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# Characterizing azobenzene disperse dyes and related compounds in house dust and their correlations with other organic contaminant classes<sup>☆</sup>

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## ABSTRACT

Azobenzene disperse dyes are the fastest-growing category of commercial dyestuffs and are implicated in the literature as potentially allergenic. In the indoor environment, these dyes may be shed from various textiles, including clothing and upholstery and accumulate in dust particles potentially leading to exposure in young children who have higher exposure to chemicals associated with dust due to their crawling and mouthing behaviors. Children may be more vulnerable to dye exposure due to their developing immune systems, and therefore, it is critical to characterize azobenzene disperse dyes in children's home environments. Here, we investigate azobenzene disperse dyes and related compounds in house dust samples ( $n = 124$ ) that were previously analyzed for flame retardants, phthalates, pesticides and per- and polyfluoroalkyl substances (PFAS). High-resolution mass spectrometry was used to support both targeted and suspect screening of dyes in dust. Statistical analyses were conducted to determine if dye concentrations were related to demographic information. Detection frequencies for 12 target dyes ranged from 11% to 89%; of the dyes that were detected in at least 50% of the samples, geometric mean levels ranged from 32.4 to 360 ng/g. Suspect screening analysis identified eight additional high-abundance azobenzene compounds in dust. Some dyes were correlated to numerous flame retardants and several antimicrobials, and statistically higher levels of some dyes were observed in homes of non-Hispanic Black mothers than in homes of non-Hispanic white mothers. To our knowledge, this is the most comprehensive study of azobenzene disperse dyes in house dust to date. Future studies are needed to quantify additional dyes in dust and to examine exposure pathways of dyes in indoor environments where children are concerned.

## 1. Introduction

Disperse azobenzene dyes are used to color synthetic fabrics such as polyester, nylon, and acrylic (Waring, 1984; Benkhaya et al., 2020a). They are currently the most abundant and fastest-growing class of dyestuffs, comprising roughly 70% of the nearly 10 million tons of industrial dye colorants used annually (Dawson, 1991; Drummond Chequer et al., 2011). While the chemical structures of azobenzene disperse dyes can vary widely, each dye is based on a p-aminoazobenzene core substructure. Extensive functionalization of this core structure with substituents including halogens – commonly bromine or chlorine – induces

electronic structure variation that in turn gives rise to the optical properties of these molecules (Chen et al., 2018; El-Ghamaz et al., 2017; Porobić et al., 2020; Overdahl et al., 2021a). Azo dyes are hydrophobic and do not dissolve well in aqueous solutions; as a result, they do not chemically bond to fibers and must be applied in conjunction with a dispersing or a fasting agent (Benkhaya et al., 2020b). As they are associated with synthetic fibers through absorption and/or adsorption, dyes can be removed from the fibers by abrasion, by leaching into water, or by partitioning onto skin when worn (Malinauskiene et al., 2013). As such, azobenzene disperse dyes are known to be aquatic environmental pollutants and enter the environment via pathways such as textile

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effluents and other waterways, as documented extensively in literature (Balakrishnan et al., 2016; Carneiro et al., 2010; Chequer et al., 2015; Chung and Stevens, 1993; De Aragão Umbuzeiro et al., 2005; Golka et al., 2004; Ohe et al., 2004; Vacchi et al., 2017; Vacchi et al., 2016; Zhang et al., 2012). However, little is known about the occurrences of azobenzene disperse dyes in the indoor environment.

Dust is a complex mixture known to contain hundreds to thousands of chemicals. Previous work examining chemicals in house dust has focused largely on presence, quantities, and co-exposures of metals such as lead (Hogervorst et al., 2007; Lanphear et al., 1998; Lanphear et al., 2011) and of semi-volatile organic compounds (SVOCs) (Hoffman et al., 2018) such as phthalates (Ait Bamai et al., 2014; Becker et al., 2004; Bekö et al., 2013; Bekö et al., 2015; Bornehag et al., 2004; Fromme et al., 2013; Kweon et al., 2018; Langer et al., 2014), brominated flame retardants (Allen et al., 2008; Fang and Stapleton, 2014; Hoang et al., 2020; Hoffman et al., 2015; Meeker and Stapleton, 2010; Phillips et al., 2018; Stapleton et al., 2014; Stapleton et al., 2012a; Stapleton and Dodder, 2008), and polyfluoroalkyl substances (PFAS) (de la Torre et al., 2019; Hall et al., 2020; Shoeib et al., 2011; Wu et al., 2020; Xu et al., 2021; Young et al., 2021; Zheng et al., 2020). Many of these chemicals, such as phthalates, are associated with increased risks of allergies and other adverse health effects in young children (Ait Bamai et al., 2014; Ait Bamai et al.; Carrer et al., 2001; Hsu et al., 2012; Jahreis et al., 2018). In fact, it is recognized that children are chronically exposed to indoor contaminants in dust at higher rates than adults due to greater behavioral differences and related dust ingestion and inhalation (Hoffman et al., 2015; Stapleton et al., 2014; Moya et al., 2004); the EPA estimates that children ingest, on average, 50 mg of house dust per day (US Environmental Protection Agency, 2011). Recent studies by our group and others have determined that azobenzene disperse dyes are present in indoor house dust (Peng et al., 2016; Ferguson and Stapleton, 2017; Dhungana et al., 2019; Kutarna et al., 2021), suggesting that dyes may be another class of chemicals chronically detected in dust. However, to date, these studies and associated toxicity studies have been limited, largely due to the lack of commercially-available reference standards and analytical methods for these compounds (Overdahl et al., 2021a).

Exposure to azo dyes in the indoor environment raise concerns about potential health impacts: azo dyes are known to have mutagenic and genotoxic properties (Vacchi et al., 2017; Vacchi et al., 2016; Chung and Cerniglia, 1992; Ventura-Camargo et al., 2016; Garner and Nutman, 1977; Platzek, 2013; Franco et al., 2018a; Franco et al., 2018b; Josephy et al., 2016), and they have also been implicated as contact allergens in clinical studies (Brookstein, 2009; Chung, 2016; Giusti et al., 2003; Heratizadeh et al., 2017; Seidenari et al., 1990; Seidenari et al., 2002; Seidenari et al., 1991; Susan and Elizabeth, 1988). Given that children may have disproportionately higher levels of exposure to azobenzene disperse dyes, and given that they may be more susceptible to known and suspected health consequences due to their developmental sensitivity, it is crucial to investigate levels and distributions of dyes in the indoor environment and to understand the home characteristics that may contribute to children's exposures to these compounds.

The goal of this study was to expand on our previous preliminary identifications of dyes in dust by utilizing a comprehensive analytical approach to characterize azobenzene disperse dyes in residential dust samples in order to understand potential exposures in children aged 3–6 years. Here, we analyzed archived dust samples that were previously collected as part of a study investigating children's exposure to semi-volatile organic chemicals (SVOCs) in the home environment. These samples were previously analyzed for several classes of organic contaminants, and we sought to understand how levels of dyes in this well-characterized cohort compare with levels of other contaminant classes. We also sought to determine if specific demographic characteristics were associated with dye levels in the home to understand if they may be predictors of potential exposure. Quantitative and non-targeted approaches were both used to maximize analytical coverage.

## 2. Materials and methods

### 2.1. Participant enrollment and cohort

Samples included in this study were previously collected as part of the Toddler's Exposure to Semivolatile Organic Chemicals in the Indoor Environment (TESIE) project. Hoffman et al. (2018) provides a detailed description of families participating in the TESIE study and the recruitment strategies (Hoffman et al., 2018). Briefly, we enrolled a total of 203 children from 190 families in the TESIE Study between August 2014 and April 2016. Study team members conducted home visits with each family enrolled in the TESIE study to collect the dust samples; staff also conducted surveys to collect information about the home environment and children's health and behavior. Legal guardians provided informed consent prior to participation in the TESIE study. All study protocols and related materials were reviewed and approved by the Duke Medicine Institutional Review Board (Duke IRB Protocol #55540).

### 2.2. Disperse azo dye standards

Twelve purified azobenzene disperse dye standards were employed in this study to enable quantification of target analytes. Table 1 lists each azobenzene disperse dye by common name, molecular formula, mono-isotopic mass, and chemical structure. These dyes were chosen based on availability; they were also previously identified in children's polyester apparel (Overdahl et al., 2021a). Seven of the 12 dyes – Disperse Blue 183:1 (DB 183:1), Disperse Blue 79:1 (DB 79:1), Disperse Orange 44 (DO 44), Disperse Orange 73 (DO 73), Disperse Red 354 (DR 354), Disperse Red 50 (DR 50), and Disperse Red 73 (DR 73) – were purified from raw dyestuffs via flash chromatography and structurally characterized by nuclear magnetic resonance (NMR) spectroscopy and high-resolution mass spectrometry (HRMS); a detailed explanation of the dye purification process is reported in our previously-published work (Overdahl et al., 2021a). In addition to these seven in-house purified dyes, we purchased analytical standards of Disperse Orange 25 (DO 25) and Disperse Orange 37 (DO 37) [Sigma; 95% purity]. Analytical standards of Disperse Orange 61 (DO 61), Disperse Violet 93 (DV 93), and Disperse Blue 373 (DB 373) were provided via a generous gift from Prof. Gisela Umbuzeiro, School of Technology, UNICAMP, Limeira, Brazil (Carneiro et al., 2010; De Aragão Umbuzeiro et al., 2005).

### 2.3. Data sample collection and processing

#### 2.3.1. House dust collection and extraction

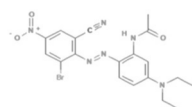
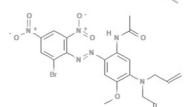
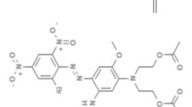
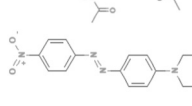
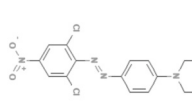
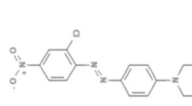
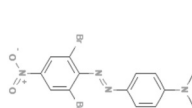
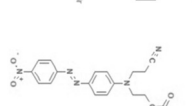
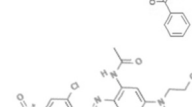
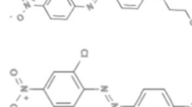

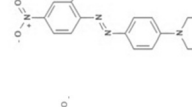
House dust collection and extraction methods for this study have previously been described in detail (Phillips et al., 2018). Briefly, to collect a house dust sample, the exposed floor area of the main living area (unvacuumed for at least two days) was vacuumed using a Eureka Mighty Mite vacuum fitted with a cellulose thimble within the hose attachment (Stapleton et al., 2012a). Each thimble was wrapped in aluminum foil and stored at  $-20^{\circ}\text{C}$  until analysis. Dust samples were sieved to  $<500\ \mu\text{m}$  prior to extraction. Extraction was performed using 1:1 dichloromethane:hexane(v/v) by sonication; extracts were concentrated to  $\sim 1\ \text{mL}$  using a SpeedVac™ Concentrator, then samples were split into three fractions. One fraction was reserved for *in vitro* assays, as reported in Kassotis et al., 2021 (Kassotis et al., 2021). Remaining fractions were spiked with internal standards (including 13C-TPHP used in this study); of those fractions, one fraction per home was utilized for untargeted analysis without further cleaning and was used to support this study. Untargeted extracts contained 92 ng/mL of 13C-TPHP in each sample. Untargeted extracts were evaporated to near-dryness, reconstituted in methanol, sonicated for 15 min, and filtered. The final volume of all untargeted dust samples was 0.5 mL in 100% methanol.

