

# Florida Department of Environmental Protection

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July 18, 2011

Mr. Scott Miller Remedial Project Manager United States Environmental Protection Agency Region IV, Superfund North Florida Section 61 Forsyth Street, SW Atlanta, Georgia 30303

RE: DEP review of April 2011 Off-site Data Summary and Fingerprinting Evaluation

Cabot Carbon/Koppers Superfund site, Gainesville, Florida

#### Dear Scott:

Thank you for the opportunity to review the above referenced document. The report summarizes the offsite soil data collected by Beazer to date, provides a discussion of fingerprinting techniques used to evaluate possible sources of PAH and dioxin contamination near the former Koppers facility, and compares offsite contaminant concentrations to proposed background concentrations. In addition, the report proposes additional offsite soil sampling locations for delineation of site related contamination as well as locations for further background determination. General comments are provided below and focus primarily on offsite contaminant delineation. Review comments from Dr.s Roberts and Stuchal at the University of Florida (UF) are enclosed and provide further discussion, particularly in the areas of fingerprinting and determination of representative background concentrations. DEP agrees with the UF review comments.

As discussed below, delineation of the extent of offsite soil contamination by arsenic, carcinogenic PAHs (expressed as BAP-TE) and dioxin (expressed as TCDD-TEQ) has not been accomplished to date. Additional soil sampling beyond that proposed in the report is necessary to adequately delineate offsite contamination to the soil cleanup target levels (SCTLs) identified in the EPA February 2011 Record of Decision. As offsite soil contamination has been confirmed, DEP recommends that future sampling be conducted on private properties, rather than limiting locations to ROWs, in order to expedite delineation and design of offsite remediation.

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#### Arsenic:

Section 2.1 erroneously concludes that offsite concentrations of arsenic above the 2.1 mg/kg SCTL do not exceed site specific residential background concentrations and therefore have been adequately delineated. As discussed in the UF comments, the non-statistical determination of an arsenic background concentration did not follow DEP guidance, nor has statistical determination of a representative background been made. As such, we recommend additional sampling west of Koppers to delineate arsenic contamination in the areas of SS-09 and SS-15 to 2.1 mg/kg. We also recommend delineation of arsenic south of Koppers in the area of SS-309. Note also that while arsenic has been delineated to the residential SCTL east of Koppers, sampling was limited to locations 200 + feet away from the property boundary. It would be prudent to conduct additional sampling between the Koppers property boundary and those sampling points to more closely determine where arsenic meets the residential criterion.

## Carcinogenic PAHs (cPAH):

A review of existing data indicates that cPAH has not been delineated to the residential SCTL west of Koppers (SS-06, -07, -13), south/southwest (SS-307, -308, -309), east/southeast (SS-305, -306, -310), or north (SS-302, -303). Site specific background levels have also not been established. As discussed by UF, fingerprinting based on PAH constituent ratios did not conclusively demonstrate other offsite sources. As such, we recommend additional delineation in the areas noted above, particularly west and south of Koppers, and east around SS-310. Please note that while there are properties characterized by commercial land use in the immediate vicinity of Koppers, particularly to the east, offsite soil contamination should be delineated to residential (unrestricted use) criterion. Site related contaminants may remain on a property above unrestricted levels only if the property owner agrees to a restrictive covenant ensuring land use is consistent with cleanup criteria.

#### Dioxin:

We are pleased to see additional offsite sampling proposed immediately west and south of the Koppers property where dioxin has not been delineated to the residential SCTL of 7 ppt, in accordance with the ROD. In addition to the proposed ROW samples, however, DEP recommends that sampling be conducted on private properties as part of this delineation effort, including the area northwest of SS-204.

A review of existing data indicates that the western extent of dioxin contamination has not been delineated and that soil sampling west of NW 6<sup>th</sup> Street is necessary to complete delineation to the residential SCTL. While the work plan asserts that

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preliminary busy residential street data suggest a site specific background concentration in the vicinity of NW 6<sup>th</sup> Street higher than the residential SCTL, there is inadequate data to support this assertion at this time. Even if this is the case, further delineation west of NW 6<sup>th</sup> Street would be necessary to evaluate contaminant trends and demonstrate that delineation of site related contamination has been accomplished. DEP recommends that additional delineation sampling not be postponed and that it be conducted on private properties west of NW 6<sup>th</sup> Street from the area just south of NW 26<sup>th</sup> Ave north to approximately NW 31st Ave.

