DEPARTMENT OF ECOLOGY
State of Washington

Addendum #2 to Quality Assurance Project Plan

Flame Retardants in General Consumer and Children's Products

February 2016

Publication No. 12-07-025B

Publication Information

Addendum

This addendum is on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1207025B.html

This addendum is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan.

Original Publication

Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products

Publication No. 12-07-025

The Quality Assurance Project Plan is available on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/summarypages/1207025.html

Author of this Addendum

Saskia van Bergen
Hazardous Waste and Toxics Reduction
Washington State Department of Ecology
Olympia, Washington 98504-7710

Addendum #2 to Quality Assurance Project Plan

Flame Retardants in Children's Products

February 2016

Approved by:

Signature: _____ Date: 2/25/2016
Kara Steward, Client, HWTR-HQ

Signature: _____ Date: 2/25/16
Samuel Iwenofu, HWTR-HQ Quality Assurance Officer

Signature: _____ Date: 2/25/16
Saskia van Bergen, Author/Project Manager, HWTR-HQ

Signature: _____ Date: 2/25/2016
Ken Zarker, Author Supervisor, HWTR-HQ

Signature: _____ Date: 2.25.16
Carol Kraege, Clients Supervisor, HWTR-HQ

HWTR-HQ: Hazardous Waste and Toxics Reduction Program, Headquarters Office

Overview

Previous Studies

In 2012, the Washington Department of Ecology (Ecology) initiated a flame retardant study to:

- Determine compliance with the Washington State ban on the polybrominated diphenyl ether (PBDE) class of flame retardants.
- Assess the levels of flame retardants in general consumer and children's products.
- Determine compliance with the state's Children's Safe Product Act (CSPA) reporting requirements for flame retardants that appear on the list of Chemicals of High Concern to Children (CHCC).

Various consumer products bought in 2012-2013 were screened for the presence of bromine using a portable XRF instrument. A total of 163 product components from 125 products were analyzed for the compounds of interest identified in the *Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products* (Ecology, 2012). The samples selected for analysis included all those indicating substantial amounts of bromine, which is used to screen for brominated flame retardants, and a number of random samples where bromine was not detected. A subsequent Addendum (Ecology 2014) included the analysis of three other compounds to determine compliance and assess levels of additional flame retardants. A second Supplemental Project (Ecology 2014b) screened three products for two more analytes to confirm the presence of additional flame retardants of interest.

These studies found that manufacturers have moved away from using polybrominated diphenyl ethers (PBDEs) and that their products comply with Washington regulations regarding PBDEs. However, while PBDEs are no longer being used, alternative flame retardants are being detected including tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(1-chloro-2-propyl) phosphate (TCPP), triphenyl phosphate (TPP), 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate (V6), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) and the mixtures Firemaster® 550 and 600 (Ecology 2014c, 2014d).

Resorcinol diphenyl phosphate (RDP) was included in the initial QAPP but was not analyzed due to lack of pure standard material. Of the products tested, foam from twelve children's chairs from nine manufacturers were sent for laboratory analysis. Eight contained flame retardants in a component at greater than the percent level.

Changes in Flammability Standards

In January 2015, Technical Bulletin (TB) 117-2013 became mandatory in California and replaced TB 117, one of the major drivers for flame retardant use in upholstered furniture in the United States. While the new standard can be met without flame retardants, it does not ban their use. In January 2015, California Senate Bill 1019 also became mandatory. This law requires any flexible polyurethane foam or upholstered furniture sold in California that must meet TB117-2013 to identify whether or not the product contains added flame retardant chemicals. Children's chairs are required in California to meet TB117-2013.Since this regulation went into effect it is likely the use of additive flame retardants in upholstered furniture has decreased. A study has not been performed to assess whether products sold in Washington were manufactured prior to this new California requirement or if the use of flame retardants in children's products has decreased.

