

# EPA Indoor Dust Study Data Report Sampling Conducted in Gainesville, Florida EPA Region 4 5/23/2013

The Stephen Foster neighborhood is adjacent to the western boundary of the Koppers portion of the Cabot Carbon-Koppers Superfund Site in Gainesville, Florida. The pattern of dioxin concentrations in the Stephen Foster Neighborhood (SFN) surface soil suggests wind-blown dust deposition from the Koppers site. In 2010, representatives of some residents reported the concentrations of dioxins in area house dust using the Chemical-Activated Luciferase Expression bioassay test (CALUX®). These results suggested dust concentrations may be much higher than levels reported in soils, and it was assumed these levels were a result of contamination from the Site, although a number of other dioxin-like compounds (DLCs) may be present in dust samples. Residents advocated for further study of levels of dioxins in their homes, evaluation of potential health risks, and actions they can take to reduce these exposures.

Environmental Protection Agency (EPA) Region 4 supported the design and implementation of a dust study. The Florida Department of Health (FDOH) formed an indoor dust workgroup of federal, County, State and community representatives recommending a work plan for the investigation. The EPA worked with Dr. Pat Cline (the principal investigator for a research study on dioxins in dust funded by the Environmental Justice Small Grant Program) and Dr. John Mousa of the Alachua County Environmental Protection Department (ACEPD) to identify background and SFN homes to be included in the EPA dust study.

EPA Scientific, Engineering, Response and Analytical Services (SERAS) personnel provided technical support to the Environmental Protection Agency/Environmental Response Team (EPA/ERT) to assist EPA Region 4 with indoor dust sampling of residential homes in the Stephen Foster neighborhood adjacent to the Cabot Carbon-Koppers hazardous waste site (Site) located in Gainesville, Florida (FL).

This memorandum provides a summary of the EPA sampling program and results. A Health Consultation on these results is provided in a separate report prepared by FDOH.

### Dioxin

The term "dioxins" typically refers to a group of chlorinated chemical compounds (dioxins and furans) sharing certain chemical structures and biological characteristics. These chemicals are widely distributed throughout the environment at low concentrations, and are generally persistent. Dioxins are by- products of a number of processes including waste incineration, but can also result from natural processes such as volcanic eruptions and forest fires. Dioxins are also present in pentachlorophenol (PCP), a wood preservative used to treat lumber at the Koppers site from approximately 1980-2000.

Only a subset of the compounds in this family of chemicals are toxic, and each of these has its own level of toxicity. To account for this, toxic equivalents (TEQs) are calculated. These TEQs assign a value describing how toxic each dioxin and dioxin-like compounds is

compared to the most toxic of these, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). To evaluate health risks for exposure to a mixture of dioxin and dioxin-like compounds, the TEQs of these compounds are summed, and this total TCDD-TEQ is used to evaluate the toxicity of the mixtures.

Chlorinated dioxins have been widely studied. Regulation of these compounds are based on concentrations of these compounds using specific approved analytical methods to isolate, detect, quantitatively measure and report these compounds. These established definitive methods are used in support of risk-based decision making.

XDS-CALUX®, the screening protocol used for initial dust testing, measures an overall response to dioxin-like compound mixtures. This is EPA Method 4435, approved as a bio-analytical screening procedure for dioxin-like compounds in soil/sediments. Interpretation of these results require a demonstration of the correlation with these screening values with the total TCDD-TEQ measured using the definitive method, recognizing that compounds other than the regulated chlorinated dioxins may be present in the dust and contribute to the overall response. The method (<a href="http://www.epa.gov/osw/hazard/testmethods/pdfs/4435.pdf">http://www.epa.gov/osw/hazard/testmethods/pdfs/4435.pdf</a>) states that potential interfering compounds include other halogenated (e.g. brominated) dioxins/furans. XDS has a patented clean up method (US patent # 6,720,431) that states there are various options to this protocol that may allow separation of other groups of compounds (including brominated dioxins) so the concentrations of these may be separately measured and quantified.

Recent studies indicate brominated dioxins associated with brominated flame retardant materials are also a potential source of dioxins in house dust that may also contribute to the TCDD-TEQ. (Brown et al. 2001). Therefore, these compounds were also analyzed. In general, these brominated compounds are not well-studied, and the sources, relative toxicity and fates are much more uncertain. To assess dioxin, EPA Superfund typically measures and makes regulatory decisions on analysis of chlorinated dioxins/furans for which we have toxicity values.