#### 2.3.2. Data acquisition

All house dust extracts (0.5 mL, in muffled amber glass LC-MS vials)

**Table 1**

Target analytes examined in indoor house dust. LogK<sub>oa</sub> values are predicted using the OPEn structure–activity/property Relationship App (OPERA) as part of the U.S. EPA's CompTox Chemistry Dashboard (Mansouri et al., 2018).

Dye Name	Molecular Formula	Monoisotopic Mass (g/mol)	CAS Number	LogK <sub>oa</sub>	InChIKey	Chemical Structure
Disperse Blue 183:1	C <sub>19</sub> H <sub>19</sub> BrN <sub>6</sub> O <sub>3</sub>	458.0702	2537-62-4	10.3	KTXMBTRTVMMWQS-UHFFFAOYSA-N	
Disperse Blue 373	C <sub>21</sub> H <sub>21</sub> BrN <sub>6</sub> O <sub>6</sub>	532.0706	51868-46-3	10.2	WXDXQSMFRITTEJ-UHFFFAOYSA-N	
Disperse Blue 79:1	C <sub>23</sub> H <sub>25</sub> BrN <sub>6</sub> O <sub>10</sub>	624.0816	3618-72-2	10.2	JSRUDOBCTLPFTFO-UHFFFAOYSA-N	
Disperse Orange 25	C <sub>17</sub> H <sub>17</sub> N <sub>5</sub> O <sub>2</sub>	323.1382	31482-56-1	9.94	ZSPPPAFDNHYXNW-UHFFFAOYSA-N	
Disperse Orange 37	C <sub>17</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	391.0603	13301-61-6	10.8	KHZRTXVUEZJYNE-UHFFFAOYSA-N	
Disperse Orange 44	C <sub>18</sub> H <sub>15</sub> ClN <sub>6</sub> O <sub>2</sub>	382.0945	4058-30-4	11.7	ZXXVVTBKBDTSE-UHFFFAOYSA-N	
Disperse Orange 61	C <sub>17</sub> H <sub>15</sub> Br <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	478.9593	55281-26-0	11.7	MWMJPPMTXZJLIK-UHFFFAOYSA-N	
Disperse Orange 73	C <sub>24</sub> H <sub>21</sub> N <sub>5</sub> O <sub>4</sub>	443.1594	40690-89-9	11.7	SCLYZFZPIKFAH-UHFFFAOYSA-N	
Disperse Red 354	C <sub>22</sub> H <sub>24</sub> ClN <sub>5</sub> O <sub>7</sub>	505.1364	1533-78-4	10.2	ORDDDDNUMJXPGOC-UHFFFAOYSA-N	
Disperse Red 50	C <sub>17</sub> H <sub>16</sub> ClN <sub>5</sub> O <sub>2</sub>	357.0993	40880-51-1	10.8	NPBDWXMKLFBNIW-UHFFFAOYSA-N	
Disperse Red 73	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub>	348.1335	16889-10-4	10.4	QEORVDCGZONWCJ-UHFFFAOYSA-N	
Disperse Violet 93	C <sub>18</sub> H <sub>19</sub> BrN <sub>6</sub> O <sub>5</sub>	478.0600	52697-38-8	10.2	WFFKSTRPZWRBEW-UHFFFAOYSA-N	

were analyzed by ultra-high performance liquid chromatography (UHPLC) [ThermoDionex Ultimate 3000] coupled to high-field orbital trapping tandem mass spectrometry [ThermoFisher Orbitrap Fusion Lumos]. UHPLC was performed with a Thermo Hypersil Gold column [1.9 μm particle size, 2.1 × 100 mm] over a 43 min water:acetonitrile (LC-MS grade, 0.1% formic acid) gradient, based on in-house optimization for untargeted small molecule separation and sensitivity. The Orbitrap was operated in ESI(+) mode at 240,000 mass resolution with internal mass calibration to achieve <2 part per million (ppm) mass

accuracy, as reported previously (Overdahl et al., 2021a). Data-dependent MS/MS acquisition was performed in the Orbitrap via stepped higher energy collisional dissociation (HCD). Ions for MS/MS analysis (approximately 15–20 precursors per second) were dynamically chosen on a per-scan basis; these MS/MS data provided fragment ion data to aid in structure elucidation, as reported previously (Overdahl et al., 2021a).

### 2.3.3. Targeted screening for azobenzene disperse dyes

We used the twelve purified azobenzene disperse dye standards listed in Table 1 to quantify individual azobenzene disperse dyes in house dust. An eight-point calibration curve was created, ranging from 0 ng/mL to 1000 ng/mL, in 75:25 acetonitrile:water; 13C-TPHP was used as the internal standard in each sample (92 ng/mL). Results were analyzed using TraceFinder software [ThermoFisher, version 5.0].

### 2.3.4. Suspect screening for additional azobenzene-based compounds

Data acquired from the LC-MS/MS analysis of dust extracts were processed using Compound Discoverer software [ThermoFisher Scientific, version 3.2] in order to identify azobenzene compounds in addition to those compounds for which we had purified standards. Analysis and data processing methods have been described in detail in our previously-published work (Overdahl et al., 2021a). Briefly, molecular features with distinct exact mass, unique retention time, and MS/MS data were identified in Compound Discoverer after removal of isotope peaks, blank contaminants, and noise artifacts from the data (Overdahl et al., 2021a). Rigorous data curation and cleaning was performed within Compound Discoverer, and in-house written software (in R) was implemented within a custom data-processing node to remove in-source fragment ions, consolidate spectral library matches across multiple databases, and generate a single consolidated compound representing each feature set (Overdahl et al., 2021b). Consolidated compounds were then processed for structure annotation using a weight-of-evidence approach incorporating results from open-source, *in silico* computational mass spectrometry tools (Getzinger and Ferguson, 2020): formula assignments were validated using Sirius (Böcker and Dührkop, 2016; Dührkop et al., 2019), then passed to four separate *in silico* spectrum-to-structure annotation tools to yield possible structural annotations for each feature (Allen et al., 2014; Dührkop et al., 2015; Ridder et al., 2012; Ruttkies et al., 2016; Wolf et al., 2010). A score of fit for each candidate structure was determined using each tool; scores of candidate structures were then ranked by percentile. Scores for all structure candidates from the four annotation tools were compared according to percentile rank to determine the molecular structure with the highest composite percentile rank score, and this result was then compared with an in-house curated database of known molecules, all of which contain the p-aminoazobenzene substructure (4665 non-halogenated azobenzenes, 220 chlorinated azobenzenes, 95 brominated azobenzenes). (Overdahl et al., 2021a).

### 2.4. Quality assurance and quality control

Quality assurance and quality control were addressed by analyzing laboratory processing blanks ( $n = 6$ ) and a house dust Standard Reference Material ( $n = 10$ ) (SRM 2585, National Institute of Standards and Technology (NIST), Gaithersburg, MD) alongside house dust samples. While the house dust SRM does not contain any certified or reference values for azobenzene disperse dyes, our laboratory and others have used this material to support QA/QC for dust analyses (Phillips et al., 2018; Hall et al., 2020; Hammel et al., 2019; Levasseur et al., 2021).

The internal standard 13C-TPHP was used to normalize all peak detections; all sample concentrations were normalized to the mass of house dust extracted per sample. Given the low abundance of dyes in some of the samples, we excluded samples with a low dust mass ( $<10$  mg) in this study to reduce the likelihood of bias in the reporting.

### 2.5. Statistical analyses

All statistical analyses were performed using GraphPad Prism statistical software (version 9.0, GraphPad Software LLC). Method detection limits (MDLs) were calculated by determining the lowest calibration sample that could be quantified in three replicate calibration samples (1 ng/mL for all analytes) and normalizing to the mass of dust extracted for the given sample and analyte. Values that were less than the MDL were

replaced with MDL/2 for the purposes of statistical analysis (Antweiler and Taylor, 2008). MDL values for each dust extract ranged from 1.3 to 48.2 ng dye/g dust.

We first conducted basic exploratory data analyses and descriptive statistics. We conducted further statistical analyses for dyes when detection frequencies were  $>50\%$  (Hoffman et al., 2018). A Shapiro-Wilkes test indicated that dyes concentrations in house dust were not normally distributed; therefore, we used non-parametric statistics to examine associations. Spearman correlations were used to assess correlations among dyes in house dust and to assess correlations with other chemicals previously measured in these dust samples.

We examined relationships between dyes and cohort characteristics (as previously reported) using questionnaire data (Hoffman et al., 2018). Variables examined included mother's race and ethnicity, mother's education level at the time of birth (a proxy for socioeconomic status or SES), average outdoor temperature during the week of sample collection, type of home (e.g. apartment, detached), living room floor type (carpeted or solid flooring), dusting frequency per month, and vacuuming frequency per month (Hoffman et al., 2018). Categorization of these variables is included in Tables SI-1 in Supplementary Information. For dichotomous cohort characteristics, we utilized Mann-Whitney tests to evaluate whether statistically significant differences existed ( $p < 0.05$ ). For cohort characteristics with three categories, we used Kruskal-Wallis tests to evaluate whether groups were significantly different; we then evaluated the statistical significance of differences between groups using Dunn's multiple comparison tests.

## 3. Results and discussion

Demographic characteristics of the TESIE study population, as well as characteristics of children's homes, have been discussed extensively in Hoffman et al., 2018 (Hoffman et al., 2018). As detailed in Section 3.2.4, we excluded samples with a low dust mass ( $<10$  mg) in this study to reduce the likelihood of bias in the reporting; our results are thus from 124 unique households. Demographics of these households are presented in Tables SI-1 in Supplementary Information.