Flammability Standards for Play Tents and Tunnels

Outdoor items, such as camping tents and sleeping bags are often certified to meet flammability standards developed by the Industrial Fabrics Association International (IFAI).[1] CPAI-84 is the standard that applies to tents. The standards do not require the use of flame retardants. Tents sold in California, Louisiana, Massachusetts, Michigan, Minnesota, New York, and New Jersey are required to meet CPAI-84.

A recent study (Keller 2014) evaluated whether additive flame retardants were being applied to camping tents. The study found that ten out of eleven tents tested contained flame retardants in the percent level. The flame retardants detected were decabromodiphenyl ether (deca-BDE), TDCPP, TBBPA, and TPP. While these products are not considered household furniture, many toy tents and tunnels designed for children to use indoors meet the same flammability requirement (CPAI-84). It is unclear if the products would be treated with the same flame retardants but researchers at Duke University (Heather Stapleton, 2014) tested ten children's play tents and tunnels purchased in 2011-2012. TDCPP and TCPP were found in four of the products at concentrations ranging from 0.1% to 1% by weight. Children's products containing TDCPP must be reported to Ecology under the Children's Safe Product Act.

Scope of Current Study

The objectives of this study are to:

- Determine how/if the changes in California regulations have impacted the upholstered children's chairs and sofa products sold in Washington.
- Assess the level of flame retardants in children's play tents and tunnels and the correlation with CPAI-84.
- Determine compliance with the state's CSPA reporting requirements for flame retardants on the CHCC list.

[1] Formerly the Canvas Products Association International (CPAI)

This addendum describes additional sampling and testing of children's products including:

- Purchasing children's chairs and couches containing polyurethane foam and children's play tents and tunnels.
- Screening all foam and fabric components for bromine, antimony, and phosphorus, which are indicators for flame retardants.
- Submitting selected samples of foam and fabric with high screening result for bromine, antimony, and phosphorous to the laboratory for additional flame retardant analyses.

Organization and Schedule

Table 1. Organization of Project Staff and Responsibilities

Staff	Title	Responsibilities
Kara Steward HWTR-HQ (360) 407-6250	Client	Reviews project scope and budget; tracks progress.
Saskia van Bergen HWTR-HQ (360) 407-6609	Project Manager	Writes QAPP Addendum; coordinates with laboratory; oversees product collection, processing, and transportation of samples to laboratory; conducts QA review of data; analyzes and interprets data.
Christina Wiseman HWTR-HQ 360-407-7672	Sampling Lead	Purchases products; conducts XRF screening of products; sends samples to laboratory; enters data into Product Testing Database.
Samuel Iwenofu HWTR-HQ (360) 407-6964	HWTR QA Officer	Reviews draft QAPP Addendum and approves final QAPP.
Ken Zarker HWTR-HQ (360) 407-6698	Section Manager for the Project Manager	Tracks progress; reviews draft QAPP Addendum; approves final QAPP Addendum.
Carol Kraege HWTR-HQ (360) 407-6906	Section Manager for the Client	Reviews project scope and budget; tracks progress; reviews draft QAPP Addendum; approves final QAPP Addendum.

HWTR-HQ: Hazardous Waste and Toxics Reduction Program-Headquarters. QAPP: Quality Assurance Project Plan.

Table 2. Proposed Schedule for Completing Field and Laboratory Work and Reports

Sample Collection and Laboratory Work	
Lead / Support staff	Saskia van Bergen/Christina Wiseman
Sample collection, XRF screening and preparation	Within two months of QAPP completion
Phosphorus screening	Three weeks after shipment for Phosphorus
Laboratory analyses for FR1 (TCPP, TDCPP, TCEP, TPP, RDP)	Two months after decision for analyses based on screening results
Laboratory analyses for FR2 (V6, HBCD, TBBPA)	Two months after decision for analyses based on FR1 results
Laboratory analyses for FR3 (TBB and TBPH)	Two months after decision for analyses based on FR1 results
Reporting to Product Testing Database	
Lead / Support staff	Saskia van Bergen/Christina Wiseman
Schedule	
Review/Qualify data	one month after receipt of data
Upload to database	one month after reviewed
Data publically available	five months after receipt of data
Final Report	
Author Lead	Saskia van Bergen
Schedule	
Draft due to client/peer reviewer	3 months after receipt of data
Final to publications coordinator	4 months after receipt of data
Final listed on the web	5 months after receipt of data

Project Budget

Proposed cost estimate for product collection and laboratory analysis totals $64,240. Table 3 shows the estimated costs for this project.

