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Addendum 1 to Quality Assurance Project Plan

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

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
EIM: Environmental Information Management database
HWTR: Hazardous Waste and Toxics Reduction
W2R: Waste 2 Resources

3.0 Background

Ecology regularly conducts studies in support of agency efforts to ensure manufacturer compliance with Washington State's Children's Safe Products Act (CSPA – RCW 70.240). In 2014-2015, Ecology's Environmental Assessment Program conducted a study to measure frequently-reported chemicals of high concern to children (CHCCs) in children's clothing, footwear, and accessories (Mathieu and McCall, 2014). Ecology tested samples of the children's products for metals (antimony, arsenic, cadmium, cobalt, lead, mercury, and molybdenum), phthalates (DEHP, BBP, DEP, DnHP, DIDP, DINP, DMP, DBP, and DnOP[1]), ethylene glycol, methyl-ethyl ketone (MEK), styrene, octamethylcyclotetrasiloxane (D4), and 4-nonylphenol.

During the process of this study, Ecology's product testing team identified a need to develop guidance for consistency in the preparation and analysis of consumer products. Little guidance is available in the literature or from governmental agencies on the necessary pre-treatment (i.e., cryomilling) of various consumer product matrices prior to analysis. Fabric may be a matrix that is easily digested and/or extracted, and may not require cryomilling. Cryomilling, as described in section 9.3, is a technique used to reduce material to a finely divided sample. There are advantages to cryomilling consumer products prior to analysis (i.e., provides a representative, homogenous sample and may be more efficient for extraction), but cryomilling also increases the time and cost of each analysis. Due to a lack of guidance in the literature or from other federal or state agencies, Ecology will reanalyze a subset of the samples from the original project to help assess the need for cryomilling fabric prior to analysis. This comparison will be limited to metal analytes.

Ecology also identified a need to ensure consistency in the analysis of consumer products for phthalates. The U.S. Consumer Products Safety Commission has a published method for the preparation and analysis of phthalates in children's toys and child care articles. However, according to the method, users may follow either the protocol outlined in CPSC-CH-C1001-09.3 or several alternative extraction and analysis methods. Ecology's Manchester Environmental Laboratory (MEL) uses modifications of EPA Method 3546 and EPA Method 8270D for extraction and analysis, respectively, which are allowed under CPSC-CH-C1001-09.3. Ecology will re-analyze one of the samples from the original project and two standard reference materials (SRM) for phthalates using both the CPSC method and MEL's current method.

[1] DEHP = di-2-ethylhexyl phthalate; BBP = butyl benzyl phthalate; DEP = diethyl phthalate; DnHP = di-n-hexyl phthalate; DIDP = diisodecyl phthalate; DINP = diisononyl phthalate; DMP = dimethyl phthalate; DBP = dibutyl phthalate; DnOP = Di-n-octyl phthalate.

3.1.3 Parameters of Interest

Ecology will analyze archived samples of children's clothing, footwear, and accessories for metals (antimony, arsenic, cadmium, cobalt, lead, mercury, and molybdenum) and phthalates (DEHP, BBP, DEP, DnHP, DIDP, DINP, DMP, DBP, and DnOP).

3.1.4 Results of previous studies

Preliminary results from the original study, CHCCs in Children's Clothing, Footwear, and Accessories, will be reviewed and used to select samples that contained the parameters of interest. Section 7.1 describes how the data will be consulted for selection of samples. Final results of the original study are expected to be published in fall 2015.

4.0 Project Description

4.1 Project Goals

Additional testing of archive samples is being carried out to:

- Provide guidance for Ecology's product testing program to achieve consistency in sample pre-treatment for fabric matrices and methods for the determination of phthalates in plastic matrices. This guidance may be incorporated into Ecology's product testing protocols.

