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**Addendum #1 to
Quality Assurance Project Plan**

**Flame Retardants in General Consumer
and Children's Products**

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Addendum

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

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Addendum #1 to Quality Assurance Project Plan

Flame Retardants in General Consumer and Children's Products

November 2013

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DEPARTMENT OF ECOLOGY
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November 15, 2013

TO: Joshua Grice, Client
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SUBJECT: Addendum #1 to Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products

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Overview

In 2012, the Washington State Department of Ecology (Ecology) initiated a study with the objectives to:

- Determine compliance with the Washington State ban on the 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 Chemicals of High Concern to Children (CHCC) list.

A portable XRF instrument was used to screen various consumer products for the presence of bromine and chlorine. A subset of these samples was analyzed for the initial compounds of interest identified in the **Quality Assurance Project Plan: Flame Retardants in General Consumer and Children's Products** (Ecology, 2012) listed in Table 1. This subset of samples included all samples showing the presence of substantial amounts of bromine and chlorine and a random selection of some of the samples where bromine and chlorine were not detected. The analyses were conducted by Ecology's Manchester Environmental Laboratory (MEL) using modified EPA methods as there are no standard approved methods for most of these analytes.

Table 1 Analytes of interest in the Original QAPP

Analytes	CAS Number
PBDEs	
Pentabromodiphenyl ether mix	32534-81-9
Octabromodiphenyl ether mix	32536-52-0
Decabromodiphenyl ether	1163-19-5

Decabromodiphenyl ethane	84852-53-9
Chlorinated phosphates	
TCEP	115-96-8
TCPP	13674-84-5
TDCPP	13674-87-8
Non-halogenated phosphates	
RDP	115-86-6
TPP	125997-21-9

Early in 2013 through the CSPA reporting requirements, Ecology was notified that a product sampled for this study contained another flame retardant on the CHCC list. This flame retardant, tetrabromobisphenol A, was not part of the original group of analytes selected for analysis. As part of the effort to determine compliance and assess levels of all pertinent flame retardants, three additional flame retardants were identified for analysis. These new flame retardants include hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate) (V6). All three flame retardants contain either chlorine or bromine and may be present in the earlier samples sent for analysis. Stapleton et al. (2011, 2012) showed the presence of V6 in both consumer's and children's products.

This addendum describes two substantive changes to the original QAPP:

- 1) A contract laboratory will measure concentrations of three additional flame retardants in 60 archived samples from the original QAPP sampling event.
- 2) The contract lab will analyze the 60 archived product samples for the chlorinated phosphate and triphenyl phosphate flame retardant compounds already analyzed by MEL to confirm the ability to measure these analytes.

Quality objectives for the chlorinated phosphates and triphenyl phosphate are described in the original Quality Assurance Project Plan (QAPP).

Experimental Design

60 samples from the original project were selected for both the analysis of the added target chemicals in Table 2 and the reanalysis of the analytes in Table 3. Samples that had XRF results reporting chlorine or bromine were selected as well as those with preliminary results reporting TCEP, which is a large impurity in "V6" (Stapleton 2011). The remaining selected samples were chosen based on the original reported results in order to test samples with a range of analyte concentrations or if the product was identified to have a California Technical Bulletin 117 label (California, 2000). This label indicates the sample may have met California flammability testing requirements through chemical addition.

The three additional target chemicals proposed for testing and recommended practical quantitation limits (PQLs) are listed in Table 2. Flame retardants are commonly used in products at the percent levels (Stapleton et al., 2011), which is two orders of magnitude above the PQLs.

Table 2. Analytes of Interest

Analytes	CAS Number	PQL (ppm+)
V6 - 2,2-bis(chloromethyl)propane-1,3-diyl-tetrakis(2-chloroethyl)bis(phosphate)	38051-10-4	100++
HBCD – Hexabromocyclododecane	3194-55-6 25637-99-4	100++
TBBPA - Tetrabromobisphenol A	79-94-7	100++

+ppm = parts per million of analyte in sample by weight

++ No PQL exists for these compounds; the PQL for PBDEs is used as a surrogate.