Table 3. Project budget and funding

Product/Parameter	Number of Samples	QC Samples**	Average Cost per Sample	Subtotal
Product Collection	80	-	$100	$8,000
Phosphorus	120	6	$40	$5,040
FR1 (TCPP, TDCPP, TCEP, TPP, RDP)	50	9	$350	$20,650
FR2 (V6, HBCD, TBBPA)	20*	3	$800	$28,800
FR3 (TBB and TBPH)	4*	3	$250	$1,750
	Total:			$64,240

** Number of samples subject to change depending on screening and results from FR1.*

***QC samples in this table include those that are not provided free of charge (matrix spikes, matrix spike duplicates, and lab duplicates). Method blanks, spike blanks and spike blank duplicates are included at no charge.*

Experimental Design

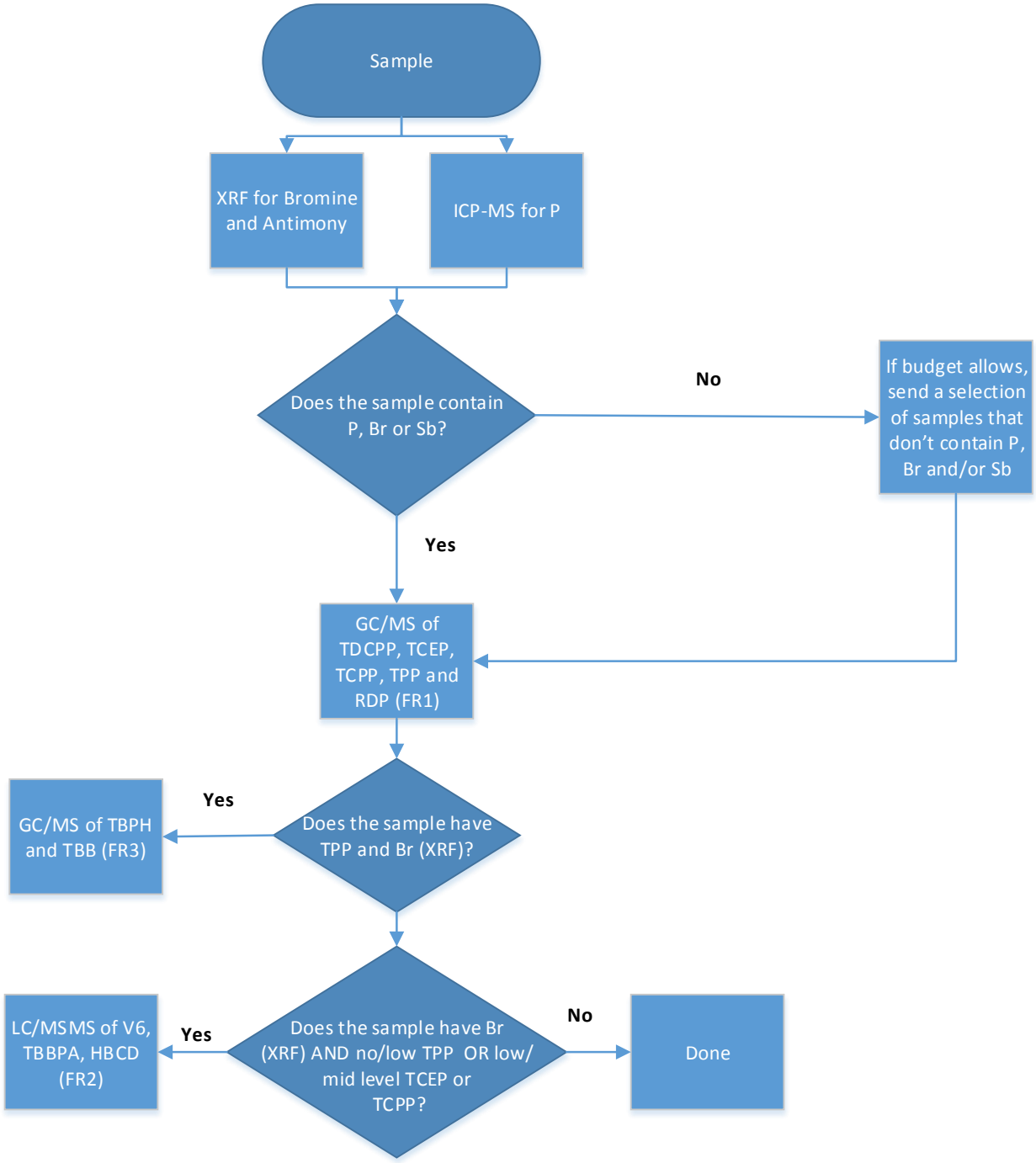
Approximately 80 children's chairs and couches containing polyurethane foam and children's play tents and tunnels from various manufacturers will be gathered for testing. Products will be collected by HWTR staff either in person or through internet retailers. An inventory will be taken of the children's chairs and couches in the department stores where products are purchased. If available, manufacture dates and California labels will be recorded. Emphasis will be given to chairs and couches with different California labels. Preference will be given to products without California labels, those with the TB-117 label and those with the SB 1019 label stating that the product does contain additive flame retardants.