4.2 Project Objectives

To meet project goals, Ecology staff will carry out the following analyses on archive samples from the original project:

- Analyze laboratory split samples consisting of fabric matrices with two different pre-treatment types: (1) cryomilled and (2) reduced in size by hand to 2 mm x 2 mm (MEL's current procedure for non-cryomilled samples), for the suite of CSPA metal analytes.
- Analyze laboratory split samples (archived material and SRM) for phthalates using both the CPSC method and MEL's current phthalates method (EPA Method 3546 and EPA Method 8270D, modified).

4.4 Target Population

Archive samples selected for analysis will consist of children's clothing (fabric) for the cryomilling portion of this project. Plastic components of children's clothing, shoes, and accessories will be targeted for the phthalates comparison.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Organization of project staff and responsibilities is documented in the original QAPP (Mathieu and McCall, 2014). The project manager will be responsible for locating and sending the archive samples to the laboratory.

5.4 Project Schedule

Table 1. Project Schedule.

Sample shipment and laboratory work	Due date	Lead staff
Archive samples shipped to lab	06/2015	Callie Mathieu
Lab analysis complete	08/2015	
Final report		
Author lead/support staff	Callie Mathieu (lead)/ Sara Sekerak (supporting)	
Schedule		
Draft due to supervisor	02/2016	
Draft due to client/peer reviewer	03/2016	
Final (all reviews done) due to publications coordinator	04/2016	
Final report due on web	05/2016	

5.6 Budget and funding

Table 2. Laboratory Budget.

Metals cryomill comparison

Treatment	Analyte	No. of samples	No. of replicates	No. of QC samples*	Cost	Total Cost
Cryomilling	Metals	5	---	1	$100	$600
Cryomilled samples	Metals	5	7	2	$200	$7,400
Non-cryomilled samples	Metals	5	7	2	$200	$7,400
					Total:	$15,400

Phthalates method comparison

Method	Analyte	No. of samples	No. of replicates	No. of QC samples*	Cost	Total Cost
Cryomilling	Phthalates	1	---	---	$100	$100
MEL method	Phthalates	3	7	---	$375	$7,875
CPSC method	Phthalates	3	7	---	$375	$7,875
					Total:	$15,850
					Total cost for both projects:	$31,250

*QC samples in this table include those that are not provided free of charge (matrix spikes, matrix spike duplicates, and cryomill rinseates).

6.0 Quality Objectives

6.2 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) will remain the same as those described for metals and phthalates in the original QAPP (Mathieu and McCall, 2014).

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Laboratory precision will be assessed through laboratory replicate samples. Each sample will be split by the laboratory after treatment (cryomilling or size reduction by hand) and analyzed in replicates of seven.

6.2.1.2 Bias

Laboratory bias will be evaluated through analysis of laboratory control samples and matrix spikes.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

To facilitate comparability between treatment and method type, samples will be split by the lab after pre-treatment (cryomilling or size reduction by hand). The use of laboratory splits will eliminate comparability issues generated by sample collection and processing prior to the laboratory.

6.2.2.2 Representativeness

Samples will be analyzed in replicates of seven to help achieve statistical representativeness of the treatment/method type. Seven is the minimum sample size required for Method Detection Limit (MDL) studies under EPA's guidelines for establishing test procedures for the analysis of pollutants (40 CFR 136).

6.2.2.3 Completeness

The project manager will consider the study to have achieved completeness if 95% of the samples are analyzed acceptably.

7.0 Sampling Process Design

7.1 Study design

Cryomilling pre-treatment

Five archive samples will be selected by the project manager and sent to MEL for analysis of metals. Samples will be selected based on preliminary laboratory results of metals from the original project (Mathieu and McCall, 2014). Archived samples with preliminary results showing at least one parameter of interest above reporting limits will be chosen for analysis. Selected samples will cover a range of metal analyte concentrations. All samples selected for analysis will consist of a fabric matrix. This project will only examine the need for cryomilling fabric matrices and will not extend to other matrices.