### 3.1. Azobenzene disperse dyes in house dust

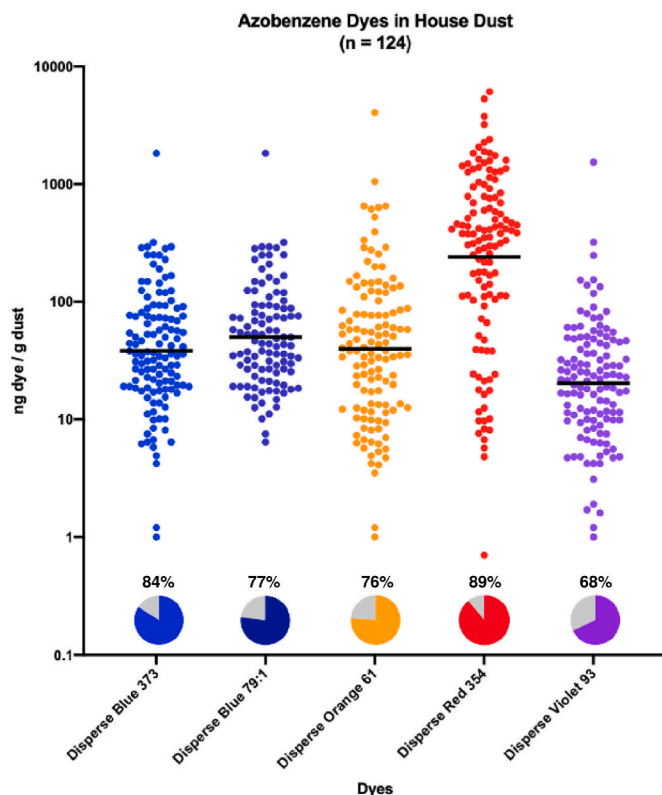
#### 3.1.1. Targeted quantification of azobenzene disperse dyes in house dust

Table 2 summarizes quantitative measurements for the twelve azobenzene disperse dyes targeted for measurement in this study. Five of the dyes were brominated, four were chlorinated, and three were non-halogenated compounds. All azobenzene disperse dyes for which we had standards were detected in one or more house dust samples. Five dyes (DB 373, DB 79:1, DO 61, DR 354, DV 93) were detected in 50% or more of the house dust samples and were further examined statistically. In general, DB 373 (84%) and DR 354 (89%) were detected most frequently, while DO 25 (11%) and DR 50 (11%) were detected least frequently. Dyes were detected at levels up to 6106 ng dye/g house dust (DR 354). Considerable variation was observed in distributions of dust concentrations for these five individual dye analytes (Fig. 1). Median levels for dyes in dust reported here ranged from tens to hundreds of ng dye/g house dust.

To our knowledge, these data are the most extensive quantitative assessment of azobenzene disperse dyes in house dust to date. While not comprehensively quantitative due to limited reference standards, no other study to date has been able to quantify this many dyes in dust. Dhungana et al. (2019) previously detected and quantified DB373 and DV93 in 13 and 12 samples, respectively, out of 37 dust samples collected from daycare centers, homes, salons, and research facilities. In dust specifically from homes, Dhungana et al. measured concentrations of DB373 and DV93 up to 338 ng/g and 453 ng/g, respectively; these measurements are an order of magnitude lower than the maximum concentrations we report here for DV373 and DV93 in dust from homes. However, in dust specifically from daycare centers, Dhungana et al.

**Table 2**  
Descriptive statistics for azobenzene disperse dyes quantified in indoor house dust samples.

Dye	% Detected	Geometric Mean (ng dye/g house dust)	Median (ng dye/g house dust)	75th Percentile (ng dye/g house dust)	90th Percentile (ng dye/g house dust)	Maximum (ng dye/g house dust)
Disperse Blue 183:1	21	n/a	n/a	n/a	845	1697
Disperse Blue 373	84	51.3	46.4	91.9	205	1827
Disperse Blue 79:1	77	11.2	11.0	22.6	515	2022
Disperse Orange 25	11	n/a	n/a	n/a	83.8	173
Disperse Orange 37	46	n/a	n/a	n/a	85.3	488
Disperse Orange 44	43	n/a	n/a	n/a	656	3223
Disperse Orange 61	76	65.6	58.2	136	290	4052
Disperse Orange 73	31	n/a	n/a	n/a	604	2167
Disperse Red 354	89	360	412	981	1638	6106
Disperse Red 50	11	n/a	n/a	n/a	66.5	109
Disperse Red 73	44	n/a	n/a	n/a	359	1894
Disperse Violet 93	68	32.4	31.0	n/a	87.9	1540



**Fig. 1.** Concentrations of azobenzene disperse dyes in indoor house dust for all dyes detected in more than 50% of all dust samples ( $n = 124$ ). Although quantitative measurements were made for all twelve targeted dyes in dust samples, data is presented here only for those five dyes detected in  $>50\%$  of samples in order to minimize bias from large numbers of measurements below the MDL. Geomeans for each dye are represented by a thick black horizontal bar on the dataset. Pie charts below each dot cluster represent the percent detection of each dye, as also shown in Table 2. Samples below the method detection limit (MDL) for each compound are represented by imputed values equal to the MDL/2 per sample.

measured concentrations of DB373 and DV93 as high as 3850 ng/g and 1190 ng/g, respectively (Dhungana et al., 2019); these concentrations in daycare center dust are within the same order of magnitude as the maximum concentrations we report here in dust from homes. Given that our house dust population ( $n = 124$ ) consists exclusively of homes that house young children, the similar levels of dye concentrations in our cohort and dye concentrations in Dhungana et al.'s daycare samples is notable. Previous work by our group (Overdahl et al., 2021a) measured these same twelve azo dyes (Table 1) in seven children's polyester athletic apparel samples, suggesting that apparel may be one possible source of these dyes to the indoor environment.

**3.1.2. Associations between dyes, and between dyes and other chemicals, in house dust**

We utilized Spearman correlations to examine pairwise associations among dyes in house dust (Tables SI-2). Moderate correlations were observed among the five dyes detected in  $>50\%$  of samples ( $r_s > 0.6$ ,  $p < 0.0001$  for all), suggesting that dyes have similar sources. The strongest associations were observed between DB 373 and DV 93 ( $r_s = 0.80$ ); between DV 93 and DO 61 ( $r_s = 0.77$ ); and between DB 373 and DO 61 ( $r_s = 0.70$ ). While we did not have access to samples of possible sources of dyes in the home, these associations are in accordance with our previously-reported observations of these dyes found together in clothing apparel (Overdahl et al., 2021a) and in measurements of black textile dyestuff powder (De Aragão Umbuzeiro et al., 2005), suggesting that black-colored textiles may be an important source of azobenzene

disperse dyes in house dust.

We also utilized Spearman correlations to examine pairwise associations between dyes in house dust and other classes of chemicals previously measured in these same dust samples (Phillips et al., 2018; Hall et al., 2020; Kassotis et al., 2021; Hammel et al., 2019; Levasseur et al., 2021), in order to gain potential insight about possible common sources of contaminants. For instance, it is known that both dyes and PFAS are associated with fabric sources in the indoor environment (e.g. stain repellants), and that compounds such as phthalates may have close associations with dye-containing materials (e.g. fabrics over polymer sources). Spearman correlations between these chemicals and each of the five dyes detected in >50% of samples, as well as the specific statistical significances of these correlations, are itemized in Tables SI-3. Generally, levels of dyes in dust were similar to levels of other classes of contaminants measured in the same dust samples, such as per- and polyfluoroalkyl substances (PFAS) (Hall et al., 2020), as shown in Figs. SI-1. However, these levels are an order of magnitude lower than the levels of phthalates (Hammel et al., 2019) previously measured in this house dust cohort, as shown in Figs. SI-2 in Supplementary Information. Weak, yet statistically significant, correlations were also observed between dyes and several types of flame retardants that are common to furniture, including TBB, TBPH, TCPP, TDCPP, and ZIPPDP, and multiple PBDEs. Because these flame retardants have been commonly applied to furniture (Cooper et al., 2016; Stapleton et al., 2012b; Stapleton et al., 2011), these correlations may indicate that azobenzene disperse dyes may also be used in furniture upholstery.

Azobenzene disperse dyes were also weakly correlated ( $r_s = 0.18-0.32$ ) with triclocarban and triclosan, two common antimicrobials. While these chemicals have traditionally been considered as personal care product antimicrobials, online databases and scientific review articles suggest that triclosan has been used as an antimicrobial in other materials such as countertops and flooring (Halden, 2014). The abundant levels of triclocarban and triclosan measured previously in this house dust cohort (Levasseur et al., 2021) indicate that these chemicals may be used as antimicrobials in household materials other than personal care products. Overall, while these correlations are suggestive of possible exposure sources of azobenzene disperse dyes within the indoor environment, further research is needed to identify specific materials from which these dyes may originate in the indoor home.

### 3.1.3. Detections and relative abundances of additional azobenzene-based compounds in dust via suspect screening analysis

In addition to the twelve dyes we quantified via reference standards, we tentatively identified eight additional azobenzene compounds using a suspect screening approach. Table 3 summarizes results of our HRMS/MS-based suspect screening analysis and illustrates tentatively identified structural candidates of azobenzene compounds in house dust using our weight-of-evidence approach, including the molecular formula of the compound (from Sirius 4.0<sup>7b</sup>), the number of isomeric structure candidates in the PubChem database having this formula, the percentile rank score generated for the overall top-ranked PubChem structural candidate from each *in silico* MS/MS structure annotation tool, and metadata in support of the annotation, including the number of PubChem sources, patents, and references for the selected top-rank structure annotation candidate. Structures were considered to be tentatively identified (Figs. SI-3, and included within Table 3) in cases where the PubChem structure candidate with the top-ranked composite score from the four *in silico* structure annotation tools matched a p-amino-azobenzene compound structure from the suspect list.

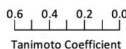
Tentatively-identified compounds (Figs. SI-3) included: Disperse Violet 93 Cl (DV93 Cl, the chlorinated analog of DV 93), Disperse Yellow 23 (DY 23), Disperse Yellow 3 (DY 3), and Yellow OB, for which we did not have standards but which had known common names; and four additional azobenzene compounds for which no common name was available (CAS #s 1533-74-0, 54888-15-2, 722-25-8, and 96662-24-7). Compounds (rows) were clustered according to structural similarity via MACCS (Molecular Access System) fingerprints and Tanimoto coefficient to examine the structural relationships of these compounds to one another (Anderson, 1984); these relationships are shown by the dendrogram in Table 3.

