

Chemicals of High Concern to Children in Children's Clothing, Footwear, and Accessories

By Callie Mathieu and Sara Sekerak, Environmental Assessment Program



Overview

In 2014/2015, the Washington State Department of Ecology (Ecology) conducted a study to evaluate the presence of chemicals of high concern to children (CHCCs) in children's clothing, footwear, and accessories. Ecology carried out this study to provide data for enforcement of Washington State's Children's Safe Products Act (CSPA). The legislation restricts levels of cadmium, lead, and phthalates in children's products to levels of 40 ppm, 90 ppm, and 1000 ppm, respectively. The legislation also requires manufacturers to report to Ecology if a product contains a CHCC.

Ecology purchased 297 articles of children's clothing, footwear, and accessories and sent a subset of those products for laboratory testing of CHCCs. A total of 112 samples consisting of individual product components were analyzed for one or more target CHCC analyte suites. Product types and sample matrices selected for analysis are displayed in Figure 1.

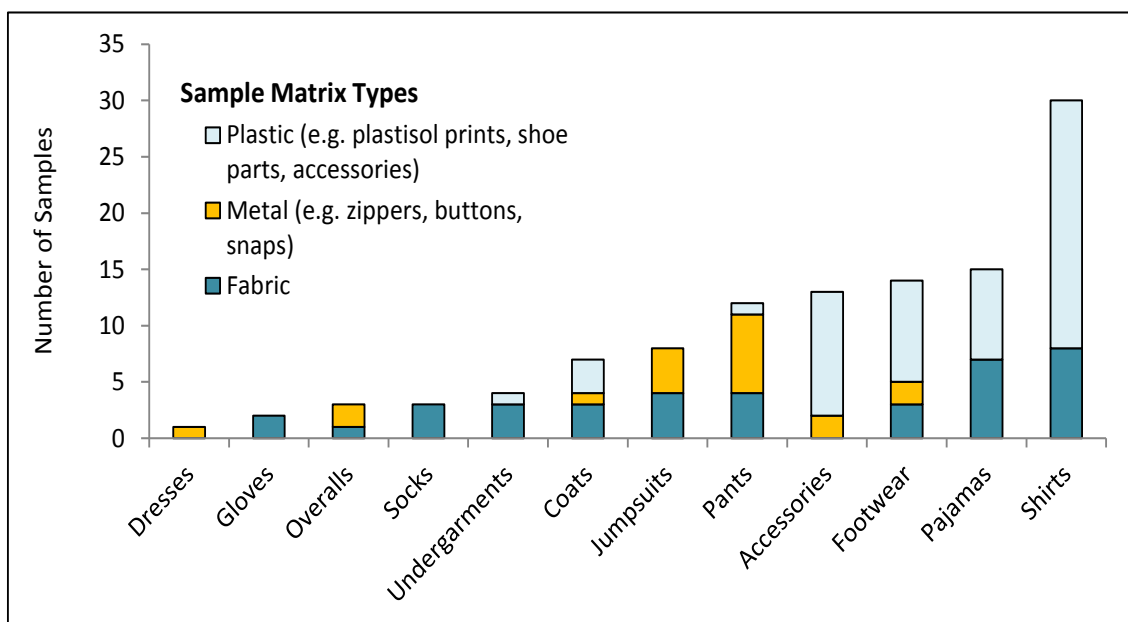


Figure 1. Types and Distribution of Products Submitted for Laboratory Testing.

Ecology selected samples for laboratory analysis of metals and phthalates based on X-ray fluorescence (XRF) screenings. Samples for solvents were selected based on a review of the CSPA manufacturer database and literature reviews.

- Fifty samples were analyzed for metals: antimony, arsenic, cadmium, cobalt, lead, mercury, and molybdenum.
- Fifty samples were analyzed for phthalates: butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di-n-hexyl phthalate (DnHP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), and di-n-octyl phthalate (DnOP).
- Fifty samples were analyzed for solvents: ethylene glycol, styrene, methyl ethyl ketone, octamethylcyclotetra-siloxane (D4), and 4-nonylphenol.