### Methods

### **Sampling Locations**

One of the first steps in evaluating the presence of dioxins is to determine concentrations in background samples. Soil samples from background areas were previously collected and analyzed for dioxins. Nine soil samples analyzed from two background residential areas west of the Site had dioxin concentrations ranging from 0.2 to 1.7 pg/g, with a median concentration of 0.4 pg/g. Letters were sent to residents in these two neighborhoods requesting interest in participating in the dust study. From these, 13 participants were identified and included in the dust study.

For the SFN, letters were sent to homes within the area previously identified as having dioxin soil above 7 pg/g. Seventeen access agreements were obtained and these homes were sampled for this study.

### Sample Collection and Processing

Samples were collected by SERAS at 30 homes between May 5, 2012 and May 15, 2012. Sampling methods for the collection of dust samples used EPA standard operating procedure (SOP) #2040, *Collection of Indoor Dust Samples from Carpeted Surfaces for Chemical Analysis Using a Niljisk GS-80 Vacuum Cleaner.* The sampling consisted of one composite dust sample per household; in addition, the resident's vacuum bags were collected as separate samples. The residents vacuum samples were included to understand the impact of the sampling protocol on dioxin concentrations in support of the EJSG research study, and will be evaluated in that report.

The composite sample collected dust from high traffic areas that were easily accessible. Dust samples were collected from carpets, rugs, tile, and wood floors using a vacuum following EPA SOP 2040. Vacuuming from a known area allows expression of results in both mass per surface area (nanograms per square meter (ng/m2) and mass of chemical per mass of dust concentration parts per trillion (ppt or pg/g).

A total of 44 samples were collected from 30 households, including 14 resident's vacuum bags. All samples were sieved with an automated system with 100-mesh sieve and weighed following EPA SOP #2040, Collection of Indoor Dust Samples from Carpeted Surfaces for Chemical Analysis Using a Nilfisk GS-80 Vacuum Cleaner procedures in SERAS lab in Edison, New Jersey (NJ). Only the fine dust which passed the 100-mesh sieve was weighed and portioned to the samples sent for analysis. Polybrominated Dioxins/Furans in Dust EPA Method 1613B and Polychlorinated Dioxins/Furans in Dust Modified EPA Method 1613B; and Xenobiotic Detection Systems (XDS)-CALUX® EPA Method 4435 each required approximately 10 grams of dust. If an insufficient amount of sample volume was collected the following rules were applied:

- For samples less than 1.6 grams analysis for TCDD/TCDF and PBDD/PBDF (both to be analyzed using the same extract from the same GC/HR MS run) samples were analyzed via EPA method 1613B.
- For samples greater than 1.6 grams 1.1 grams or 50 % of the total, dust whichever is greater, for TCDD/TCDF and PBDD/PBDF analysis. The other portion was sent for CALUX analysis via EPA Method 4435.

### **Analytical Methods**

Resident's vacuum bag samples were divided into 10 grams of sample for EPA Method 4435 and the remaining sample volume for EPA method 1613B (High Resolution Gas Chromatography/High Resolution Mass Spectrometry or HRGC/HRMS)

A total of 36 samples were sent to Vista Analytical Laboratory, El Dorado Hills, California (CA) for analysis following Method 1613B. A total of 33 samples were sent to XDS, Durham, North Carolina (NC) for analysis following Method 4435. XDS received three fewer samples due to insufficient sample volume.

### **Data Validation**

SERAS data validation group reviewed the data packages produced by the analytical laboratories for completeness for EPA Method 1613B and EPA Method 4435. A qualitative review was completed on the Method 1613B data package from Vista Analytical Laboratory including the review of mass resolution checks, window defining mixtures, lock mass channels, initial calibrations, continuing calibrations, internal standards and column performance checks as to their acceptability to method criteria. A review of QC samples (method blanks, laboratory control samples (LCS) and Matrix spikes/duplicates (MS/MSD) as to their acceptability to method criteria. A review of sample data: qualitative (presence or absence of compound) and quantitative (correct concentration is reported). Determination of the data quality was documented by placing qualifiers on the sample results based on QC parameters.