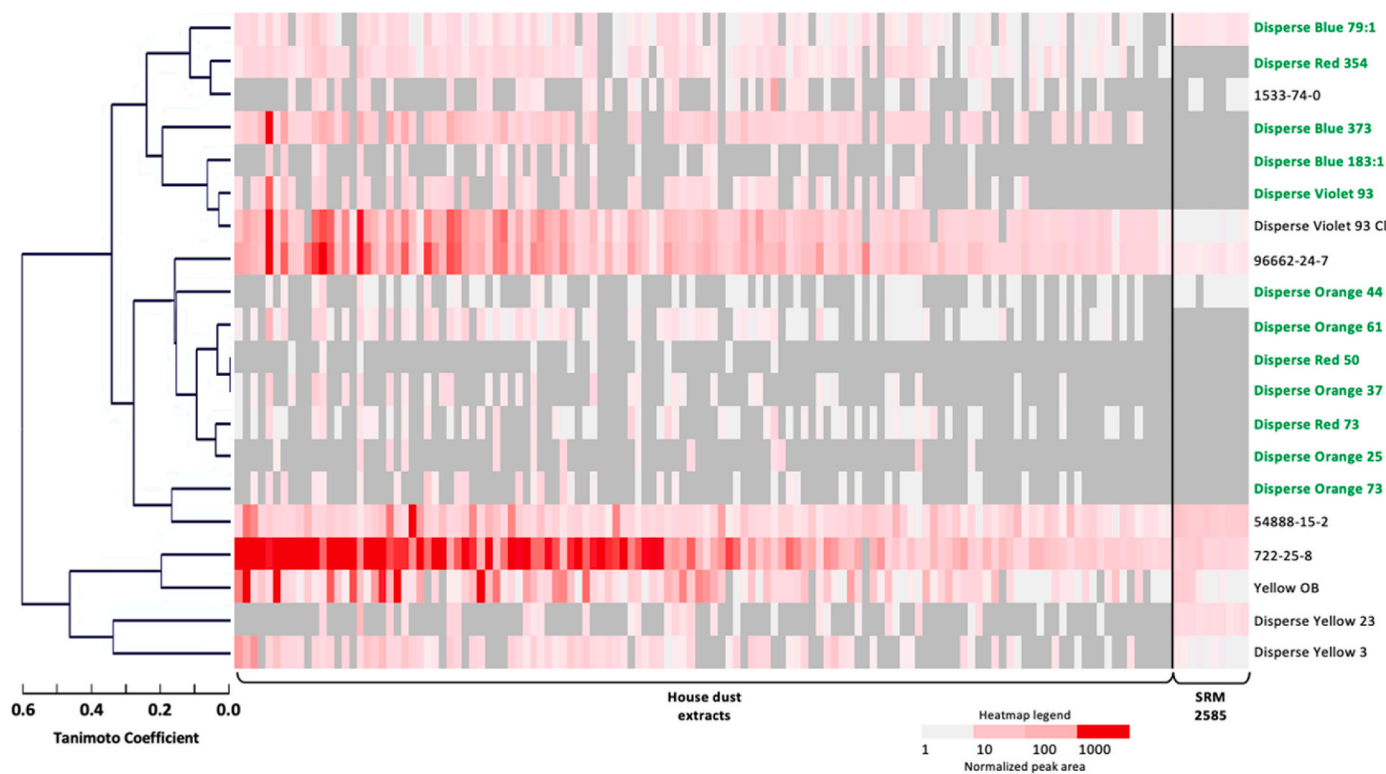
Although the lack of analytical standards precluded us from generating quantitative measurements of tentatively-identified azobenzene compounds, we utilized chromatographic peak areas to generate relative abundances of all confirmed and tentatively-identified compounds in house dust samples in order to compare relative abundances across house dust samples and to examine structural similarities across all compounds detected. Peak areas were first normalized to the peak area of the 13C-TPHP internal standard, then normalized to the house dust mass in each sample. Log-transformed relative abundances of confirmed and tentatively-identified compounds are shown in Fig. 2, in which dust extract samples (columns) are clustered according to similarity in

**Table 3**

Azobenzene compounds tentatively identified in house dust through our weight-of-evidence approach using the computational mass spectrometry tools MAGMa, MetFrag, CSI:FingerID, and CFMID; percentile scores of fit to the compound fragmentation spectra are shown, generated by each of the four fragmenters, and are color coded from red (0th percentile score of fit predicted by the fragmenter) to green (100th percentile score of fit predicted by the fragmenter). Numbers of sources, patents, and references in PubChem are also included as additional metadata for substantiation of compound identification. Compounds (rows) are ordered according to chemical similarity, evaluated using MACCS fingerprints and Tanimoto coefficient. Common names are listed if available; compounds with no common name listed are not known by any azo dye name in open-source databases.

Common Name (if applicable)	CAS	Molecular Formula	# Structure Candidates	Percentile Scores				PubChem # Sources	PubChem # Patents	PubChem # References
				MAGMa	MetFrag	CSI:FingerID	CFMID			
	96662-24-7	C <sub>22</sub> H <sub>19</sub> N <sub>5</sub> O <sub>2</sub>	1586	100	99.9	81.5	97.2	6	2	0
	54888-15-2	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>3</sub>	489	100	100	n/a	100	10	0	0
	1533-74-0	C <sub>22</sub> H <sub>25</sub> N <sub>5</sub> O <sub>7</sub>	41	97.5	100	100	97.5	22	0	0
Disperse Violet 93 Cl	66557-45-7	C <sub>18</sub> H <sub>19</sub> ClN <sub>6</sub> O <sub>5</sub>	10	100	100	100	100	18	6	0
	722-25-8	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub>	1180	99.7	98.8	99.4	76.4	36	53	0
Yellow OB	131-79-3	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub>	853	100	100	100	100	36	51	7
Disperse Yellow 23	6250-23-3	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> O	1076	99.9	99.8	38	98.5	41	0	0
Disperse Yellow 3	2832-40-8	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	6055	100	99.3	51.3	97.3	82	0	20





**Fig. 2.** Relative abundances of all confirmed and tentatively-identified azobenzene-based compounds in house dust samples. Relative abundances of each compound were calculated by normalizing chromatographic peak area of each detection first to the peak area of the 13C-TPHP internal standard, then normalizing the ratio of compound peak area: 13C-TPHP peak area to the mass of dust in each house dust extract. Normalized peak areas are log-scaled and are colored from white (lowest detection limit calculations and values, please see the Supplementary Information.) Each column represents an individual dust extract; dust extract samples are binned according to TESIE house dust extracts vs. SRM replicate extracts, and within bins are clustered according to similarity. Rows (azobenzene compounds) are sorted according to chemical fingerprint similarity, calculated by MACCS fingerprints and represented by the dendrogram to the left of the heatmap. Azo dye names in bolded green type are those that we were able to confirm and quantify via authentic reference standard.

abundance profiles, and detected azo compounds (rows) are clustered according to chemical similarity. Because chromophore activity is determined by the electronic properties of a compound (primarily dictated by type, number, and position of chemical functional groups), azo compounds with similar structures are likely to exhibit similar color behavior (Aljamali, 2015; Choi et al., 2000; Wojciechowski, 1997). We therefore utilized the MACCS fingerprint clustering to compare the un-named compounds identified from suspect screening with named dyes detected in both target and suspect screening methods. Structural similarity clustering indicated that CAS# 1533-74-0 clustered closely with DR 354 and DB 79:1; CAS# 1533-74-0 may therefore be a blue or red dye. CAS# 96662-24-7 clustered closely with orange dyes, specifically DO 44, and is thus likely an orange dye. Similarly, CAS #54888-15-2 clustered closely with orange dyes, specifically DO 73, and is also likely an orange dye. CAS #722-25-8 clustered closely with yellow dyes and is likely a yellow colorant; patents mentioning this compound (Helmut-Martin et al., 2013) indicate that CAS #722-25-8 is commonly used to produce brown dyes.

Fig. 2 also demonstrates several notable patterns of relative abundances and co-occurrences of dyes within and among samples. Five compounds were detected in more than 90% of house dust extracts: DV 93 Cl, Yellow OB, and CAS #s 54888-15-2, 722-25-8, and 96662-24-7. These compounds also displayed the highest overall relative abundances within dust extracts and across all extracts. In fact, CAS #s 54888-15-2 and 96662-24-7, both of which may be orange dyes, were detected in 100% of house dust samples. Notably, all five of the most frequently detected and highly abundant (based on peak area) disperse azobenzene dyes in house dust samples were identified through suspect screening and were not quantifiable. Three of the five dyes are so poorly

represented in the literature that they have no known common names. The targeted dyes DB 373, DB 79:1, and DR 354 (for which quantitative data are shown in Fig. 1) were detected in more than 75% of house dust extracts, but at relative abundances that were an order of magnitude lower than the most abundant compounds described above. This observation highlights a need to obtain reference standards for disperse azobenzene dyes in order to completely quantify these compounds in the indoor environment and elsewhere. The co-occurrence of DV 93 Cl and CAS #96662-24-7 is notable: these two compounds were present in almost all house dust samples at near-identical relative abundances. Additionally, in nearly every sample where DV 93 Cl and 96662-24-7 co-occurred, at least one blue dye was also detected. These results are concordant with our Spearman correlation results demonstrating positive relationships between blue, orange and violet dyes, and with our previous work showing blue, orange, and violet dyes as the main component in black dyestuff and black polyester apparel (Overdahl et al., 2021a), suggesting that black textiles may be primary drivers to the azobenzene disperse dye profile of indoor house dust.

Interestingly, DV 93 (a brominated dye) was detected at only a fraction of the frequency of its chlorinated analog. While quantitative data shows that DV 93 was present in 68% of house dust samples, Fig. 2 shows that DV 93 Cl was detected in all but four dust samples, and was one of the most abundant compounds in the dataset. Kutarna et al. (2021) observed a similar phenomenon in a study of 24 house dust samples, detecting DV 93 Cl in all samples and noting that abundances of the chlorinated analog were 4.9 times higher than corresponding brominated compound abundances, and higher than all 39 chlorinated compounds tentatively annotated from a Toxic Substances Control Act (TSCA) database (Kutarna et al., 2021). Our results in this study, coupled

with Kutarna et al.'s findings, indicate that DV 93 Cl is a ubiquitous component of indoor house dust.

Across all samples, CAS #722-25-8 was the most prominent azobenzene compound in both abundance and frequency. This prominence is concerning as CAS #722-25-8 is on the list of ECHA's "Annex III" substances predicted to meet criteria for carcinogenicity, mutagenicity, or reproductive toxicity. (-(p-tolylazo)aniline) Given these potential hazards, and given that house dust is a potential source of exposure to many chemicals – particularly for young children – further studies to confirm these putative annotations and evaluate toxic properties such as mutagenicity (e.g. via the Ames mutagenicity assay (Chung and Cerniglia, 1992; Ventura-Camargo et al., 2016; Franco et al., 2018a; Franco et al., 2018b)) at exposure-relevant concentrations are needed. 3.1.4 Azobenzene compounds detected in SRM 2585.

In addition to measurements in house dust samples, we identified azobenzene disperse dyes and related compounds in NIST SRM 2585 (National Institute of Standards & Technology (NIST), 2018). DB 79:1 and DO 44 were measured at levels of  $123 \pm 26$  ng dye/g dust and  $33.5 \pm 12$  ng dye/g dust, respectively, while the other 10 dyes for which we had analytical standards available were not quantifiable above the method detection limits in this material (Tables SI-4). We also tentatively identified azobenzene compounds DV 93 Cl, DY 23, DY 3, Yellow OB, and CAS #s 1533-74-0, 54888-15-2, 722-25-8, and 96662-24-7 via normalized peak areas (Tables SI-5). To our knowledge, these are the first reported detections of azobenzene disperse dyes in this commonly studied SRM.

### 3.2. Associations between azobenzene disperse dye concentrations and housing characteristics

Using data collected from surveys, we examined associations between dye abundances and demographic and housing characteristics. While significant associations were not observed between dyes and the majority of demographic and housing characteristics we evaluated, associations were observed between maternal race and ethnicity of the home occupants and several of the azobenzene dyes and compounds measured in indoor house dust. For example, significant associations with maternal race and ethnicity were observed for DB 373, DV 93 Cl, and CAS #96662-24-7 (Tables SI-6). More specifically, dust samples from the homes of non-Hispanic Black mothers had concentrations of DB 373 ( $p = 0.03$ ), DV 93 Cl ( $p < 0.01$ ), and CAS #96662-24-7 ( $p < 0.01$ ) that were twice as high, on average, than samples from the homes of non-Hispanic white mothers (Fig. 3a). While we did not have access to samples of textiles within the home, one possible reason for these socioeconomic associations might be related to differences in textile purchasing. For example, synthetic polyester clothing, for which azobenzene disperse dyes are predominant colorants, comprises the majority of affordable, easily accessible "fast fashion." Purchasing habits may differ based on these socioeconomic factors; however, further investigations are needed to determine if these findings would be replicated in additional studies.