Methods

Sample Collection, Processing, and Selection

During October - December, 2014, Ecology purchased 297 children's products from 14 large retail stores within the south Puget Sound area. The practice of statewide distribution by most of the retail chain stores ensures that products purchased from Puget Sound area stores are representative of products sold across the state. Products collected included children's clothing (74% of samples), children's shoes (17%), and children's accessories (9%). The intended age for the products purchased ranged from newborn (infant) to 12 years.

Products were separated into 1,653 individual components, and screened for metals and chlorine using an XRF analyzer. Fifty component samples that contained the highest levels of XRF-measured metals were selected for analysis of metal analytes. Fifty components with XRF-measured chlorine greater than 15%, which this study used as an indication that the sample consisted of polyvinyl chloride (PVC) material, were selected for analysis of phthalates. Phthalates are added to PVC plastic and PVC-based inks to impart flexibility. Fifty additional components were chosen for analysis of solvents (ethylene glycol, styrene, MEK, D4, and 4-nonylphenol) based on product types identified through a literature review and the CSPA manufacturer reporting database as likely to contain these compounds. A total of 112 samples were sent to the laboratory for analysis, with some samples being sent for analysis of multiple target analyte suites.

Complete laboratory results for this study can be downloaded from Ecology's Product Testing Database <https://fortress.wa.gov/ecy/ptdbpublicreporting/>, by selecting Download Data/Study: *Chemicals of High Concern to Children in Children's Clothing, Footwear, and Accessories - 2014-2015*.

Laboratory Procedures

Table 1 outlines the sample preparation and instrumentation for all analyses. Manchester Environmental Laboratory (MEL) cryomilled, by means of cryogenically freezing and grinding, the laboratory samples prior to analysis. All samples were successfully cryomilled with the exception of 7 samples that consisted of metal matrices.

Data Quality

Cryomill rinseate blanks were analyzed for the target parameters in this study. No analytes were detected above the reporting limit with the following exception: Two cryomill rinseate blanks contained trace levels of DBP (ppb). All concentrations in samples were greater than 10 times the level of the rinseate blank.

Quality control (QC) tests and measurement quality objectives (MQOs) are outlined in the project plan (Mathieu and McCall, 2014). All metal analyte data met MQOs. The solvent analyses met MQOs, with the following minor exceptions: The target method reporting limit (RL) for ethylene glycol could not be obtained due to extraction complications and matrix issues during analysis. A duplicate sample was inadvertently left out of a batch analysis of ethylene glycol samples; however, all other batch QC was analyzed within acceptable ranges and no qualifications were made.

Five DEHP samples were qualified "J", as estimates, for either back calculation or continuing calibration verification checks exceeding QC limits. Six DEHP results, as well as one sample for BBP, DBP, DHP, and DINP, did not meet isotope abundance ratio acceptance limits and were qualified "NJ", indicating that the presence of the analyte was

Table 1. Laboratory Methods.

Analyte	Preparation Method	Analysis Method	Analysis Instrument
Metals	EPA 3052	EPA 200.8	ICP-MS
Phthalates	EPA 3546 mod	EPA 8270D mod	GC-MS
Ethylene Glycol	n/a	EPA 8015C	GC-FID
Styrene	EPA 5030B mod	EPA 8260C	GC-MS
MEK	EPA 5030B mod	EPA 8260C	GC-MS
D4	ALS SOP SVM-D4SO	ALS SOP SVM-D4SO	GC-MS
4-Nonylphenol	EPA 3546 mod	EPA 8270D	GC-MS

tentatively identified and the associated concentration is an estimate. Several QC tests were outside of MQOs, and the associated samples were qualified “UJ” instead of “U”. The qualifier “U” indicates that the analyte was not detected at the quantitation limit, and “UJ” signifies that the quantitation limit is an estimate.

