XRF Screening of Packaging Components: Cadmium Continues to be Present in Flexible Polyvinyl Chloride (PVC)

This research bulletin provides an update on projects performed by the Toxics in Packaging Clearinghouse (TPCH) related to the presence of lead (Pb) and cadmium (Cd) found in flexible PVC packaging above legal thresholds established by state toxics in packaging laws. The bulletin summarizes the results of x-ray fluorescent (XRF) analysis of flexible PVC packaging samples in 2015 to assess current compliance with state toxics in packaging laws. The Bulletin also assesses trends in compliance with state laws using XRF data collected since 2006. The analysis shows continuing but potentially declining rates of non-compliance in the packaging of products from specific retail product sectors. The continuing presence of noncompliant packaging found in the marketplace demonstrates the need for continued monitoring of packaging components for compliance with state toxics in packaging laws by the packaging supply chain and product brand owners who select packaging and introduce packaging into the market in the U.S.

Since 2006, the Toxics in Packaging Clearinghouse (TPCH) has screened packaging for compliance with state laws using XRF technology, a rapid and inexpensive screening tool for measuring the elemental composition of samples including the four metals restricted by state laws—cadmium, lead, mercury, and hexavalent chromium.[1] These screening projects found elevated levels of lead and cadmium in flexible PVC packaging. The levels found by TPCH may be functional levels as a stand-alone additive or part of a mixture, or they could be non-functional impurity or contaminant levels in an additive. Most PVC additives work as plasticizers to provide resin flexibility or as stabilizers that maintain integrity of the packaging and therefore, its retail shelf life.

Since its first screening project in 2006, TPCH has observed a shift away from the use of both lead and cadmium in flexible PVC packaging. This may be due to tighter restrictions and surveillance of lead and cadmium in children's and consumer products, as well as mandated and voluntary industry actions to reduce the use of lead and cadmium in a wide range of other PVC products.

[1] XRF measures total chromium, not hexavalent chromium. If chromium is detected using XRF, laboratory analysis would be needed to determine if the chromium is hexavalent chromium.

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The 2015 TPCH screening project analyzed flexible PVC packages for the presence of the regulated metals in a variety of products such as home furnishings, pet supplies, and sporting goods. The results confirmed the continued presence of cadmium above legal limits in flexible PVC packaging, although the overall rate of non-compliant packaging has decreased since 2006 in the limited sample populations tested by TPCH. Lead was found in screened packaging in 2006 and 2008 but was not found in the 2015 sample population. Packaging identified as potentially non-compliant through XRF technology was also analyzed for total metals content by the Manchester Environmental Laboratory of the Washington State Department of Ecology (WA Ecology). The results of the laboratory analysis supported the use of XRF screening for the detection of non-compliant flexible PVC packaging.

TPCH also worked cooperatively with over a dozen brand owners of non-compliant packaging to bring their packaging into compliance with state laws and further educate the packaging supply chain about U.S. toxics in packaging laws.

Background

The use of four metals—lead, cadmium, mercury, and hexavalent chromium— is restricted in packaging in nineteen states in the U.S. by toxics in packaging laws. These state laws prohibit the intentional use of any amount of these four metals in any packaging or packaging component, such as plastic sheets, glass bottles, inks and colorants. If the metals are incidentally present (defined as an unintended or undesired ingredient) in the packaging component or material, the laws restrict the total concentration of these four metals to less than 100 parts per million.

The TPCH supports and helps coordinate the implementation of toxics in packaging laws in 9 member states -- California, Connecticut, Iowa, Minnesota, New Hampshire, New Jersey, New York, Rhode Island, and Washington. The TPCH serves as a central location for general education on toxics in packaging requirements, processing information requests from external constituencies, and promoting compliance with the laws.

The TPCH also undertakes research projects, such as compliance screening, which assist member states by:

- Identifying potential material types and retail product sources of non-compliant packaging, and
- Conducting outreach to industry to increase compliance with state laws.

Methodology

The TPCH and its member states collected random retail packaging samples over a 7-month period (November 2014 through May 2015). TPCH member states secured 109 unique flexible PVC packaging samples and shipped the packages and copies of the purchase receipts directly to either TPCH or WA Ecology staff for XRF screening (see below).

The packages were assessed for their concentration of restricted metals and their potential compliance status. XRF screening found that twenty-one samples were likely non-compliant and these samples are the primary focus of this report. Member states obtained four additional samples of the likely non-compliant packaging, if available in their state, or a similar product from the same manufacturer or distributor. These duplicate packages were also screened using XRF technology to determine their potential compliance status. The original twenty-one non-compliant samples and the four additional samples, also found to be non-compliant, are the focus of this report.