All products will have at least one component screened for bromine and antimony using a portable XRF. The matrices of interest are foam and fabric. Photos of the California labels for the children's chairs and couches and the CPAI-84 label on the play tents and tunnels will be recorded and stored in Ecology's Product Testing Database.

Samples will follow the screening and analytical flow in Figure 1. Product components will be screened for bromine and antimony using XRF. Approximately 120 components will be screened for phosphorus using EPA 3050B for sample digestion and EPA method 6020 for analysis. The objective of both screening methods is to evaluate a large number of samples for bromine, antimony, and phosphorous. Detection of antimony and/or bromine will indicate the potential presence of halogenated flame retardants. Detection of phosphorous will indicate the potential presence of phosphate-based flame retardants, either halogenated or non-halogenated alternatives. The screening methodologies will enable limited sampling funds to focus on those samples most likely to contain one of the flame retardants of interest. An overview of the sample preparation and XRF screening is discussed in the Original QAPP. Ecology's *Standard Operating Procedures for Product Testing* is available upon request.

Based on the screening results, a subset of samples will then be selected and analyzed for TCEP, TCPP, TDCPP, TPP and RDP. Depending on the screening results, samples may also be sent out for TBPH and TBB and/or HBCD, V6 and TCEP.

Figure . Flow Chart



Analytical Laboratory

Manchester Environmental Laboratory (MEL) or a contract laboratory will conduct the analytical work. The Original QAPP and Addendum #1 had the laboratory methods and reported limits for all the analyses except phosphorus. TBB and TBPH were qualitatively analyzed in a Supplemental QAPP. The method used for the analysis of TBB and TBPH will be determined by the number of samples. The options are listed in Table 4.

Table 4. Laboratory Methods and Reporting Limits (RL) for FR3

Analyte	Digestion Method	Instrumentation	Method	RL (ppm)++
Phosphorus	3050B	ICP-MS+	EPA 6020	10.0
TBB	3540C, 3545A or 3546	GC/MS+++ or GC/ECNI-MS++++	EPA 8270 or as described by Stapleton 2012	100
TBPH	3540C, 3545A or 3546	GC/MS+++ or GC/ECNI-MS++++	EPA 8270 or as described by Stapleton 2012	100

+ ICP-MS = Inductively coupled plasma mass spectrometry
++ppm = parts per million of analyte in sample by weight
+++ GC/MS = Gas chromatography/mass spectroscopy
++++ GC/ECNI-MS = Gas chromatograph electron capture negative ionization mass spectroscopy

The reporting limits in the original plans were not achievable and were increased to 100 ppm for organic analyses. The methods are repeated below for clarity in Tables 5 and 6.