Ecology headquarters staff will reduce the product component material into 2 cm x 2 cm pieces and store in 8 oz glass jars prior to sending the archive sample to MEL. MEL staff will then divide the sample into two equally-weighed subsamples. Each subsample will be either (1) cryomilled or (2) reduced in size to 2mm x 2mm using stainless steel scissors. Subsamples will then be split by the laboratory into seven aliquots of each treatment type. The fourteen aliquots of each sample will then be analyzed for the target metal analyte list by the same method.

This analysis is being carried out to determine the necessity of cryomilling samples consisting of fabric matrices prior to laboratory analysis. The two data sets will be assessed for within-sample-treatment variation through calculation of relative standard deviations for each subsample (7 aliquots), as well as Levene's Test for equality of variance. Depending on the distribution of the data, either parametric or non-parametric tests will be conducted to identify differences in group means among samples.

Phthalates Method Comparison

Due to a lack of material left over from the original study, only one appropriate sample was identified as having sufficient material for further analysis by the laboratory. Two SRMs will also be analyzed by the laboratory – one consisting of polyethylene and one of polyvinyl chloride matrix – that contains the target phthalate list.

Similar to above, the archive sample will be reduced by Ecology headquarters staff into 2 cm x 2 cm pieces, placed in a 4 oz glass jar, and sent to MEL. MEL staff will then cryomill the archive and SRM samples and divide each sample into fourteen aliquots after cryomilling. Seven aliquots of each sample will be analyzed for the target phthalate list using MEL's current method, EPA 3546/EPA 8270D modified, and seven aliquots will be analyzed for the target phthalate list following the CPSC Method (CPCS-CH-C1001-09.3). As noted earlier, the CPSC

Method allows for the use of several other analytical methods, including EPA 3546/EPA 8270D modified. A more detailed description of the two analytical methods is included in Section 9.2.

The phthalate data will be assessed using the same approach as the metals data.

7.5 Characteristics of existing data

Ecology has not conducted any studies to determine the necessity of cryomilling product matrices prior to analysis. There is little guidance in the literature concerning appropriate pre-treatment techniques for matrices other than plastic. The CPSC method for phthalates (CPSC-CH-C1001-09.3) requires a pre-treatment step of either cryomilling or reducing the plastic material in size to 2 mm x 2 mm. The cryomilling component of this project will fill this data gap for fabric matrices only.

Ecology has previously conducted studies of phthalates in consumer products (Mathieu and Bookter, 2014; Stone, 2014) and other studies of phthalates in products is currently underway (Mathieu and McCall, 2014; Stone, 2015). MEL has conducted the phthalates analysis for all but one of these studies, using EPA 3546/EPA 8270D, modified. A contract laboratory conducted analysis of phthalates using the CPSC method for Stone (2014). No side-by-side studies of consumer products that have compared differences in phthalate methods allowed under CPSC-CH-C1001-09.3 were identified when writing this QAPP addendum.

9.0 Measurement Methods

9.2 Laboratory procedures table

Laboratory procedures for the analyses are presented in Table 3.

Table 3. Laboratory Procedures.

Analyte	Samples (number/ arrival date)	Expected Range of Results	Matrix	RL (ppm)	Extraction Method	Analysis Method	Analysis Instrument
Metals	5, 6/15/2015	<1 - 1,000 ppm	Fabric	1.0	EPA 3052	EPA 6020	ICP-MS
Phthalates	3, 6/15/2015	<5 - 50,000 ppm	Plastic	25 - 50	EPA 3546 mod	EPA 8270D mod	GC-MS
Phthalates				25 - 50	CPSC-CH-C1001-09.3	CPSC-CH-C1001-09.3	GC-MS

MEL's current method of extraction for phthalates follows a modification of EPA 3546. In this method, surrogates and spikes are added to 0.2 g of properly prepared samples and then 20 mL of a 70:30 acetone hexane mix is added. The samples are extracted by microwave, solvent exchanged to iso-octane, and brought to a final volume of 10 mL. The CPSC method (CPSC-CH-C1001-09.3) extraction consists of the following sequence: 5 mL of tetrahydrofuran (THF) is added to 0.05 g of properly prepared sample then shaken, stirred, or mixed with gentle heat for at least 30 minutes. 10 mL of hexane is then added to precipitate out the polyvinyl chloride for at least 5 minutes. Internal standards are then added to 0.3 mL of the extract and diluted to 1.5 mL with cyclohexane.