TPCH and WA Ecology staff shared the packaging screening task. TPCH screened packaging using an Olympus Innov-X Systems DELTA handheld XRF instrument, following manufacturer recommended procedures for RoHS mode.[2] WA Ecology utilized a Niton XL3t 700 portable XRF analyzer. All samples were analyzed for a minimum of 60 seconds. A single measurement was taken of each sample unless confirmation was needed[3].

All but two of the samples that failed the XRF screening (>100 ppm) for cadmium or lead were sent to the Washington State Manchester Environmental Laboratory for confirmatory testing. Chain of custody was maintained in accordance with the TPCH QAPP throughout the project. The laboratory followed EPA SW 846 Method 3052 for the preparation of samples and Method 6020 for analysis. TPCH recommends EPA SW 846 Method 3052 for extraction and analysis of metals in PVC packaging samples based on the results of the PVC round robin study.

TPCH contacted companies that manufactured or distributed the products in non-compliant packaging to advise them of the presence of restricted metals in their packaging and the need to bring their packaging into compliance with state laws, including existing inventory on retail shelves or in the distribution channel.

Packaging Samples

TPCH staff and member states obtained 109 unique flexible PVC packaging samples from seven states with toxics in packaging laws, from New Hampshire to California. The samples represented diverse product sectors, with the greatest number of unique samples from home furnishings (46), pet supplies (16), sporting goods (16), and personal care (11).

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[2]Olympus Innov-X System User Manual, Delta Family: Handheld XRF Analyzers, June 2010; and Quick Start Guide, DELTA Family of Handheld XRF Analyzers, August 2010. The RoHS Mode is described in the User Manual (page 67) as "RoHS regulated elements - Cr, Hg, As, Pb, Br, Cd, PLUS Cl, Ti, Fe, Co, Ni, Cu, Zn, Sn, Sb, and Ba. Analysis software for measurement of restricted elements in electronics and **consumer** goods. Auto-compensations built in for metal, polymer, and mixed matrices."

[3] This study selected 100 ppm as the threshold for passing or failing XRF screening (indicating likely non-compliance) for two reasons: 1) an assumption that <100 ppm is from incidental presence of the metals (i.e., not intentionally added); and 2) confidence in XRF results for PVC samples at this level of detection.

Table 1 summarizes the product sectors for all samples.

Table 1: PVC Packages Screened by Product Sector

Product Sector	No. of Samples
Home Furnishings	46
Pet Supplies	16
Sporting Goods	16
Personal Care	11
Children/Baby	9
Toys/Games	6
Apparel	2
Crafts	1
Medical	1
Kitchen	1
Total	**109**

Results

Twenty-one of the initial 109 samples (19%) exceeded the 100 ppm limit for the restricted metals in packaging upon initial XRF analysis. All twenty-one initial failed samples and the four additional failed replicate samples contained cadmium (Cd) over 100 ppm.

Table 2 shows the distribution of the 21 initial failed samples by cadmium concentration as detected using XRF analysis.

Table 2: XRF detection of Cadmium Concentrations for 21 Initial Failed PVC Samples