Dye concentrations were also found to be significantly associated with flooring type (from where each dust sample was collected). Significant associations with floor type were observed for DB 373, DO 61,

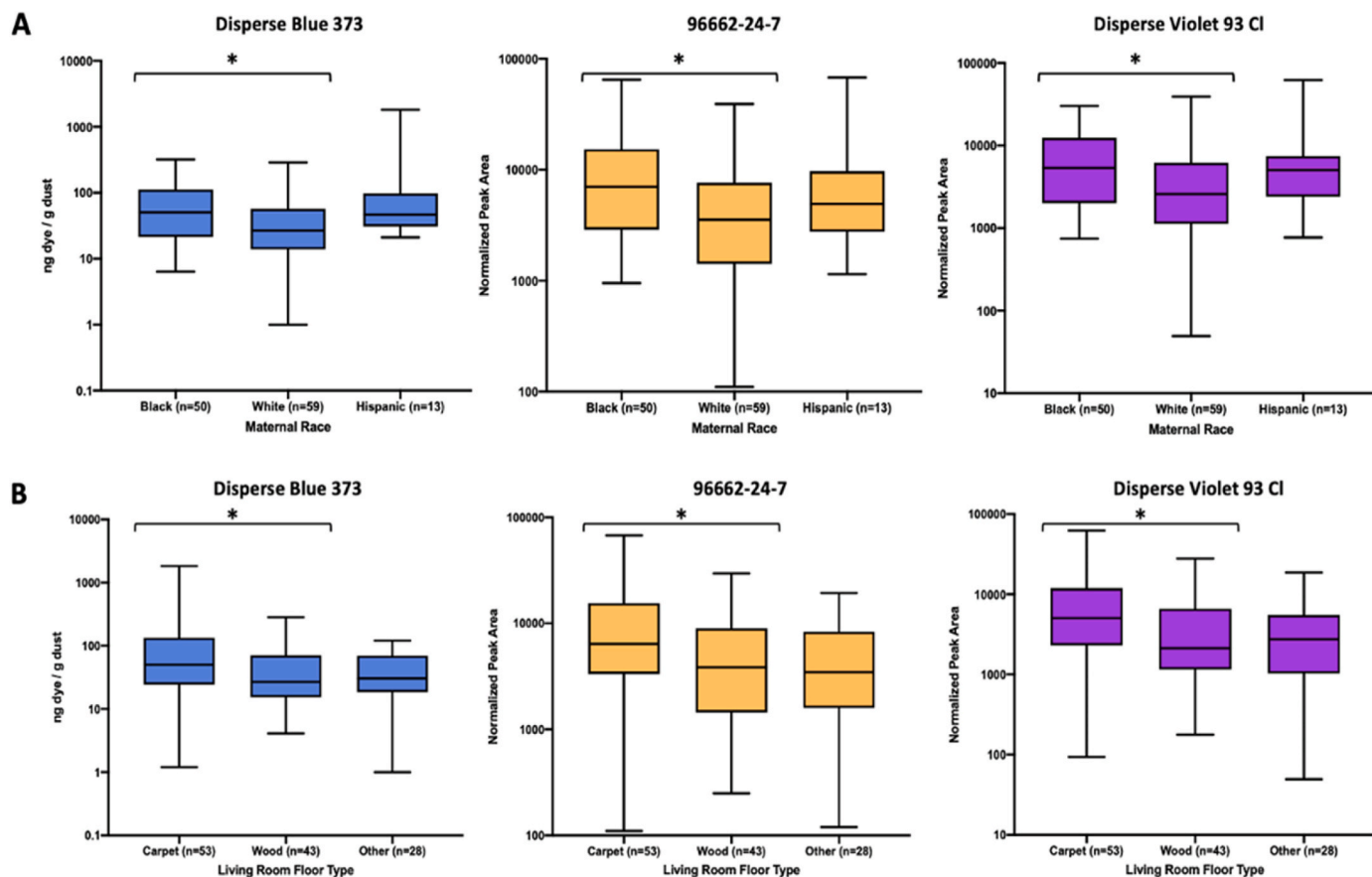


Fig. 3. Significant associations between levels of select compounds in house dust and maternal race (4A), and between levels of select compounds in house dust and living room floor type (4B). Significant associations across all variables within a category were determined via Kruskal-Wallis tests (Tables SI-5); significant associations between individual variables were then determined via Dunn's Multiple Comparisons testing (other differences were not significant, as seen in Tables SI-6). Values for quantitated dyes are reported in ng dye/g house dust on the y-axis; values for tentatively-identified azobenzene compounds are reported in normalized peak area on the y-axis. Asterisks grouping two categories (\*) indicates  $p < 0.05$ .

DV 93 Cl, Yellow OB, and CAS #96662-24-7 (Tables SI–6). More specifically, homes with carpeted living rooms were associated with higher dust concentrations of DB 373 ( $p = 0.03$ ), CAS #96662-24-7 ( $p = 0.03$ ), and DV 93 Cl ( $p = 0.05$ ) (Fig. 3b); higher dust concentrations of Yellow OB ( $p = 0.04$ ) and DO 61 ( $p = 0.03$ ) were also observed in homes with carpeted living areas (results in Tables SI–6). Dhungana et al. (2019) previously showed that DB 373 and DV 93 Cl were detectable in synthetic carpeting, albeit at abundances that were orders of magnitude lower than in cloth samples (Dhungana et al., 2019). Carpet can be both a reservoir for and a source of chemicals in the indoor environment (Haines et al., 2020); for example, carpet has been established as a significant source of exposure for other chemical classes such as PFAS (Wu et al., 2020). More work is needed to determine the extent to which carpet may be a source of dyes in the indoor environment.

### 3.3. Study limitations and future directions

The results of this study should be interpreted in the context of several potential limitations. First, our house dust samples were collected in North Carolina; regional product uses and textile availabilities throughout the United States may lead to potentially variant house dust profiles, and the generalizability of this study to nationwide households may be limited. Additionally, we only sampled dust from one microenvironment – the main living area of the home – which may not correctly account for the total house dust profile within the home. Because these dust samples were collected without the intent of analyzing them for dyes, we did not have an opportunity to collect additional samples to characterize potential sources of dyes in the home. It is therefore also unclear to what degree the dust samples may be influenced by textiles in the main living area, such as upholsteries or curtains, as opposed to all possible azobenzene disperse dye sources that may contribute to total dye loading in the home (e.g. clothing). Furthermore, detection frequencies coupled with Spearman correlation analyses suggest that the dye colors known to be found in black textiles are those that appear most commonly in house dust. However, it is unclear to what degree this difference could be driven by the use or wearing of specific textiles within homes. Future work should be directed at examining different possible sources of azobenzene disperse dyes, such as different type of textiles in the main living area, and also examine different combinatorial matrices of these sources.

To our knowledge, this study represents the largest-scale and most comprehensive characterization of azobenzene disperse dyes in house dust to date in which azo dyes are explored, and the use of suspect screening employing a library of all p-aminoazobenzene-based compounds in CAS provides the broadest coverage of any azo dye study to date. However, we were able to quantify only 12 dyes. It is known that thousands of azobenzene disperse dyes and related compounds exist, and future studies should prioritize the purifications of additional reference standards in order to obtain more accurate measurements of dyes in house dust.

## 4. Conclusions

This study builds off of previous studies that detected azobenzene disperse dyes in indoor house dust, but were limited in scope due to the lack of commercially-available reference standards and analytical methods for these compounds. By utilizing in-house purified reference standards and an in-house curated database of known azobenzene molecules to conduct both targeted and suspect screening of dyes in a previously-collected cohort of house dust, we sought to characterize azobenzene disperse dyes in dust in order to understand potential exposures for young children. Collectively, results of our work suggest that azobenzene disperse dye concentrations in indoor house dust represent a potential source of human exposure, particularly for children. It is well-established that exposures to contaminants in indoor house dust are of concern for children (Mercier et al., 2011; Bonvallot et al., 2010;

Glorennec et al., 2011). Furthermore, dust chemical profiles paired with biomonitoring studies have established (Salthammer et al., 2018) that house dust is known to be a critical pathway of exposure to the human body (Butte and Heinzow, 2002), and dermal contact and hand-to-mouth behaviors of children exacerbate these exposures (Hammel et al., 2019). However, to date no biomarkers of exposure have been established for azobenzene disperse dyes. Future studies should prioritize dye biomarker identification in order to investigate children's internal dose of azobenzene disperse dye. Given that dust is a complex mixture of multiple contaminants, and that dyes co-occur with other contaminants in dust, mixture effects should also be assessed moving forward. While toxicity testing of azobenzene disperse dyes is beyond the scope of this study, previous studies have established that azobenzene disperse dyes have known mutagenic and genotoxic properties (Vacchi et al., 2017; Vacchi et al., 2016; Chung and Cerniglia, 1992; Ventura-Camargo et al., 2016; Garner and Nutman, 1977; Platzek, 2013; Franco et al., 2018a; Franco et al., 2018b; Josephy et al., 2016) and are suspected immune sensitizers (Brookstein, 2009; Chung, 2016; Giusti et al., 2003; Heratizadeh et al., 2017; Seidenari et al., 1990; Seidenari et al., 2002; Seidenari et al., 1991; Susan and Elizabeth, 1988); the potential for disproportionate exposure to children is therefore concerning. Given the suggested toxicities of additional azo compounds identified in dust in this study, such as Yellow OB and CAS #722-25-8, further studies examining toxicities of these compounds and examining exposures of children to these compounds in homes are crucial.

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## CRedit authorship

**KEO:** Study design; Sample collection; Investigation; Data analysis; Visualization; Writing – original draft; Writing – review & editing; **CDK:** Investigation; Data analysis; **KH:** Conceptualization; Study design; Sample collection; Data analysis; Writing – review & editing; **GJG:** Data interpretation; **AP:** Sample collection; Data analysis; **SH:** Sample Collection; Data analysis; **PLF:** Study design; Investigation; Data interpretation; Visualization; Writing-review & editing; **HMS:** Conceptualization; Study design; Sample collection; Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

De-identified data will be made available upon request.

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## Abbreviations

DB 79:1	Disperse Blue 79:1
DB 183:1	Disperse Blue 183:1
DB 373	Disperse Blue 373
DO 25	Disperse Orange 25
DO 37	Disperse Orange 37
DO 44	Disperse Orange 44
DO 61	Disperse Orange 61
DO 73	Disperse Orange 73
DR 50	Disperse Red 50
DR 73	Disperse Red 73
DR 354	Disperse Red 354
DV 93	Disperse Violet 93
DV 93 Cl	Disperse Violet 93, chlorine analog
DY 3	Disperse Yellow 3
DY 23	Disperse Yellow 23
MDL	Method Detection Limit
SRM	Standard Reference Material

TESIE Toddlers' Exposures to SVOCs in the Indoor Environment

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2023.122491>.