For analysis of phthalates, MEL follows a modification of EPA 8270D, using gas chromatography-mass spectrometry (GC-MS) in selected-ion monitoring (SIM) mode. The instrument is calibrated with 6 or more standards using a quadratic curve meeting internal calibration linearity, back-calculation, and calibration verification limits. Continuing calibration verification checks are analyzed every 12 hours. The CPSC method (CPSC-CH-C1001-09.3) also uses GC-MS in SIM mode for analysis of phthalates. With the CPSC method, the instrument is calibrated using at least 4 standards, a certified reference material is analyzed to ensure a proper calibration, and the sample is analyzed qualitatively in GC-MS full scan mode. Sample results are then quantitated using GC-MS in SIM mode.

9.3 Sample preparation method

Samples selected for analysis of metals will be split by the lab. One subsample will be cryomilled and the other subsample will be reduced in size to 2 mm x 2 mm using stainless steel scissors or snips. Cryomilling is the process of reducing a sample to very small particle sizes (~5-50 microns) by lowering the product to cryogenic temperatures and mechanically milling it with a stainless steel magnetic shaker. This process provides a homogenous, finely divided solids sample for efficient extraction.

All samples being analyzed for phthalates will be cryomilled prior to analysis and split by the laboratory after cryomilling.

10.0 Quality Control (QC) Procedures

Quality Control procedures for this project are outlined in Table 4.

Table 4. Quality Control Procedures.

Analyte	Cryomill Rinseates	Method Blank	Laboratory Control Sample	Matrix Spike	Matrix Spike Duplicate	Surrogates
Metals	1/batch	1/batch	1/batch	1/batch	1/batch	n/a
Phthalates	n/a	1/batch	1/batch	none	none	every sample

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

Original product data and laboratory results will be stored in Ecology's Product Testing Database (https://fortress.wa.gov/ecy/ptdbpublicreporting/). Results from additional testing of archive samples outlined in this QAPP addendum will not be stored in the database because the results are considered to be for QC purposes. QC data are not stored in the database.

12.0 Audits and Reports

12.3 Frequency and distribution of report

A report summarizing findings for the additional testing outlined in this QAPP will be published after an internal review period. The final report will include:

- Results of laboratory analyses.
- Statistical summary and statistical analysis of laboratory results.
- Recommendations for type of pre-treatment to use for analysis of metals in fabric matrices and analytical method to request for phthalates in plastic consumer products.

14.0 Data Quality (Usability) Assessment

14.2 Data analysis and presentation methods

The final report will include a statistical summary of the laboratory results. Laboratory data will be assessed for within-sample-treatment variation through calculation of relative standard deviations for each subsample (7 aliquots), as well as the Levene's Test for equality of variance.

Depending on the distribution of the data and number of censored data, either parametric or non-parametric two-sample tests will be conducted to identify differences in lab results between each treatment/method, for each sample. Parametric tests may include t-tests, if all assumptions are satisfied. If the distribution of the data set cannot be identified as normal, or if the data set contains censored ("non-detect") data, a Wilcoxon rank-sum test will be used. Depending on the number of censored data and whether reporting limits varied, a Tarone-Ware two-sample test may be used instead of a Wilcoxon rank-sum test.

14.3 Treatment of non-detects

Statistical tests will be conducted on individual compound laboratory results (i.e., phthalates will not be summed). If all laboratory results for one sample are below detection limits, no statistical tests will be conducted on that sample. Non-parametric methods suitable for censored data will be used if both detects and non-detects are present in a sample.

References

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