### **Calculation of Toxicity Equivalency (TEQ)**

EPA published a report titled, Recommended Toxicity Equivalence Factors (TEFs) for Human Health Risk Assessments of 2,3,7,8-Tetrachlorodibenzo-p-dioxin and Dioxin-Like Compounds (TEF report) (U.S. EPA, 2010). The TEF report describes EPA's updated approach for evaluating the human health risks from exposures to environmental media containing DLCs. In the TEF report, EPA recommends use of the consensus TEF values for TCDD and DLCs published in 2005 by the World Health Organization for all cancer and noncancer effects mediated through aryl hydrocarbon (AH) receptor binding. Further, EPA recommends that the TEF methodology, a component mixture method, be used to evaluate human health risks posed by these mixtures, using TCDD as the index chemical. The TEFs are factors that scale individual DLC exposures to toxicity equivalence (TEQ) units of TCDD. To assess health risks for a given exposure to a mixture of DLCs, the TEQ's of those DLCs are summed, and the sum (i.e., total TEQ) is used with the dose-response information for TCDD. For the results summarized in this report, the minimum TEQ was calculated, summing the TEQs for the detected congeners.

While the TEFs for chlorinated DLCs have been widely accepted, the relative potency of brominated dioxins/furans is not well established and is not typically used by the EPA Superfund program to assess risks. The toxicity relative to TCDD have been estimated using the response in the CALUX assay as an indication of relative binding to the AH receptor. These TEFs were used for the calculation of an estimated TCDD-TEQ for the brominated dioxins.

The CALUX assay is a direct measurement of total binding to the AH receptor, quantified relative to the response of TCDD. Therefore, the CALUX-TEQ measures the total toxic potency (relative to a TCDD standard), while HRGC-HRMS first determines the concentration of each congener and calculates the total TCDD-TEQ. In general, studies of the correlation between CALUX-TEQ and TCDD-TEQ by HRGC/HRMS suggest the CALUX values tend to be higher, possibly due to contribution of other compounds not measured by HRGC/HRMS.

The TEFs used in the calculation of TCDD-TEQs are shown in Attachment 1.

### **Results**

The concentration of the chlorinated dioxins (as TCDD-TEQ), TEQ for the detected brominated dioxins and furans, and bio-TEQ measured using the CALUX assay are shown in Table 1 for the Gainesville area background homes, and Table 2 for those homes sampled in the Stephen Foster Neighborhood. These include only those results sampled using the EPA sampling protocol (EPA SOP #2040). These results allow comparison of the TCDD-TEQs, allowing comparison of the relative toxicity for different compound groups or methods. Table 1. Gainesville Area Background Houses: Contaminant Concentrations in Indoor Dust

Background	TCDD-TEQ	Brominated Dioxin &	CALUX® Screening
House	Concentration	Furan-TEQ*	Bioassay Concentration
	(pg/g)	Concentration (pg/g)	(pg/g)
A	34.0	5.7	11.5
В	5.37	1159.9	47.51
С	35.1	104.6	51.97
D	2.66	33.8	27.93
Е	6.34	19.9	30.49
F	6.45	3.4	12.03
G	47.6	62.4	84.45
Н	6.69	12.2	24.16
I	18.3	below detection limits	insufficient sample size
J	6.52	635	8.32
K	77.3	below detection limits	insufficient sample size
L	18.2	206.3	200.73
M	15.3	18.9	insufficient sample size
median	15.3	33.8	29.21
geometric mean	13.6	47.8	31.59

TCDD - TEQ = 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents  $CALUX^{®} = Chemical-Activated Luciferase Expression bioassay$ 

pg/g = picograms per gram (parts per trillion, ppt) \*Brominated Dioxin & Furan TEQ concentration based on relative potency factors in D'Silva, et al 2004. Source of data: EPA 2012

Table 2. Select Stephen Foster Area Houses: Contaminant Concentrations in Indoor Dust

Stephen Foster	TCDD-TEQ	Brominated Dioxin &	CALUX® Screening
House	Concentration	Furan-TEQ*	Bioassay Concentration
	(pg/g)	Concentration (pg/g)	(pg/g)
A	11.4	0.5	15.30
В	72.3	1.1	22.15
С	29.2	6.2	33.46
D	38.1	161.8	74.36
Е	8.92	27.8	42.39
F	13.4	36.0	42.54
G	27.6	32.1	7.06
Н	50.6	605.2	39.21
I	42.9	0.4	53.55
J	60.3	10.2	53.87
K	17.5	28.6	55.03
L	37.6	0.3	25.02
M	44.9	1.2	29.24
N	6.78	7.7	8.45
О	27.7	2.8	16.38
P	90.9	3.9	149.58
Q	19.0	5.7	33.97
median	29.2	6.2	33.97
geometric mean	27.9	7.0	31.78