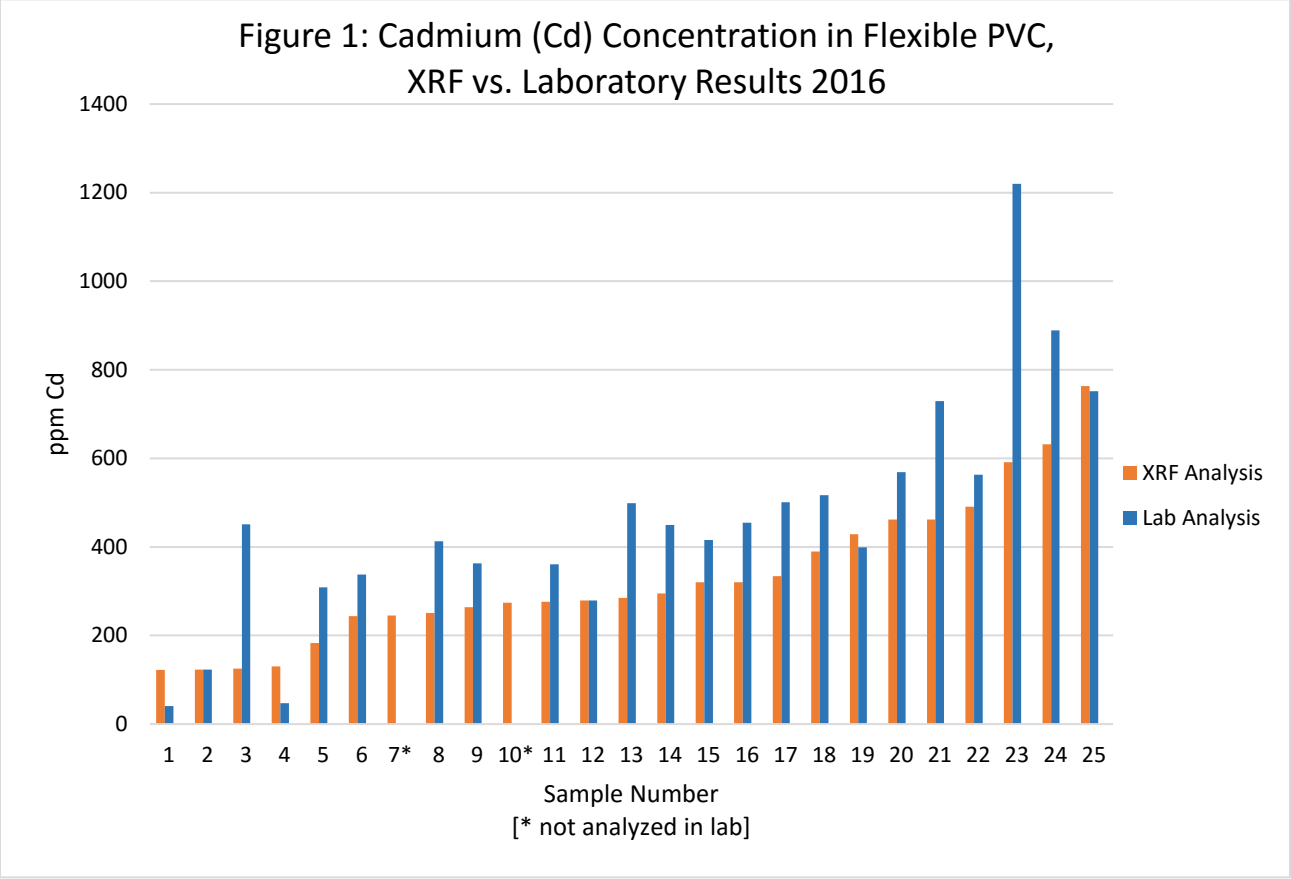
Cd Concentration	Number of Samples by Cd Concentration
100 - 200 ppm	5
201 - 300 ppm	9
301 - 400 ppm	3
401 - 500 ppm	2
501 - 600 ppm	1
601 - 700 ppm	0
701 - 800 ppm	1

The Manchester Environmental Laboratory analyzed 23 of the 25 failed initial and replicate packaging samples, and confirmed, with two exceptions, that the failed packaging samples were not in compliance with state laws. Laboratory analysis detected less than 100 ppm of cadmium for two packages where cadmium measured between 100 and 200 ppm by XRF analysis.

For the three other samples with XRF results of 100 – 200 ppm, XRF and laboratory results were identical for one sample, and laboratory results were significantly higher for the other two.

Figure 1 provides a comparison of cadmium concentrations as measured by XRF (blue) and Laboratory Method 3052 (orange) for each of the 25 initial and additional samples. Highlights of Figure 1 include:

- Two samples (7 and 10) found non-compliant with the XRF were not analyzed in the laboratory;
- Two samples found non-compliant with the XRF in the 100 – 200 ppm range had lab results below 100 ppm;
- Two samples had identical results with the two analytical methods (123 and 279 ppm);
- Two samples had laboratory results that were more than 100 percent greater than XRF results;
- Five samples had laboratory results that were between 50 percent and 75 percent greater than XRF results, and;
- The remaining twelve samples had laboratory results ranging from 7 percent lower to 50 percent greater than XRF results. The replicate sample pairs are samples 14/19, 15/18, 21/22, and 24/25.



At least 14 of the 21 packaging samples failing the initial XRF screening (>100 ppm cadmium) were for products labeled as "made in China." One product was made in the U.S. and one in Mexico. The country of origin was not available for five products. It is important to note the country of origin for the *product* may not be the country of origin for the *packaging*. As an illustration, in this project, for the products made in the US and Mexico, the brand owner later documented that the packaging was imported from China.