Many of the phthalate samples contained a large co-eluting peak from the non-target analyte bis-2-ethylhexyl terephthalate (DEHT), which prevented quantitation of DnOP at the method reporting limit. As a result of the interference, the reporting limit for DnOP was raised to the amount of the co-eluting peak. Because of the large amounts of DEHT in these samples, the reporting limits for DnOP were much higher than is useful for verifying compliance with CSPA restrictions. The project manager for this study determined that the DnOP results affected by the co-eluting peak did not meet data usability requirements, and she rejected the data.

Metals

A total of 50 product component samples were analyzed by the laboratory for seven metal analytes. Figure 2 displays the results graphically. Mercury results were omitted from the figure.

Samples sent to the laboratory for metals were pre-screened by XRF and targeted for the highest levels of metal analytes across a range of the analytes. Ninety-six percent of samples (48 out of 50) selected for analysis contained one or more of the metals above the reporting limit.

Antimony had the highest detection frequency of any of the analytes, being present in 72% of samples. Antimony was primarily found in fabric and plastisol prints of children’s clothing. Plastisol is a suspension of PVC particles in a liquid plasticizer. It is commonly used as a textile ink for screen-printing. Antimony concentrations ranged from <1 - 2,500 ppm, with a median of 5.9 ppm, for all sample types. In fabric samples alone, antimony was present in all but 2 samples, with a median of 126 ppm. Samples with concentrations from 50 to 300 ppm included primarily polyester clothing. This is in the range expected from the use of antimony trioxide as a catalyst in the process of making polyester.

The highest concentration, 2,500 ppm, was found in a pair of children’s pajamas labeled as flame resistant. This sample also had an XRF-measured bromine level of 4.6%, which may be an indication of the presence of brominated flame retardants. More information about the relationship of antimony and flame retardants can be found in the 2015 report to the Washington State Legislature at:

<https://fortress.wa.gov/ecy/publications/documents/1404047.pdf>

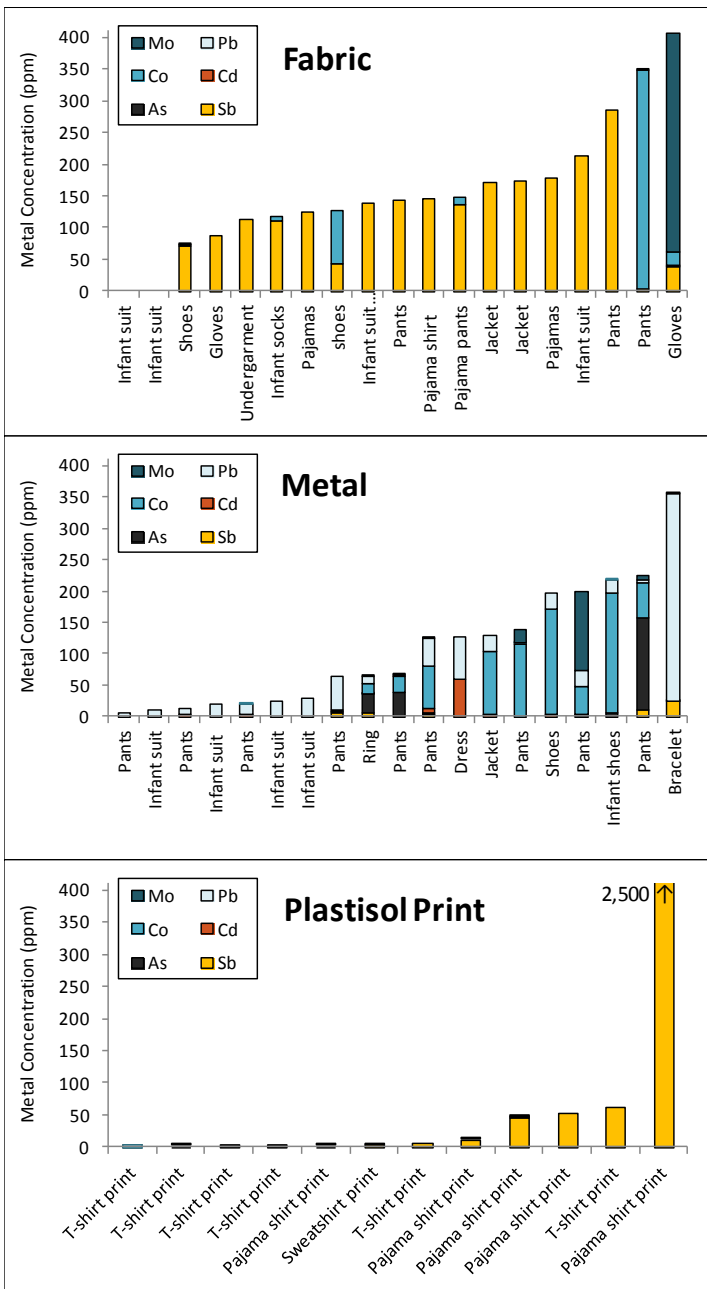


Figure 2. Metal Concentrations in Children’s Products.

Metals - *continued*

Lead was the second-most frequently detected metal analyte (48% of samples), with concentrations ranging from <1 - 329 ppm. Only one sample contained lead higher than Washington's restricted level of 90 ppm. This sample, a metal bracelet, contained 329 ppm of lead. Other samples that contained lead were of much lower concentrations (range = 1.03 - 68 ppm) and primarily consisted of buttons, zipper pulls, and snaps made from metal.

Cobalt was detected in 38% of samples, with higher concentrations (>50 ppm) found in 8 samples. Fabric from a pair of green pants contained the highest cobalt concentration, 344 ppm, and several metal components (i.e. zipper pulls and snaps) had levels ranging from 44 - 190 ppm.

Arsenic had a detection frequency of 34%, with most results near the reporting limit. One sample, a metal strap adjustment on a pair of overalls, contained arsenic at 147 ppm. Cadmium and molybdenum were detected infrequently, with two detections higher than 50 ppm in metal components of clothing. Mercury was not detected above 1 ppm in any of the samples. Summary statistics for all detected metals can be reviewed in Table 2.

Table 2. Summary Statistics of Detected Metals in Children's Products.

Analyte	Antimony	Arsenic	Cadmium	Cobalt	Lead	Mercury	Molybdenum
n	50	50	50	50	50	50	50
# > RL	36	17	7	19	24	4	9
% > RL	72%	34%	14%	38%	48%	8%	18%
Minimum (ppm)*	1.1	1	1.08	1.24	1.03	0.026	1.24
Maximum (ppm)*	2500	147	59.3	344	329	0.05	343
Mean (ppm)*	137	15	11	66	31	0	56
Median (ppm)*	44.1	3.17	1.73	25.2	14.7	0.032	3.92

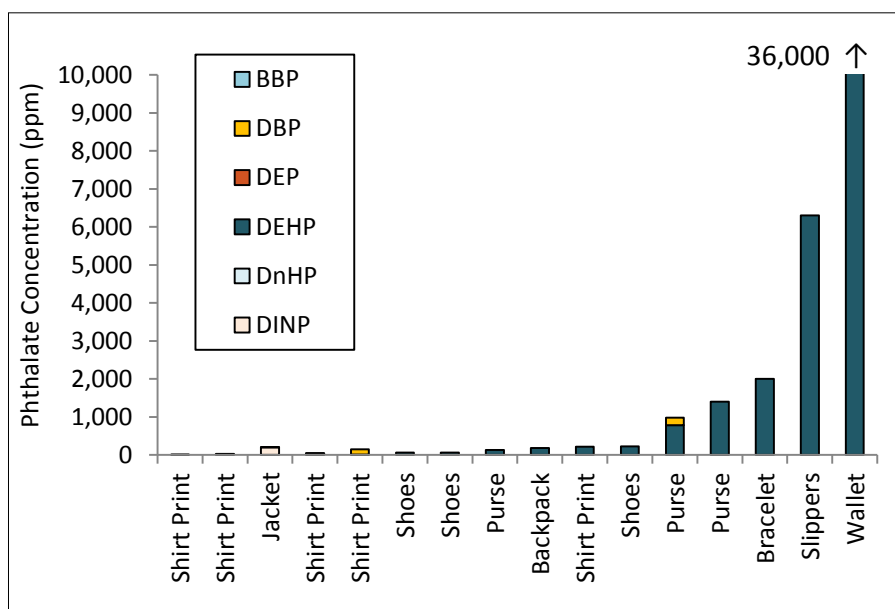
RL= Reporting (quantitation) limit.