## References

- Ait Bamai, Y., Araki, A., Kawai, T., Tsuboi, T., Saito, I., Yoshioka, E., Cong, S., Kishi, R., Exposure to phthalates in house dust and associated allergies in children aged 6–12 years. *Environ. Int.* 96: 16–23. doi:10.1016/j.envint.2016.08.025.
- Ait Bamai, Y., Shibata, E., Saito, I., Araki, A., Kanazawa, A., Morimoto, K., Nakayama, K., Tanaka, M., Takigawa, T., Yoshimura, T., Chikara, H., Saijo, Y., Kishi, R., 2014. Exposure to house dust phthalates in relation to asthma and allergies in both children and adults. *Sci. Total Environ.* 485–486, 153–163. <https://doi.org/10.1016/j.scitotenv.2014.03.059>.
- Aljamali, N.M., 2015. Review in azo compounds and its biological activity. *Biochem. Anal. Biochem.* 4 (2), 1–4. <https://doi.org/10.4172/2161-1009.1000169>.
- Allen, J.G., McClean, M.D., Stapleton, H.M., Webster, T.F., 2008. Critical factors in assessing exposure to PBDEs via house dust. *Environ. Int.* 34 (8), 1085–1091. <https://doi.org/10.1016/j.envint.2008.03.006>.
- Allen, F., Greiner, R., Wishart, D., 2014. Competitive fragmentation modeling of ESI-MS/MS spectra for putative metabolite identification. *Metabolomics* 11, 98–110. <https://doi.org/10.1007/s11306-014-0676-4>.
- Anderson, S., 1984. Graphical representation of molecules and substructure-search queries in MACCSm. *J. Mol. Graph.* 2 (3), 83–90. [https://doi.org/10.1016/0263-7855\(84\)80060-0](https://doi.org/10.1016/0263-7855(84)80060-0).
- Antweiler, R.C., Taylor, H.E., 2008. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets: I. Summary statistics. *Environ. Sci. Technol.* 42 (10), 3732–3738. <https://doi.org/10.1021/es071301c>.
- Balakrishnan, V.K., Shirin, S., Aman, A.M., de Solla, S.R., Mathieu-Denoncourt, J., Langlois, V.S., 2016. Genotoxic and carcinogenic products arising from reductive transformations of the azo dye, Disperse Yellow 7. *Chemosphere* 146, 206–215. <https://doi.org/10.1016/j.chemosphere.2015.11.119>.
- Becker, K., Seiwert, M., Angerer, J., Heger, W., Koch, H.M., Nagorka, R., Rosskamp, E., Schlüter, C., Seifert, B., Ullrich, D., 2004. DEHP metabolites in urine of children and DEHP in house dust. *Int. J. Hyg. Environ. Health* 207 (5), 409–417. <https://doi.org/10.1078/1438-4639-00309>.
- Bekö, G., Weschler, C.J., Langer, S., Callesen, M., Toftum, J., Clausen, G., 2013. Children's phthalate intakes and resultant cumulative exposures estimated from urine compared with estimates from dust ingestion, inhalation and dermal absorption in their homes and daycare centers. *PLoS One*. <https://doi.org/10.1371/journal.pone.0062442>.
- Bekö, G., Callesen, M., Weschler, C.J., Toftum, J., Langer, S., Sigsgaard, T., Høst, A., Jensen, T.K., Clausen, G., 2015. Phthalate exposure through different pathways and allergic sensitization in preschool children with asthma, allergic rhinoconjunctivitis and atopic dermatitis. *Environ. Res.* 137, 432–439. <https://doi.org/10.1016/j.envres.2015.01.012>.
- Benkhaya, S., M'rabet, S., El Harfi, A., 2020a. A review on classifications, recent synthesis and applications of textile dyes. *Inorg. Chem. Commun.* 115, 107891. <https://doi.org/10.1016/j.inoche.2020.107891>.
- Benkhaya, S., M'rabet, S., El Harfi, A., 2020b. Classifications, properties, recent synthesis and applications of azo dyes. *Heliyon* 6 (1), e03271. <https://doi.org/10.1016/j.heliyon.2020.e03271>.
- Böcker, S., Dührkop, K., 2016. Fragmentation trees reloaded. *J. Cheminf.* 8 (5) <https://doi.org/10.1186/s13321-016-0116-8>.
- Bonvallot, N., Mandin, C., Mercier, F., Le Bot, B., Glorennec, P., 2010. Health ranking of ingested semi-volatile organic compounds in house dust: an application to France. *Indoor Air* 20 (6), 458–472. <https://doi.org/10.1111/j.1600-0668.2010.00667.x>.
- Bornehag, C.G., Sundell, J., Weschler, C.J., Sigsgaard, T., Lundgren, B., Hasselgren, M., Hägerhed-Engman, L., 2004. The association between asthma and allergic symptoms in children and phthalates in house dust: a nested case-control study. *Environ. Health Perspect.* 112 (14), 1393–1397. <https://doi.org/10.1289/ehp.7187>.
- Brookstein, D.S., 2009. Factors associated with textile pattern dermatitis caused by contact allergy to dyes, finishes, foams, and preservatives. *Dermatol. Clin.* 27 (3), 309–322. <https://doi.org/10.1016/j.det.2009.05.001>.
- Butte, W., Heinzow, B., 2002. Pollutants in house dust as indicators of indoor contamination. *Rev. Environ. Contam. Toxicol.* 175, 1–46.
- Carneiro, P.A., Umbuzeiro, G.A., Oliveira, D.P., Zanoni, M.V.B., 2010. Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. *J. Hazard Mater.* 174 (1–3), 694–699. <https://doi.org/10.1016/j.jhazmat.2009.09.106>.
- Carrer, P., Maroni, M., Alcini, D., Cavallo, D., 2001. Allergens in indoor air: environmental assessment and health effects. *Sci. Total Environ.* 270 (1–3), 33–42. [https://doi.org/10.1016/S0048-9697\(00\)00791-9](https://doi.org/10.1016/S0048-9697(00)00791-9).
- Chen, B., Ni, S., Sun, L., Luo, X., Zhang, Q., Song, Y., Zhong, Q., Huang, C., Chen, S., Wu, W., 2018. Intramolecular charge transfer tuning of azo dyes: spectroscopic characteristic and third-order nonlinear optical properties. *Dyes Pigments* 158, 474–481. <https://doi.org/10.1016/j.dyepig.2018.05.063>.
- Chequer, F.M.D., Lizier, T.M., de Felício, R., Zanoni, M.V.B., Debonsi, H.M., Lopes, N.P., de Oliveira, D.P., 2015. The azo dye Disperse Red 13 and its oxidation and reduction products showed mutagenic potential. *Toxicol. Vitro* 29 (7), 1906–1915. <https://doi.org/10.1016/j.tiv.2015.08.001>.
- Choi, J.H., Hong, S.H., Lee, E.J., Towns, A.D., 2000. Structure-wet fastness relationships of some blue disperse dyes for polyester. *J. Soc. Dye. Colour.* 116 (9), 273–278. <https://doi.org/10.1111/j.1478-4408.2000.tb00046.x>.
- Chung, K.T., 2016. Azo dyes and human health: a review. *J. Environ. Sci. Health Part C Environ. Carcinog. Ecotoxicol. Rev.* 34 (4), 233–261. <https://doi.org/10.1080/10590501.2016.1236602>.
- Chung, K.T., Cerniglia, C.E., 1992. Mutagenicity of azo dyes: structure-activity relationships. *Mutat. Res. Genet. Toxicol.* 277 (3), 201–220. [https://doi.org/10.1016/0165-1110\(92\)90044-A](https://doi.org/10.1016/0165-1110(92)90044-A).
- Chung, K.T., Stevens, S.E., 1993. Degradation azo dyes by environmental microorganisms and helminths. *Environ. Toxicol. Chem.* 12, 2121–2132. <https://doi.org/10.1002/etc.5620121120>.
- Cooper, E., Kroeger, G., Davis Warnell, K., Clark, C.R., Ferguson, P.L., Stapleton, H.M., 2016. Results from screening polyurethane foam based consumer products for flame retardant chemicals: assessing impacts on the change in the furniture flammability standards. *Environ. Sci. Technol.* 50 (19), 10653–10660. <https://doi.org/10.1021/acs.est.6b01602>.
- Dawson, J.F., 1991. Azobenzene disperse dyes-past development and future prospects. *J. Soc. Dye. Colour.* 107 (11), 395–400. <https://doi.org/10.1111/j.1478-4408.1991.tb01285.x>.
- De Aragão Umbuzeiro, G., Freeman, H.S., Warren, S.H., de Oliveira, D.P., Terao, Y., Watanabe, T., Claxton, L.D., 2005. The contribution of azo dyes to the mutagenic activity of the Cristais River. *Chemosphere* 60 (1), 55–64. <https://doi.org/10.1016/j.chemosphere.2004.11.100>.
- de la Torre, A., Navarro, I., Sanz, P., Martínez, M., de los, Á., 2019. Occurrence and human exposure assessment of perfluorinated substances in house dust from three European countries. *Sci. Total Environ.* 685, 308–314. <https://doi.org/10.1016/j.scitotenv.2019.05.463>.
- Dhungana, B., Peng, H., Kutarna, S., Umbuzeiro, G., Shrestha, S., Liu, J., Jones, P.D., Subedi, B., Giesy, J.P., Cobb, G.P., 2019. Abundances and concentrations of brominated azo dyes detected in indoor dust. *Environ. Pollut.* 252, 784–793. <https://doi.org/10.1016/j.envpol.2019.05.153>.
- Drumond Chequer, F.M., Junqueira, D., de Oliveir, D.P., 2011. Azo Dyes and Their Metabolites: Does the Discharge of the Azo Dye into Water Bodies Represent Human and Ecological Risks? *Advances in Treating Textile Effluent*, pp. 27–48. <https://doi.org/10.5772/19872>.
- Dührkop, K., Shen, H., Meusel, M., Rousu, J., Böcker, S., 2015. Searching molecular structure databases with tandem mass spectra using CSI:FingerID. *Proc. Natl. Acad. Sci. USA* 112 (41), 12580–12585. <https://doi.org/10.1073/pnas.1509788112>.
- Dührkop, K., Fleischauer, M., Ludwig, M., Aksenov, A.A., Melnik, A.V., Meusel, M., Dorrestein, P.C., Rousu, J., Böcker, S., 2019. SIRIUS 4: a rapid tool for turning tandem mass spectra into metabolite structure information. *Nat. Methods* 16, 299–302. <https://doi.org/10.1038/s41592-019-0344-8>.
- El-Ghamaz, N.A., El-Bindary, A.A., El-Boz, R.A., 2017. Electrical and optical properties of new azo dyes derived from m-aminophenol. *Synth. Met.* 226, 207–214. <https://doi.org/10.1016/j.synthmet.2017.02.005>.
- Fang, M., Stapleton, H.M., 2014. Evaluating the bioaccessibility of flame retardants in house dust using an in vitro Tenax bead-assisted sorptive physiologically based method. *Environ. Sci. Technol.* 48 (22), 13323–13330. <https://doi.org/10.1021/es503918m>.
- Ferguson, P.L., Stapleton, H.M., 2017. Comment on “mutagenic azo dyes, rather than flame retardants, are the predominant brominated compounds in house dust. *Environ. Sci. Technol.* 51 (6), 3588–3590. <https://doi.org/10.1021/acs.est.7b00372>.