TCDD - TEQ = 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents  $CALUX^{\otimes} = Chemical$ -Activated Luciferase Expression bioassay pg/g = picograms per gram (parts per trillion, ppt) \*Brominated Dioxin & Furan concentration based on relative potency factors in D'Silva, et al 2004. Source of data: EPA 2012

The chemical concentrations are helpful in comparing concentrations with background data or results from other locations. However, the dust loading, or amount of dust over a given surface area, can influence the exposure. It was requested that residents limit vacuuming prior to sample collection so that sufficient sample would be obtained for testing. The amount of dust collected varied among the homes, however, it is not certain if these values accurately represent typical levels. The dust loading (mg/m2) for these locations as measured using the standard sampling protocols are summarized in Table 3.

Table 3. Dust Loading in Sampled Homes

Background House	Dust Load (mg/m²)	Stephen Foster House	Dust Load (mg/m²)
A	43	A	1,003
В	58	В	78
С	55	С	34
D	56	D	741
Е	411	Е	32
F	274	F	265
G	188	G	816
Н	9	Н	1,108
I	52	I	182
J	66	J	110
K	47	K	497
L	22	L	901
M	64	M	1,240
		N	970
		О	25
		Р	157
		Q	85

### Discussion

All samples have detected concentrations of chlorinated dioxins and a measurable response in the CALUX TEQ bioassay. Brominated dioxins were detected in all dust samples with the exception of two that had only a small sample size available for the analysis.

Wood treating is a potential source of the chlorinated dioxins. While all but one of the SFN samples were within concentrations detected in background samples, the median TCDD-TEQ concentration in the SFN homes of 29.2 pg/g is higher than the median in background samples of 15.3 pg/g. None of the TCDD-TEQ concentrations exceeded 100 pg/g, with approximately 85% below 50 pg/g.

Brominated dioxins are not related to the former wood treating operations, but are generally associated with potential flame retardant materials found in homes. Of the 30 homes tested, five had brominated TCDD-TEQ estimates above 100 pg/g, with a maximum of 1160 pg/g. Concentrations were typically lower in the SFN homes, with a median TEQ of 6.2 pg/g as compared to 33.8 pg/g for the background homes. The highest concentrations appear to be sporadic, possibly associated with specific sources within these homes. In approximately 40% of the samples, chlorinated dioxins accounted for 80-99% of the total

TEQ. Brominated compound TEQs exceeded chlorinated TCDD-TEQs in over half the samples, with 8 of the 27 samples exceeding by more than 20 pg/g.

The CALUX-TEQ results ranged from 7.06 to 200.73 pg/g, with median values of 29 and 34 pg/g for background and SFN homes respectively. Only 2 of 27 samples (~7%) had CALUX-TEQ values above 100 pg/g. Three dust samples had TCDD-TEQ concentrations for brominated compounds ranging from 605-1160 pg/g, however, the CALUX-TEQ for these samples ranged from 8.3-48 pg/g, suggesting that these brominated compounds were not included in the CALUX-TEQ. The ratio of the chlorinated TCDD-TEQ result to the CALUX-TEQ ranged from 0.09 to 3.91, with the CALUX-TEQ underestimating the TCDD-TEQ in over 25% of the samples.

By contrast, the CALUX-TEQ from 2010 results showed concentrations exceeding 100 pg/g in over 65% of the samples, with concentrations more similar to the sum of the chlorinated and brominated TEQs found in this EPA study. As summarized by Windal et al. 2005, several factors impact the CALUX assay result, particularly the extraction and sample cleanup protocols. EPA Method 4435 and the XDS patented clean up method (US patent # 6,720,431) do not specify one exact protocol for sample cleanup. While XDS has reported the response of brominated compounds using the CALUX bioassay (Brown et al. 2001; Brown et al. 2004), the sample processing protocol may be altered to provide results for specific chemical groups. To interpret the results of the CALUX assay, the specific protocols for sample processing must be documented for each set of samples tested.