Table 5. Laboratory Methods and Reporting Limits for FR1

Analyte	Digestion Method	Instrumentation	Method	RL+ (ppm)++
TCEP	3546	GC/MS+++	EPA 8270	100
TCPP	3546	GC/MS+++	EPA 8270	100
TDCPP	3546	GC/MS+++	EPA 8270	100
TPP	3546	GC/MS+++	EPA 8270	100
RDP	3546	GC/MS+++	EPA 8270	100

+RL = Reporting Limit
++ppm = parts per million of analyte in sample by weight
+++ GC/MS = Gas chromatography/mass spectroscopy

Table 6. Laboratory Methods and Reporting Limits for FR 2

Analyte	Digestion Method	Instrumentation	Method	RL+ (ppm)++
V6	3540C or 3546	LC/MSMS+++	EPA 1694	100
HBCD	3540C or 3546	LC/MSMS+++	EPA 1694	100
TBBPA	3540C or 3546	LC/MSMS+++	EPA 1694	100

+RL = Reporting Limit
++ppm = parts per million of analyte in sample by weight
+++ LC/MSMS = Liquid chromatography/mass spectroscopy/mass spectroscopy

Quality Objectives

Measurement Quality Objectives (MQOs) for TCEP, TCPP, TDCPP, TPP and RDP are listed in Table 8 of the original QAPP and for V6, TBBPA and HBCD in Table 5 of the Addendum #1 (Ecology, 2012, Ecology 2013, respectively). Some of the values have been adjusted from the original QAPP and Addendum based on the results from the previous study. The updated MQOs are listed below. Any deviations from these MQOs will be noted in the final report.

Table 7. Updated MQOs for Laboratory Analyses in previous QAPP

Analyte	Laboratory Control Samples (LCS) (recovery)	Matrix+ Spikes (recovery)	Duplicates+ (RPD) ++	Method Blanks (ppm) +++	Surrogate Recovery (recovery)
V6	60-140%	60-140%	± 40%	< 5.0	50-150%
HBCD	60-140%	60-140%	± 40%	< 5.0	50-150%
TBBPA	60-140%	60-140%	± 40%	< 5.0	50-150%
TDCPP	60-140%	60-140%	± 40%	< 5.0	50-150%
TCEP	60-140%	60-140%	± 40%	< 5.0	50-150%
TCPP	60-140%	60-140%	± 40%	< 5.0	50-150%
TPP	60-140%	60-140%	± 40%	< 5.0	50-150%
RDP	50-150%	50-150%	50-150%	< 5.0	50-150%

XRF standard acceptance criteria for the XRF standards are in Ecology's *Standard Operating Procedures for Product Testing*. Readings of an additional standard containing bromine (PE-H-30A, Database ID STD-1-2-1) will be taken at the beginning and ending of each screening session.

Additional MQOs are listed in Tables 8 and 9 below.

Table 8. Additional MQOs for Added Laboratory Analyses

Analyte	Laboratory Control Samples (LCS) (recovery)	Duplicates (RPD) +	Method Blanks (ppm) ++
Phosphorus	80-120%	± 20%	<10 ppm

[+]RPD = Relative Percent Difference

[++]ppm = parts per million

As mentioned previously, the analysis of TBB and TBPH will be determined once the study is initiated. It will either be qualitative as described in the Supplemental QAPP or quantitative. If quantitative, the MQOs are listed in Table 9.