The PVC packaging samples fell into ten product sectors. Six out of ten product sectors had non-compliant packaging samples. Flexible PVC used for pet supplies had the highest percentage (31%) of non-compliant samples. Five of 16 flexible PVC samples for pet supplies such as animal treats and play toys were non-compliant with state toxics in packaging laws.

Eleven of 46 PVC packaging samples (24%) in the home furnishings product sector were non-compliant; home furnishings products included window and shower curtains, blankets, and pillow protectors, among others. Cadmium was also found in the packaging of products in the sporting goods, personal care, and children's products sectors.

Table 4 summarizes the failed packaging samples using XRF analysis by product sector.

Table 4: Failed PVC Packaging Samples Using XRF by Product Sector

Product Sector	Number of Samples	Number of Failed Samples >100 ppm Cd	Percentage of Failed Samples
Home Furnishings	46	11	23.9%
Pet Supplies	16	5	31.3%
Sporting Goods	16	2	12.5%
Personal Care	11	1	9.1%
Children/Baby	9	1	11.1%
Toys/Games	6	0	-
Apparel	2	0	-
Crafts	1	0	-
Medical	1	0	-
Kitchen	1	1	100%
Total	**109**	**21**	**19.3%**

Given the limited number of samples screened for the products sectors where there were no failed samples, the results should not be interpreted to mean that the packaging in these sectors will always be in compliance. Further, the samples are not representative of all product sectors that use flexible PVC packaging.

Discussion

Over time, TPCH has observed a decrease in the percentage of non-compliant flexible PVC packaging among all the packages in our limited sample population. Table 5 summarizes the XRF screening results for flexible PVC in 2006, 2008, and 2015 (this report).

The first XRF screening project conducted by the TPCH found that 61% of flexible PVC samples were non-compliant with state toxics in packaging laws. The percentage dropped to 52% in 2008, and was lower yet in 2015 at 18%. Historically and in the current study, the flexible PVC packaging for home furnishing and pet supplies consistently has the highest percentage of non-compliant packaging compared to other product sectors.

These sectors also show a decrease in non-compliant packages between 2006 and 2015. The non-compliance rate of sampled packaging of home furnishing products decreased from a high of 81% in 2006 to 22% in 2015. The non-compliance rate of sampled pet supplies packaging follows a similar trend, from a high of 80% in 2006 to 31% in 2015. The majority of non-compliant packages tested still appear to be manufactured in China.

Table 5: Comparison of XRF Results 2006 – 2015 for Flexible PVC

Product Sector	% Samples Failing Screening in 2006 (>100 ppm) For Cd and/or Pb		% Samples Failing Screening in 2008 (>100 ppm) For Cd and/or Pb		% Samples Failing Screening in 2015 (>100 ppm) For Cd and/or Pb	
All Samples	N=45	Fail 58% Cd only 42% Pb only 4% Both 11%	N=71	Fail 55% Cd only 44% Pb only 0% Both 11%	N=109	Fail 19.3% Cd only 19.3% Pb only 0% Both 0%
Home Furnishings	N=16	Fail 87.5% Cd only 69% Pb only 0% Both 19%	N=40	Fail 52.5% Cd only 45% Pb only 0% Both 7.5%	N=46	Fail 22% Cd only 22% Pb only 0% Both 0%
Pet Supplies	N=5	Fail 80% Cd only 80% Pb only 0% Both 0%	N=8	Fail 63% Cd only 38% Pb only 0% Both 25%	N=16	Fail 31% Cd only 31% Pb only 0% Both 0%

A trend detected by XRF screening from 2006 to 2015 was the type of metals detected in the flexible PVC packaging samples. In the 2006 and 2008 projects, Cd was detected in nearly all (over 95%) of the non-compliant packaging samples, but a few contained only Pb. TPCH also found Pb in over 15% of the non-compliant packaging samples. In the 2015 project, only Cd was detected in the non-compliant packaging samples.

It is possible that the tighter restrictions, awareness of hazards, increased surveillance of lead in children's and consumer products, and voluntary industry efforts to phase out lead in PVC [see side bar] have resulted in a shift away from its use as a plasticizer and UV stabilizer in flexible PVC packaging. There has also been a decrease in the use of Cd in the tested packaging. Known alternatives for Cd stabilizers include barium-zinc, calcium-zinc, antimony, organotin, and organic compound stabilizers. It is not in the scope of this Bulletin to evaluate the safety of these relative to Cadmium.