* Statistic includes only detected results.

Phthalates

Fifty product-component samples were analyzed by the laboratory for a suite of nine phthalates: BBP, DEHP, DBP, DEP, DMP, DnHP, DIDP, DINP, and DnOP. Components were selected for analysis if the XRF screening measured a chlorine content of 15% or greater, which this study used as an indication that the sample consisted of PVC material. Target samples included soft plastics, synthetic polymeric-fiber (faux fur), and plastisol prints.

Sixteen individual samples (32.1%) were found to contain phthalates, with 6 of the 9 phthalates detected across the sample set (Figure 3; Table 3). DEHP had the highest detection frequency, with 14 samples containing DEHP ranging from 7.4 - 36,000 ppm. DEHP was the only phthalate found in products at concentrations consistent with plasticizer use. Four samples contained DEHP at concentrations higher than 0.1% (1,000 ppm). One sample, the plastic covering of a boy's wallet, had a particularly high level of DEHP, at 3.6% (36,000 ppm).



Four samples contained DBP, with concentrations ranging from 5.3 ppm - 200 ppm, and a median concentration of 69.0 ppm. DEP and DnHP were found separately in two samples at levels of 26 ppm and 14 ppm, respectively.

One plastisol print on a set of pajamas was found to contain four separate phthalates, with detectable levels of DEHP, BBP, DnHP and DINP at low concentrations (12 ppm, 13 ppm, 5.3 ppm, and 14 ppm, respectively).

Forty-six samples contained the non-target analyte bis-2-ethylhexyl terephthalate (DEHT). DEHT is a non-ortho phthalate plasticizer used as a replacement for DEHP and DINP in plastics.

Figure 3. Detected Phthalate Concentrations in Children's Products.

Table 3. Summary Statistics of Detected Phthalates in Children's Products.

Analyte	BBP	DEHP	DBP	DEP	DnHP	DIDP	DINP	DMP	DnOP
n	50	50	50	50	50	50	50	50	4**
# > RL	1	14	4	1	1	0	1	0	0
% > RL	2%	28%	8%	2%	2%	0%	2%	0%	0%
Min (ppm)*	13	7.4	5.3	26	14	---	200	---	---
Max (ppm)*	13	36,000	200	26	14	---	200	---	---
Mean (ppm)*	---	3,390	85.8	---	---	---	---	---	---
Median (ppm)*	---	200	69.0	---	---	---	---	---	---

RL= Reporting (quantitation) limit.

* Statistic includes only detected results. **Includes only DnOP results that were not rejected.

Solvents

Fifty product-component samples were submitted for laboratory analysis of ethylene glycol, methyl ethyl ketone (MEK), 4-nonylphenol (including branched and linear isomers), octamethylcyclotetrasiloxane (D4), and styrene. One third of the samples tested consisted of a plastic matrix (including plastisol prints), and the remaining samples consisted of fabric material.

Twelve of the samples (24%) were found to contain one or more of the target analytes (Table 4). A single sample had detectable levels of ethylene glycol, MEK and D4, resulting in a combined solvent concentration of 140 ppm. Six additional samples contained ethylene glycol as the only solvent, and the remaining five samples had only D4 present. Figure 4 illustrates the combined detected solvent concentrations by type of children's product.

The samples containing solvents were distributed equally between the plastisol print (n=6) and fabric (n=6) matrices. Children's pajamas (33%) and shirts (33%) accounted for a majority of the product types containing solvents. Solvents were also detected in two pairs of gloves, one coat, and one underwear garment.