Table 9. MQOs for Laboratory Analyses

Analyte	Laboratory Control Samples (LCS) (recovery)	Matrix+ Spikes (recovery)	Duplicates+ (RPD) ++	Method Blanks (ppm) +++	Surrogate Recovery (recovery)
TBB	50-150%	50-150%	50-150%	< 5.0	50-150%
TBPH	50-150%	50-150%	50-150%	< 5.0	50-150%

Quality Control Procedures

Laboratory QC tests will consist of laboratory control samples, matrix spikes, matrix spike duplicates, laboratory duplicates, and method blanks. Laboratory QC tests for TCEP, TCPP, TDCPP, TPP and RDP are listed in Table 9 of the original QAPP and V6, TBBPA and HBCD in Table 6 of Addendum #1 (Ecology, 2012, Ecology 2013). Final flame retardant results will be corrected for surrogate recovery.

Measurement quality objectives (MQOs) for phosphorus are listed in Table 10.

Table 10. Quality Control Tests

Analyte	LCS	Spike Blank Duplicate	Laboratory Duplicates	Method Blanks
Phosphorus	1/batch	1/batch	1/batch	1/batch

LCS: laboratory control sample (spike blank)
Batch: 20 or fewer samples

Data Management

All project data will be stored in Ecology's Product Testing Database. Product descriptions, purchase receipts, photos of the products, XRF data, laboratory data, and case narratives will be stored in the database.

All data management procedures including data verification, validation, and quality evaluation will follow those stated in the original QA Project Plan (Ecology, 2012). If an independent third party data validation and review is necessary, the Project Manager will consult with the HWTR QA Officer.

Report

A report summarizing the findings will be published after an internal review period. The final report will include:

- A summary of screening and laboratory analysis
- Any deviations from the QAPP and addendum in terms of sample preparation, QA/QC requirements, etc.
- Data on specific product components and whether the levels of flame retardants found would require reporting as dictated by the CSPA legislation

References

Keller, A. S.; Raju, N. P.; Webster, T. F.; Stapleton, H. M.; 2014. *Flame Retardant Applications in Camping Tents and Potential Exposure.* Environmental Science and Technology Letters, Vol. 1(2): 152-155.

Stapleton, Heather, private correspondence, 8/21/2014.

State of California (California), 2000. Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation, Technical Bulletin 117, Requirements, *Test Procedure and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture*, 8 pages, http://www.bhfti.ca.gov/industry/117.pdf.

U.S. Environmental Protection Agency (EPA) *Test Methods for Evaluating Solid Waste*, SW-846, Method 3050B.

U.S. Environmental Protection Agency (EPA) *Test Methods for Evaluating Solid Waste*, SW-846 Method 3546.

U.S. Environmental Protection Agency (EPA) *Test Methods for Evaluating Solid Waste*, SW-846 Method 3540C.

U.S. Environmental Protection Agency (EPA) *Test Methods for Evaluating Solid Waste*, SW-846 Method 6020B.

U.S. Environmental Protection Agency (EPA) *Test Methods for Evaluating Solid Waste*, SW-846 Method 8270D.

Washington State Department of Ecology (Ecology), 2012. *Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products*, publication number 12-07- 025, 29 pages, https://fortress.wa.gov/ecy/publications/publications/1207025.pdf.

Washington State Department of Ecology (Ecology), 2014. *Addendum #1 to Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products*, Publication number 12-07- 025a, 8 pages, https://fortress.wa.gov/ecy/publications/SummaryPages/1207025a.html.

Washington State Department of Ecology (Ecology), 2014b. *Quality Assurance Project Plan: Supplemental Analysis of Flame Retardants in General Consumer and Children's Products*, publication number 14-03-111, 25 pages, https://fortress.wa.gov/ecy/publications/SummaryPages/1403111.html

Washington State Department of Ecology (Ecology), 2014c. *Flame Retardants in General Consumer and Children's Products*, publication number 14-04-021, 41 pages, https://fortress.wa.gov/ecy/publications/SummaryPages/1404021.html

Washington State Department of Ecology (Ecology), 2014d. *Flame Retardants- A Report to the Legislature*, publication number 14-04-047, 100 pages, https://fortress.wa.gov/ecy/publications/documents/1404047.pdf