The TPCH and member states are encouraged by these results, which may indicate manufacturers and distributors of packaging and packaging components are paying more attention to sourcing and testing for compliance with toxics in packaging laws. Since the release of the 2006 results, extensive outreach by TPCH to build awareness of heavy metals in flexible PVC packaging, in addition to member state enforcement initiatives, appears to be yielding positive results.

PVC Industry Initiatives to Reduce and Eliminate Lead and Cadmium

The Vinyl Institute (United States trade association of PVC manufacturers) provided TPCH with information on voluntary initiatives and mandates in the US to eliminate lead, cadmium, and other chemicals of concern from a range of PVC products. The Vinyl Institute cites the ***PVC Handbook*** (2005), which states that lead and cadmium were removed from all PVC products manufactured in the US in the early 2000's, except for wire and cable, where lead was phased out between 2006 and 2009. TPCH requested additional information since the information provided by the Vinyl Institute did not directly address flexible PVC packaging. In response, the Vinyl Institute provided information on two national/multinational trade association-level research and policy initiatives that addressed a range of products, including flexible PVC packaging. These initiatives led to the replacement of lead- and cadmium-based PVC stabilizers by manufacturers in Europe and Australia. A report by the European Vinyl Council notes that these replacements have been instituted by their members and required significant financial and technical investments. (***The European PVC industry's experience in replacing lead and cadmium-based stabilizers***, *Brussels 30 May 2014, VinylPlus; http://www.stabilisers.eu/wp-content/uploads/2015/11/VinylPlus_Contribution-Cefic_Eu-Industry.pdf*)

A report from the Vinyl Council of Australia provides a list of 7 sustainable practice commitments made by their members, including Commitment #2, the phase-out of lead and cadmium stabilizers by 31 December 2003. (***Product Stewardship Commitment of the Vinyl Council of Australia***, *November 2002*).

Conclusion

The results of the current screening project are encouraging since lead was not found and cadmium was present at lower non-compliant levels in about 20 percent of the total sample population. However, the results of the current screening project confirm that cadmium is still present in flexible PVC, either at functional levels or as a contaminant in an additive or mixture. State toxics in packaging laws require self-surveillance by the supply chain. Product manufacturers and distributors must remain vigilant when purchasing flexible PVC packages or packaging components, or products packaged in this material. Product manufacturers, distributors, and retailers should require compliance with state toxics in packaging laws as a condition of sale.

The TPCH Quality Assurance Considerations for Toxics in Packaging provides practical suggestions on steps companies should consider in the procurement of packaging, especially packaging at high risk for non-compliance, including:

- Incorporate toxics in packaging requirements into packaging specifications.
- Discuss toxics in packaging requirements directly with suppliers. Verify that suppliers have read, understand and will adhere to the packaging specifications. Suppliers may not be aware of restrictions on the use of heavy metals in packaging.
- Require suppliers to submit a Certificate of Compliance with supporting documentation. Ask suppliers to provide the testing/analytical data on which they base their compliance claim. Require suppliers to submit new Certificates of Compliance with supporting documentation whenever they change suppliers or raw materials.
- Test incoming feedstocks, packaging materials, and packaging components of all new suppliers and occasional suppliers prior to issuing a purchasing contract. X-ray fluorescence (XRF) analysis or conventional laboratory testing are both acceptable screening methods. Provide the laboratory with both the sample preparation and test method that will result in full dissolution of the sample, and request they analyze for **total concentration** of each metal. Test methods that only measure leachable metals are not appropriate to determine toxics in packaging compliance.
- For more information on test methods, see:
  - Frequently Asked Questions
  - TPCH guidance on laboratory analysis
  - TPCH report, Laboratory Round Robin Test Project: Assessing Performance in Measuring Toxics in Packaging.
- Initiate an on-going program for monitoring or "spot-checking" incoming raw materials or packaging components to make sure that heavy metals are not subsequently introduced into your packaging materials and supplies after initial shipments that are in compliance.
- If a company self-discovers non-compliant packaging, it must proactively take steps to correct the problem as detailed in the Frequently Asked Question section on the TPCH website.

The TPCH and its member states will continue to monitor flexible PVC packaging for compliance with state toxics in packaging laws. When TPCH or member states identify non-compliant packaging, the manufacturer, distributor, and/or retailer is contacted with a request to bring the packaging into compliance and immediately stop the sale and distribution of all non-compliant packages, including existing inventory on retail shelves or in the distribution channel. Failure to act can result in state enforcement and monetary penalties.