Ethylene glycol was detected in concentrations ranging from 43 - 590 ppm, with a median of 91 ppm, across both matrix types. The two highest concentrations of ethylene glycol were found in fabric samples. The submitted fabrics were from two shirts, with concentrations of 370 and 590 ppm. The plastisol print samples with detectable ethylene glycol ranged in concentration from 43 - 92 ppm, with a median of 84 ppm.

Methyl ethyl ketone was detected in one of the samples, which also contained ethylene glycol. The plastisol print from the pajama set contained 4.14 ppm of methyl ethyl ketone

Table 4. Summary Statistics of Detected Solvents in Children's Products.

Analyte	Ethylene Glycol	MEK	4-NP**	D4	Styrene
n	50	50	50	50	50
# > RL	7	1	0	6	0
% > RL	14%	2%	0%	12%	0%
Min (ppm)*	43	4.14	---	0.21	---
Max (ppm)*	590	4.14	---	1.21	---
Mean (ppm)*	188	---	---	0.46	---
Median (ppm)*	91	---	---	0.30	---

RL = Reporting (quantitation) limit. * Statistic includes only detected results.

**Includes combined isomers of branched and linear 4-nonylphenol.

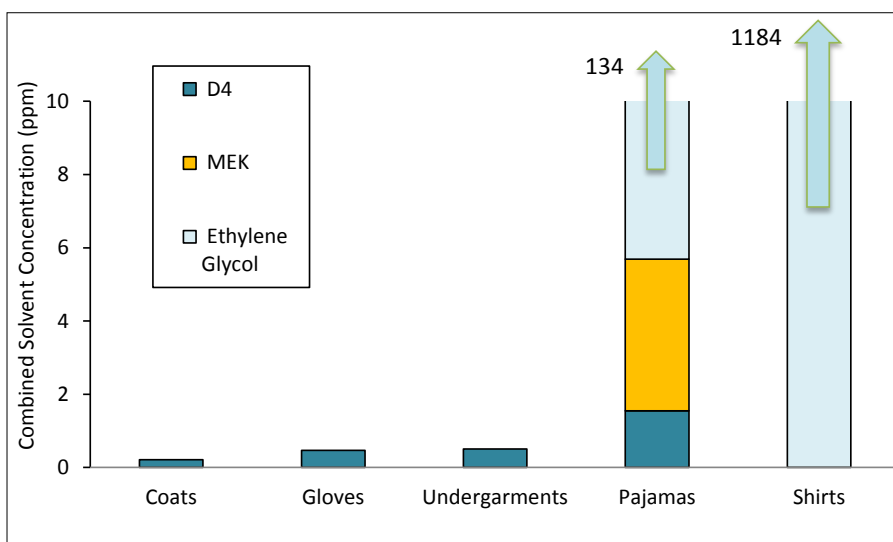


Figure 4. Combined Solvent Concentrations by Type of Children's Product.

Styrene was not detected above 1 ppm in any of the samples. The combined isomers of 4-nonylphenol (branched and unbranched) were not detected in concentrations above variable detection levels (4.7 - 130 ppm).

D4 was detected at low levels in six samples, with concentrations ranging from 0.211 - 1.21 ppm, with a median of 0.299 ppm.

Conclusions

In 2014, Ecology evaluated children's products for the presence of select chemicals from Washington State's Chemicals of High Concern to Children (CHCC) list to support enforcement of the Children's Safe Products Act. Ecology staff purchased 297 articles of children's clothing, footwear, and accessories from 14 large retail stores in Washington and screened the product components for metals and chlorine with an XRF analyzer. A subset of product samples were sent to laboratories for analysis of metals, phthalates, and solvents: ethylene glycol, MEK, styrene, D4, and 4-nonylphenol.