- Franco, J.H., da Silva, B.F., Dias, E.F.G., de Castro, A.A., Ramalho, T.C., Zanoni, M.V.B., 2018a. Influence of auxochrome group in disperse dyes bearing azo groups as chromophore center in the biotransformation and molecular docking prediction by reductase enzyme: implications and assessment for environmental toxicity of xenobiotics. *Ecotoxicol. Environ. Saf.* 160, 114–126. <https://doi.org/10.1016/j.ecoenv.2018.04.066>.
- Franco, J.H., da Silva, B.F., Oliveira, R.V., Meireles, G., de Oliveira, D.P., de Castro, A.A., Ramalho, T.C., Zanoni, M.V.B., 2018b. Identification of biotransformation products of disperse dyes with rat liver microsomes by LC-MS/MS and theoretical studies with DNA: structure-mutagenicity relationship using Salmonella/microsome assay. *Sci. Total Environ.* 613–614, 1093–1103. <https://doi.org/10.1016/j.scitotenv.2017.08.271>.
- Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Dietrich, S., Sievering, S., Burghardt, R., Schuster, R., Bolte, G., Völkel, W., 2013. Phthalates in German daycare centers: occurrence in air and dust and the excretion of their metabolites by children (LUPE 3). *Environ. Int.* 61, 64–72. <https://doi.org/10.1016/j.envint.2013.09.006>.
- Garner, C.R., Nutman, C.A., 1977. Testing of some azo dyes and their reduction products for mutagenicity using Salmonella typhimurium TA 1538. *Mutat. Res., Fundam. Mol. Mech. Mutagen.* 44 (1), 9–19. [https://doi.org/10.1016/0027-5107\(77\)90110-5](https://doi.org/10.1016/0027-5107(77)90110-5).
- Getzinger, G.J., Ferguson, P.L., 2020. Illuminating the exposome with high-resolution accurate-mass mass spectrometry and nontargeted analysis. *Curr. Opin. Environ. Sci. Heal* 15, 49–56. <https://doi.org/10.1016/j.coesh.2020.05.005>.
- Giusti, F., Massone, F., Bertoni, L., Pellacani, G., Seidenari, S., 2003. Contact sensitization to disperse dyes in children. *Pediatr. Dermatol.* 20 (5), 393–397. <https://doi.org/10.1046/j.1525-1470.2003.20504.x>.
- Glorennec, P., Mercier, F., Blanchard, O., Bonvallot, N., Ramalho, O., Mandin, C., 2011. Cumulative indoor exposures to semi-volatile organic compounds (SVOCs) in France: the ECOS project. In: 12th International Conference on Indoor Air Quality and Climate 2011.
- Golka, K., Kopps, S., Myslak, Z.W., 2004. Carcinogenicity of azo colorants: influence of solubility and bioavailability. *Toxicol. Lett.* 151 (1), 203–210. <https://doi.org/10.1016/j.toxlet.2003.11.016>.
- Haines, S.R., Adams, R.I., Boor, B.E., Bruton, T.A., Downey, J., Ferro, A.R., Gall, E., Green, B.J., Hegarty, B., Horner, E., Jacobs, D.E., Lemieux, P., Misztal, P.K., Morrison, G., Perzanowski, M., Reponen, T., Rush, R.E., Virgo, T., Alkhatry, C., Bope, A., Cochran, S., Cox, J., Donohue, A., May, A.A., Nastasi, N., Nishioka, M., Renninger, N., Tian, Y., Uebel-Niemeier, C., Wilkinson, D., Wu, T., Zambrana, J., Dannemiller, K.C.w., 2020. Ten questions concerning the implications of carpet on indoor chemistry and microbiology. *Build. Environ.* 170, 106589 <https://doi.org/10.1016/j.buildenv.2019.106589>.
- Halden, R., 2014. On the need and speed of regulating triclosan and triclocarban in the United States. *Environ. Sci. Technol.* 48 (7), 3603–3611. <https://doi.org/10.1021/es500495p>.
- Hall, S.M., Patton, S., Petreas, M., Zhang, S., Phillips, A.L., Hoffman, K., Stapleton, H.M., 2020. Per- and polyfluoroalkyl substances in dust collected from residential homes and fire stations in North America. *Environ. Sci. Technol.* 54 (22), 14558–14567. <https://doi.org/10.1021/acs.est.0c04869>.
- Hammel, S.C., Levasseur, J.L., Hoffman, K., Phillips, A.L., Lorenzo, A.M., Calafat, A.M., Webster, T.F., Stapleton, H.M., 2019. Children's exposure to phthalates and non-phthalate plasticizers in the home: the TESIIE study. *Environ. Int.* 132, 105061 <https://doi.org/10.1016/j.envint.2019.105061>.
- Helmüt-Martin, M., Christof, H., Klaus, S., 2013. CN103228738 (A), 07-31. [https://worldwide.espacenet.com/publicationDetails/biblio?CC=CN&NR=103228738A&KC=A&FT=D&ND=&date=20130731&DB=&locale=en\\_EP](https://worldwide.espacenet.com/publicationDetails/biblio?CC=CN&NR=103228738A&KC=A&FT=D&ND=&date=20130731&DB=&locale=en_EP). (Accessed 26 June 2021).
- Heratizadeh, A., Geier, J., Molin, S., Werfel, T., 2017. Contact sensitization in patients with suspected textile allergy. Data of the Information Network of Departments of Dermatology (IVDK) 2007–2014. *Contact Dermatitis* 77 (3), 143–150. <https://doi.org/10.1111/cod.12760>.
- Hoang, A.Q., Tran, T.M., Tu, M.B., Takahashi, S., 2020. Polybrominated diphenyl ethers in indoor and outdoor dust from Southeast Asia: an updated review on contamination status, human exposure, and future perspectives. *Environ. Pollut.* 272, 116012 <https://doi.org/10.1016/j.envpol.2020.116012>.
- Hoffman, K., Garantziotis, S., Birnbaum, L.S., Stapleton, H.M., 2015. Monitoring indoor exposure to organophosphate flame retardants: hand wipes and house dust. *Environ. Health Perspect.* 123 (2), 160–165. <https://doi.org/10.1289/ehp.1408669>.
- Hoffman, K., Hammel, S.C., Phillips, A.L., Lorenzo, A.M., Chen, A., Calafat, A.M., Ye, X., Webster, T.F., Stapleton, H.M., 2018. Biomarkers of exposure to SVOCs in children and their demographic associations: the TESIIE Study. *Environ. Int.* 119, 26–36. <https://doi.org/10.1016/j.envint.2018.06.007>.
- Hogervorst, J., Plusquin, M., Vangronsveld, J., Nawrot, T., Cuypers, A., Van Hecke, E., Roels, H.A., Carleer, R., Staessen, J.A., 2007. House dust as possible route of environmental exposure to cadmium and lead in the adult general population. *Environ. Res.* 103, 30–37. <https://doi.org/10.1016/j.envres.2006.05.009>.
- Hsu, N.Y., Lee, C.C., Wang, J.Y., Li, Y.C., Chang, H.W., Chen, Y.C., Bornehag, C.G., Wu, P. C., Sundell, J., Su, H.J., 2012. Predicted risk of childhood allergy, asthma, and reported symptoms using measured phthalate exposure in dust and urine. *Indoor Air* 22 (3), 186–199. <https://doi.org/10.1111/j.1600-0668.2011.00753.x>.
- Jahreis, S., Trump, S., Bauer, M., Bauer, T., Thürmann, L., Feltens, R., Wang, Q., Gu, L., Grützmann, K., Röder, S., Averbek, M., Weichenhan, D., Plass, C., Sack, U., Borte, M., Dubourg, V., Schüürmann, G., Simon, J.C., von Bergen, M., Hackermüller, J., Eils, R., Lehmann, I., Polte, T., 2018. Maternal phthalate exposure promotes allergic airway inflammation over 2 generations through epigenetic modifications. *J. Allergy Clin. Immunol.* 141 (2), 741–753. <https://doi.org/10.1016/j.jaci.2017.03.017>.
- Joseph, P.D., Zahid, M., Dhanoa, J., de Souza, G.B.D., Groom, H., Lambie, M., 2016. Potent mutagenicity in the Ames test of 2-cyano-4-nitroaniline and 2,6-dicyano-4-nitroaniline, components of disperse dyes. *Environ. Mol. Mutagen.* 57 (1), 10–16. <https://doi.org/10.1002/em.21983>.
- Kassotis, C.D., Hoffman, K., Phillips, A.L., Zhang, S., Cooper, E.M., Webster, T.F., Stapleton, H.M.a., 2021. Characterization of adipogenic, PPAR $\gamma$ , and TR $\beta$  activities in house dust extracts and their association with organic contaminants. *Sci. Total Environ.* 758, 143707 <https://doi.org/10.1016/j.scitotenv.2020.143707>.
- Kutarna, S., Tang, S., Hu, X., Peng, H., 2021. Enhanced nontarget screening algorithm reveals highly abundant chlorinated azo dye compounds in house dust. *Environ. Sci. Technol.* 55 (8), 4729–4739. <https://doi.org/10.1021/acs.est.0c06382>.
- Kweon, D.J., Kim, M.K., Zoh, K.D., 2018. Distribution of brominated flame retardants and phthalate esters in house dust in Korea. *Environ. Eng. Res.* 23 (4), 354–363. <https://doi.org/10.4491/eer.2018.005>.
- Langer, S., Bekö, G., Weschler, C.J., Brive, L.M., Toftum, J., Callesen, M., Clausen, G.B., 2014. Phthalate metabolites in urine samples from Danish children and correlations with phthalates in dust samples from their homes and daycare centers. *Int. J. Hyg. Environ. Health* 217 (1), 78–87. <https://doi.org/10.1016/j.ijheh.2013.03.014>.
- Lanphear, B.P., Matte, T.D., Rogers, J., Clickner, R.P., Dietz, B., Bornschein, R.L., Succop, P., Mahaffey, K.R., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P., Jacobs, D.E., 1998. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels: a pooled analysis of 12 epidemiologic studies. *Environ. Res.* 79 (1), 51–68. <https://doi.org/10.1006/ENRS.1998.3859>.
- Lanphear, B.P., Michael 16Weitzman, M.D., Winter, N.L., Eberly, S., Yakir, B., Tanner, M., Emond, M., Matte, T.D., 2011. Lead-contaminated house dust and urban children's blood lead levels. *Am. J. Publ. Health* 86 (10), 1416–1421. <https://doi.org/10.2105/AJPH.86.10.1416>.
- Levasseur, J.L., Hammel, S.C., Hoffman, K., Phillips, A.L., Zhang, S., Ye, X., Calafat, A.M., Webster, T.F., Stapleton, H.M., 2021. Young children's exposure to phenols in the home: associations between house dust, hand wipes, silicone wristbands, and urinary biomarkers. *Environ. Int.* 147, 106317 <https://doi.org/10.1016/j.envint.2020.106317>.
- Malinauskienė, L., Bruze, M., Ryberg, K., Zimerson, E., Isaksson, M., 2013. Contact allergy from disperse dyes in textiles—a review. *Contact Dermatitis* 68 (2), 65–75. <https://doi.org/10.1111/cod.12001>.
- Mansouri, K., Grulke, C.M., Judson, R.S., Williams, A.J., 2018. OPERA models for predicting physicochemical properties and environmental fate endpoints. *J. Cheminf.* 10 (10) <https://doi.org/10.1186/s13321-018-0263-1>.
- Meeker, J.D., Stapleton, H.M., 2010. House dust concentrations of organophosphate flame retardants in relation to hormone levels and semen quality parameters. *Environ. Health Perspect.* 118 (3), 318–323. <https://doi.org/10.1289/ehp.0901332>.
- Mercier, F., Glorennec, P., Thomas, O., Le Bot, B., 2011. Organic contamination of settled house dust, a review for exposure assessment purposes. *Environ. Sci. Technol.* 45 (16), 6716–6727. <https://doi.org/10.1021/es200925h>.
- Moya, J., Bearer, C.F., Etzel, R.A., 2004. Children's behavior and physiology and how it affects exposure to environmental contaminants. *Pediatrics* 113 (4), 996–1006.
- National Institute of Standards & Technology (NIST), 2018. Certificate of Analysis Standard Reference Material (R) 2585 Organic Contaminants in House Dust (January):16. <https://www.s-nist.gov/srmors/certificates/2585.pdf>.
- Ohe, T., Watanabe, T., Wakabayashi, K., 2004. Mutagens in surface waters: a review. *Mutat. Res. Mutat. Res.* 567 (2–3), 109–149. <https://doi.org/10.1016/j.mrrev.2004.08.003>.
- Overdahl, K.E., Gooden, D., Bobay, B., Getzinger, G.J., Stapleton, H.M., Ferguson, P.L., 2021a. Characterizing azobenzene disperse dyes in commercial mixtures and children's polyester clothing. *Environ. Pollut.* 287 (15), 117299 <https://doi.org/10.1016/j.envpol.2021.117299>.
- Overdahl, K.E., Sutton, R., Sun, J., DeStefano, N.J., Getzinger, G.J., Ferguson, P.L., 2021b. Assessment of emerging polar organic pollutants linked to contaminant pathways within an urban estuary using non-targeted analysis. *Environ. Sci.: Process. Impacts* 23, 429–445. <https://doi.org/10.1039/D0EM00463D>.
- Peng, H., Saunders, D.M.V., Sun, J., Jones, P.D., Wong, C.K.C., Liu, H., Giesy, J.P., 2016. Mutagenic azo dyes, rather than flame retardants, are the predominant brominated compounds in house dust. *Environ. Sci. Technol.* 50 (23), 12669–12677. <https://doi.org/10.1021/acs.est.6b03954>.
- Phillips, A.L., Hammel, S.C., Hoffman, K., Lorenzo, A.M., Chen, A., Webster, T.F., Stapleton, H.M.7., 2018. Children's residential exposure to organophosphate ester flame retardants and plasticizers: investigating exposure pathways in the TESIIE study. *Environ. Int.* 116, 176–185. <https://doi.org/10.1016/j.envint.2018.04.013>.
- Platzek, T., 2013. Overview on toxicity and exposure to azo dyes and aromatic amines. *Toxicol. Lett.* 221, S53. <https://doi.org/10.1016/j.toxlet.2013.06.193>.
- Porobić, S.J., Božić, B., Dramićanin, M.D., Vitnik, V., Vitnik, Z., Marinović-Cincović, M., Mijin, D.Z., 2020. Absorption and fluorescence spectral properties of azo dyes based on 3-amido-6-hydroxy-4-methyl-2-pyridone: solvent and substituent effects. *Dyes Pigments* 175, 108139. <https://doi.org/10.1016/j.dyepig.2019.108139>.
- Ridder, L., Van Der Hoof, J.J.J., Verhoeven, S., De Vos, R.C.H., Van Schaik, R., Vervoort, J., 2012. Substructure-based annotation of high-resolution multistage MSn spectral trees. *Rapid Commun. Mass Spectrom.* 26 (20), 2461–2471. <https://doi.org/10.1002/rcm.6364>.
- Ruttkies, C., Schymanski, E.L., Wolf, S., Hollender, J., Neumann, S., 2016. MetFrag relaunched: incorporating strategies beyond in silico fragmentation. *J. Cheminf.* 8 (3) <https://doi.org/10.1186/s13321-016-0115-9>.
- Salthammer, T., Zhang, Y., Mo, J., Koch, H.M., Weschler, C.J., 2018. Multidisciplinary approaches for the assessment of human exposure to organic pollutants in the indoor environment. *ISEE Conf. Abstr.* <https://doi.org/10.1289/isesisee.2018.p03.3640>.