### Risk

Soils in residential properties adjacent to the Site show concentrations of dioxins above the Florida Soil Target Cleanup Levels for dioxin TEQ, raising questions regarding concentrations and exposure to these chemicals in house dust. It was known (and confirmed in this study) that dioxins (aka TCDD-TEQ) are present in all house dust samples, including background areas. The purpose of the sampling was to compare concentrations in household dust that may be related to the former Koppers facility (located at 200 NW 23<sup>rd</sup> Avenue) to background levels and consider possible actions to reduce exposures.

Background samples were taken in homes well away from the Site which would not have been impacted by site contamination. EPA has reviewed the results considering background data and a risk-based screening value. It was determined that no remedial actions are required. The risk-based screening value for dioxin derived by EPA for potential exposure to dust in homes is 190 pg/g (ppt) dioxin. (TCDD-TEQ)

EPA derived this risk-based screening value for dioxin by utilizing a July 2011 document entitled the *Indoor Dust Investigation/Interpretation Plan*, *Stephen Foster Neighborhood*, *Gainesville*, *Florida* (hereafter referred as "Plan")- which includes exposure assumptions and a toxicity values that were agreed to by the Indoor Dust Dioxin Workgroup convened by the Florida Department of Health made up of federal, County, State and community representatives.

There were no contaminants detected that exceeded any applicable EPA health-based benchmarks for Koppers Site-related compounds. EPA is providing support to research and report on sources of dioxins in homes, actions that may help reduce exposures and anticipates reductions in concentrations following soil remediation.

The highest chlorinated dioxin/furan dose from accidentally ingesting (swallowing) indoor dust in 13 Gainesville area background houses and 17 houses near the Koppers facility is below health guidelines. The highest estimated increased cancer risk from lifetime exposure is 1 in 100,000 or  $1 \times 10$ -5. This estimate means that 1 person out of 100,000 people exposed over a lifetime might develop cancer, or that an individual has an increased risk of 1 in 100,000 of developing cancer over his/her lifetime.

### **Conclusions**

This study evaluated patterns of dioxins and dioxin like compounds using the definitive method for analysis of chlorinated dioxins/furans by HRGC/HRMS. Although protocols are not routine, brominated dioxins/furans were also quantified using this method.

- Chlorinated dioxin compounds are somewhat higher in the SFN dust samples as compared to background, but generally within the concentration range measured in these samples. The maximum chlorinated TCDD-TEQ concentration detected was 90.9 pg/g.
- Brominated dioxins are reported in selected background and SFN samples at levels much higher than the chlorinated dioxins, with a maximum brominated TCDD-TEQ of 1160 pg/g.
- The CALUX-TEQ has been shown in the literature to measure responses to both chlorinated and brominated dioxins, however, cleanup methods may be used to separate these chemical groups. The 2012 samples analyzed in this study do not include the response to the brominated dioxin/furans. However, historical dust samples from this area have concentration ranges more consistent with the sum of the halogenated dioxins.

For the SFN, properties with soil concentrations exceeding the Florida Soil Cleanup Target Level (SCTL) of 7 pg/g will be remediated, reducing potential future tracking of impacted soils into homes and reducing concentrations of chlorinated dioxins following mitigation. In addition, reducing dust loading will reduce potential exposures.

Soil remediation will not reduce concentrations of dioxins attributed to other sources within the home, particularly those attributed to presence of brominated flame retardants. EPA has developed an Action Plan to phase out/ reduce exposures to brominated flame retardants.

### References

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XDS, April 13, 2004. Methods and apparatus for separating and detecting specific polyhalogenated diaromatic hydrocarbons. US Patent #6720431 B2. <a href="http://www.google.com/patents/US6720431">http://www.google.com/patents/US6720431</a>

## **Attachment 1**

# **Dioxin Toxicity Equivalence Factors**

	TEF
Chlorinated dibenzo-p-dioxins	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
Chlorinated dibenzofurans	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003
Brominated dibenzo-p-dioxins	
2,3,7,8-TBrDD	0.54
1,2,3,7,8-PeBrDD	0.49
1,2,3,4,7,8/1,2,3,6,7,8-HxBrDD	0.001
Brominated dibenzofurans	
2,3,7,8-TBrDF	0.49
1,2,3,7,8-PeBrDF	0.41
2,3,4,7,8-PeBrDF	0.09
1,2,3,4,7,8-HxBrDF	0.001
1,2,3,4,6,7,8-HpBrDF	0.002
Chlorinated Dioxin TEFs, EPA 2010	

Brominated Dioxin & Furan TEFs based on relative potency factors in D'Silva, et al 2004. Source of data: EPA 2012