Table 3. Analytes from the Original QAPP to be measured by a second laboratory

Analytes	CAS Number	PQL (ppm+)
Chlorinated phosphates		
TCEP	115-96-8	100++
TCPP	13674-84-5	100++
TDCPP	13674-87-8	100++
Non-halogenated phosphates		
TPP	125997-21-9	100++

+ppm = parts per million of analyte in sample by weight

++ No PQL exists for these compounds; the PQL for PBDEs is used as a surrogate.

The analytical results from the reanalysis of the analytes in Table 3 will be compared to the original MEL data by calculating Relative Percent Difference and, if applicable, sorting the samples by matrix type.

Analytical Laboratory

MEL will send samples to ALS Canada Ltd for extraction and analysis. Previous work has shown V6 can be analyzed by LC/MSMS (Stapleton 2012). ALS will base their work on the laboratory methods and estimated reporting limits described in Table 3 for the three new target analytes.

Table 4. Laboratory Methods and Reporting Limits

Analyte	Digestion Method	Instrumentation	Method	RL+ (ppm)++
V6	3540C	LC/MSMS+++	EPA 1694	10.0
HBCD	3540C	LC/MSMS+++	EPA 1694	10.0
TBBPA	3540C	LC/MSMS+++	EPA 1694	10.0

+RL = Reporting Limit

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

ALS is planning to use a different standard extraction method yet similar analytical method to confirm the analytical results reported by MEL described in Table 4. Both laboratories will perform a total extraction of the sample, rather than by leaching. MEL based their procedure on EPA Method SW-846 3546 (Microwave) while ALS will perform a soxhlate extraction.

Table 5. Laboratory Methods and Reporting Limits

Analyte	Digestion Method	Instrumentation	Method	RL+ (ppm)++
TCEP	3540C	GC/MS+++	EPA 8270	10.0
TCPP	3540C	GC/MS+++	EPA 8270	10.0
TDCPP	3540C	GC/MS+++	EPA 8270	10.0
TPP	3540C	GC/MS+++	EPA 8270	10.0

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

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality to determine the amount of flame retardant compounds in a representative subsample of general consumer and children’s products. Details are listed in the original QAPP (Ecology, 2012). Additional measurement quality objectives (MQOs) are listed in Table 5.

Table 6. MQOs for Laboratory Analyses

Analyte	Laboratory Control Samples (LCS) (recovery)	Matrix+ Spikes (recovery)	Duplicates+ (RPD) ++	Method Blanks (ppm) +++	Surrogate Recovery (recovery)
V6	70-130%	70-130%	± 25%	< 1.0	30-150%
HBCD	70-130%	70-130%	± 25%	< 1.0	30-150%
TBBPA	70-130%	70-130%	± 25%	< 1.0	30-150%

+ Matrix spike duplicates and split duplicates
 ++RPD = Relative Percent Difference
 +++ppm = parts per million

Quality Control Procedures

Table 6 displays the laboratory QC tests planned for the analysis. Laboratory QC tests will consist of laboratory control samples, matrix spikes, matrix spike duplicates, laboratory duplicates, and method blanks. Final flame retardant results will be corrected for surrogate recovery.

Table 7. Quality Control Tests

Analyte	LCS	Matrix spike	Matrix spike Duplicates	Laboratory Duplicates	Method Blanks	Surrogates
V6	1/batch	1/batch	1/batch	1/batch	1/batch	Every sample
HBCD	1/batch	1/batch	1/batch	1/batch	1/batch	Every sample
TBBPA	1/batch	1/batch	1/batch	1/batch	1/batch	Every sample

LCS: laboratory control sample

Batch: 20 or fewer samples

Data Management

All data management procedures including data verification and validation and data quality evaluation will follow those stated in the original QA Project Plan (Ecology, 2012).

Report

The final report is described in the original QAPP. Additional items added from this addendum will include:

- Determination of the levels of the three additional flame retardants found in the samples analyzed.
- A comparison of MEL and ALS results.

References

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