- Seidenari, S., Manzini, B.M., Danese, P., Motolese, A., 1990. Patch and prick test study of 593 healthy subjects. *Contact Dermatitis* 23 (3), 162–167. <https://doi.org/10.1111/j.1600-0536.1990.tb04777.x>.
- Seidenari, S., Manzini, B.M., Danese, P., 1991. Contact sensitization to textile dyes: description of 100 subjects. *Contact Dermatitis* 24 (4), 253–258. <https://doi.org/10.1111/j.1600-0536.1991.tb01718.x>.
- Seidenari, S., Giusti, F., Massone, F., Mantovani, L., 2002. Sensitization to disperse dyes in a patch test population over a five-year period. *Am. J. Contact Dermatitis* 13 (3), 101–107. <https://doi.org/10.1053/ajcd.2002.34570>.
- Shoeib, M., Harner, T.M., Webster, G., Lee, S.C., 2011. Indoor sources of poly- and perfluorinated compounds (PFCS) in Vancouver, Canada: implications for human exposure. *Environ. Sci. Technol.* 45 (19), 7999–8005. <https://doi.org/10.1021/es103562v>.
- Stapleton, H.M., Dodder, N.G., 2008. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. *Environ. Toxicol. Chem.* 27 (2), 306–312. <https://doi.org/10.1897/07-301R.1>.
- Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., Webster, T.F., Blum, A., 2011. Identification of flame retardants in polyurethane foam collected from baby products. *Environ. Sci. Technol.* 45, 5323–5331. <https://doi.org/10.1021/es2007462>.
- Stapleton, H.M., Eagle, S., Sjödin, A., Webster, T.F., 2012a. Serum PBDEs in a North Carolina toddler cohort: associations with handwipes, house dust, and socioeconomic variables. *Environ. Health Perspect.* 120 (7), 1049–1054. <https://doi.org/10.1289/ehp.1104802>.
- Stapleton, H.M., Sharma, S., Getzinger, G., Ferguson, P.L., Gabriel, M., Webster, T.F., Blum, A., 2012b. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. *Environ. Sci. Technol.* 46 (24), 13432–13439. <https://doi.org/10.1021/es303471d>.
- Stapleton, H.M., Misenheimer, J., Hoffman, K., Webster, T.F., 2014. Flame retardant associations between children's handwipes and house dust. *Chemosphere* 116, 54–60. <https://doi.org/10.1016/j.chemosphere.2013.12.100>.
- Susan, E.F., Elizabeth, A.D., 1988. Sensitization to dyes in textiles and other consumer products. *Cutan. Ocul. Toxicol.* 7 (3), 195–222. <https://doi.org/10.3109/15569528809052329>.
- US Environmental Protection Agency, 2011. *Exposure Factors Handbook: 2011 Edition*. US Environ Prot Agency.
- Vacchi, F.I., Vendemiatti, J.A.S., Brosselin, V., da Silva, B.F., Zanoni, M.V.B., DeMeo, M., Bony, S., Devaux, A., de Aragão Umbuzeiro, G., 2016. Combining different assays and chemical analysis to characterize the genotoxicity of waters impacted by textile discharges. *Environ. Mol. Mutagen.* 57 (7), 559–571. <https://doi.org/10.1002/em.22034>.
- Vacchi, F.I., Vendemiatti, J.A. de S., da Silva, B.F., Zanoni, M.V.B., de Aragão Umbuzeiro, G., 2017. Quantifying the contribution of dyes to the mutagenicity of waters under the influence of textile activities. *Sci. Total Environ.* 601–602, 230–236. <https://doi.org/10.1016/j.scitotenv.2017.05.103>.
- Ventura-Camargo, B.C., de Angelis, D.F., Marin-Morales, M.A., 2016. Assessment of the cytotoxic, genotoxic and mutagenic effects of the commercial black dye in *Allium cepa* cells before and after bacterial biodegradation treatment. *Chemosphere* 161, 325–332. <https://doi.org/10.1016/j.chemosphere.2016.06.085>.
- Waring, D.R., 1984. Heterocyclic dyes and pigments. In: *Comprehensive Heterocyclic Chemistry*. <https://doi.org/10.1016/B978-008096519-2.00012-6>.
- Wojciechowski, K., 1997. Structure - property relationships in azo disperse dyes, derivatives of naphthalimide. *Dyes Pigments* 33 (2), 149–165. [https://doi.org/10.1016/S0143-7208\(96\)00039-3](https://doi.org/10.1016/S0143-7208(96)00039-3).
- Wolf, S., Schmidt, S., Müller-Hannemann, M., Neumann, S., 2010. In silico fragmentation for computer assisted identification of metabolite mass spectra. *BMC Bioinf.* 11 (148) <https://doi.org/10.1186/1471-2105-11-148>.
- Wu, Y., Romanak, K., Bruton, T., Blum, A., Venier, M., 2020. Per- and polyfluoroalkyl substances in paired dust and carpets from childcare centers. *Chemosphere* 251, 126771. <https://doi.org/10.1016/j.chemosphere.2020.126771>.
- Xu, F., Chen, D., Liu, X., Guan, Q., Tan, H., Zhou, D., Shi, Y., Liu, J., Hu, Y., 2021. Emerging and legacy per- and polyfluoroalkyl substances in house dust from South China: contamination status and human exposure assessment. *Environ. Res.* 192, 110243 <https://doi.org/10.1016/j.envres.2020.110243>.
- Young, A.S., Sparer-Fine, E.H., Pickard, H.M., Sunderland, E.M., Peaslee, G.F., Allen, J. G., 2021. Per- and polyfluoroalkyl substances (PFAS) and total fluorine in fire station dust. *J. Expo. Sci. Environ. Epidemiol.* 31, 930–942. <https://doi.org/10.1038/s41370-021-00288-7>.
- Zhang, W., Liu, W., Zhang, J., Zhao, H., Zhang, Y., Quan, X., Jin, Y., 2012. Characterisation of acute toxicity, genotoxicity and oxidative stress posed by textile effluent on zebrafish. *J. Environ. Sci.* 24 (11), 2019–2027. [https://doi.org/10.1016/S1001-0742\(11\)61030-9](https://doi.org/10.1016/S1001-0742(11)61030-9).
- Zheng, G., Boor, B.E., Schreder, E., Salamova, A., 2020. Indoor exposure to per- and polyfluoroalkyl substances (PFAS) in the childcare environment. *Environ. Pollut.* 258, 113714 <https://doi.org/10.1016/j.envpol.2019.113714>.