Laboratory results of this study include the following:

- One or more of the target metal analytes were detected above the reporting limit in 96% of samples (48 out of 50).
- Antimony was detected in 72% of samples, at concentrations ranging from <1 - 2,500 ppm. Antimony in fabric samples had a median concentration of 126 ppm. The highest antimony result, 2,500 ppm, was found in a pair of children's pajamas labeled as flame resistant; this sample also had an XRF-measured bromine level of 4.6%.
- Lead was the second-most frequently detected metal analyte (48% of samples), with concentrations ranging from <1 - 329 ppm. The sample containing 329 ppm of lead, a children's bracelet, was the only sample above the state's restricted level of 90 ppm. Lower concentrations of lead (1.08 - 68 ppm) were found in metal buttons, zipper pulls, and snaps.
- Cobalt was detected in 38% of samples, with concentrations above 50 ppm in 8 samples. Arsenic, cadmium, and molybdenum were detected less frequently, at low levels. No samples contained mercury above 1 ppm.
- One or more of the target phthalates were detected above the reporting limit in 32% of samples (16 out of 50). DEHP was detected at the highest frequency, with 14 samples ranging from 7.4 - 36,000 ppm. DEHP was the only phthalate found at concentrations consistent with plasticizer use. Four samples contained DEHP at concentrations higher than the state restriction of 0.1% (1,000 ppm).
- Ethylene glycol, MEK, and/or D4 were detected in 24% of samples (12 out of 50) submitted for solvent analyses. Ethylene glycol was detected the most frequently and at the highest concentrations, with detections ranging from 43 - 590 ppm. MEK and D4 were found at very low levels (0.21 - 4.1 ppm), and 4-nonylphenol and styrene were not detected above reporting limits in any sample.

Recommendations

The laboratory data for this project were submitted to Ecology's Children's Safe Products Act (CSPA) enforcement coordinator for assessment of compliance with Washington State laws. Responsible parties (manufacturers, distributors, and/or retailers) of products that appear to violate restrictions, or have not reported as required by the CSPA reporting rule, have been notified and enforcement actions are ongoing. Where violations are pre-empted by federal law, results have been provided to the Consumer Product Safety Commission for enforcement.

Department of Ecology Contacts

Lead Author: Callie Mathieu

callie.mathieu@ecy.wa.gov

Environmental Assessment Program

P.O. Box 47600

Olympia, WA 98504-7600

Communications Consultant

Phone: 360-407-6764

Washington State Department of Ecology: www.ecy.wa.gov

Headquarters, Olympia: 360-407-6000

If you need this document in a format for the visually impaired, call 360-407-6764.

Persons with hearing loss can call 711 for Washington Relay Service.

Persons with a speech disability can call 877-833-6341.

Publication Information

This report is available on the Department of Ecology's website at: <https://fortress.wa.gov/ecy/publications/1503039.html>

The Quality Assurance Project Plan for this study is available on at:

<https://fortress.wa.gov/ecy/publications/SummaryPages/1403125.html>

Data for this project are available at Ecology's Product Testing Database at:

<https://fortress.wa.gov/ecy/ptdbpublicreporting/>

Select Study, *Chemicals of High Concern to Children in Children's Clothing, Footwear, and Accessories - 2014-2015*.

Websites

Children's Safe Products Act: <http://www.ecy.wa.gov/programs/hwtr/RTT/cspa/index.html>

List of Chemicals of High Concern to Children: <http://www.ecy.wa.gov/programs/hwtr/RTT/cspa/chcc.html>

References

Mathieu, C. and M. McCall, 2014. Quality Assurance Project Plan: Chemicals of High Concern to Children in Children's Clothing, Footwear, and Accessories. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-125. <https://fortress.wa.gov/ecy/publications/SummaryPages/1403125.html>

Van Bergen, S.; Davies, H.; Grice, J.; Mathieu, C.; Stone, A., 2015. Flame Retardants—A Report to the Legislature. Washington State Department of Ecology, Olympia, WA. Publication No. 14-04-047. <https://fortress.wa.gov/ecy/publications/SummaryPages/1404047.html>