DEP recommends additional dioxin delineation east of Koppers, particularly in the area of SS-301 where dioxin was detected at 23 ppt. As noted above, delineation should be to the residential criterion, so that properties with site related concentrations above unrestricted use may be identified. Contaminants may remain on a property above unrestricted levels only if the property owner agrees to a restrictive covenant ensuring land use is consistent with cleanup criteria.

It is unclear why additional delineation has not been proposed to the north where dioxin was detected at 35 and 38 ppt (SS-303 and SS-300, respectively).

## **Background:**

Beazer has proposed to collect additional background samples at both busy residential street background areas and commercial/industrial background areas. We agree that existing data is insufficient to develop site specific background levels. DEP is not convinced, however, that the selection of industrial areas is appropriate to support development of commercial background levels for the immediate vicinity of Koppers. Previous background sampling in an industrial area showed dioxin concentrations much higher than other commercial areas sampled. Further, we question whether or not a busy residential street scenario should be applied to residences within the Stephen Foster neighborhood, particularly where houses do not front 6th Street. While Beazer may elect to conduct additional sampling in comparable locations further away from the site to support development of background, DEP recommends that soil samples also be collected along the NW 6th Street corridor directly west of Koppers as well as further north and south along the corridor to determine if trends in concentrations support a site specific busy street background level above the SCTL. Similar trend analyses of the spatial pattern of contamination should be conducted by sampling commercial areas and ROWs moving away from the Koppers property to the east and south, to determine when delineation of site related contamination is complete.

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# **Incremental Sampling:**

DEP understands that Incremental Sampling Methodology (ISM) is being considered as a soil sampling method for offsite soil delineation and determination of site specific background at the Koppers site. We appreciate the importance of timely delineation of offsite contamination at the Koppers site as well as EPA's desire to apply a statistically robust approach to delineate contamination and characterize the risk posed by dioxin at Superfund sites.

DEP staff participated with EPA and others in the development of ITRC ISM guidance and is currently evaluating how this approach can be applied under Chapter 62-780, FAC. DEP will be happy to work with EPA and Beazer in development of the work plan such that applicable requirements of Chapter 62-780 are satisfied.

If EPA and Beazer decide to utilize ISM in offsite delineation at Koppers, we strongly urge EPA to require a detailed work plan that clearly identifies the proposed "decision units" (DU) (both size and specific geographic locations), and the number of increments (samples) and replicates per DU. Of particular importance is the selection of the ISM "decision unit" as it relates to the "exposure unit" defined in Chapter 62-780, particularly under a residential use scenario. We understand that EPA's User Guide indicates that the standard residential DU should be 0.25 acres. This is consistent with Chapter 62-780, which specifies the same default residential property size and exposure unit. Note that there may be circumstances when the DU size may be adjusted to facilitate evaluation of potential source areas or "hot spots".

It is also important to keep in mind the strengths and weaknesses of the ISM approach, particularly those areas where guidance has not been developed including use of ISM to determine site specific background concentrations, identifying contaminant heterogeneity or "hot spots" within a DU or exposure unit, and evaluating broader spatial trends in contaminant distribution using both ISM and discrete sample data. In addition, experienced field and laboratory personnel are necessary to ensure that appropriate sampling methods and lab sample preparation procedures are followed. DEP is available to discuss this further.

Please let me know if you would like to discuss these comments or have any questions. I can be reached at 850-245-8969 or <u>kelsey.helton@dep.state.fl.us</u>.

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Sincerely,

Vubry A Helh

Bureau of Waste Cleanup

Enclosure

cc: Zoe Kulakowski, DEP

Ligia Mora-Applegate, DEP



### Center for Environment & Human Toxicology

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May 17, 2011

Ligia Mora-Applegate Bureau of Waste Cleanup Florida Department of Environmental Protection 2600 Blair Stone Road Tallahassee, FL 32399-2400

Re: Off-site soil data evaluation and fingerprint analysis for the Koppers site

Dear Ms. Mora-Applegate:

At your request, we have reviewed the *Off-Site Data Summary and Fingerprinting Evaluation, Cabot Carbon/Koppers Superfund Site, Gainesville, Florida.* This document was prepared by Arcadis and is dated April 6, 2011. It summarizes arsenic, polynuclear aromatic hydrocarbon (PAH), and dioxin concentration data in off-site soil. Fingerprinting techniques including profile evaluation and multivariate analysis were used to identify the possible source(s) of PAH and dioxin contamination near the site. Chemical concentrations in soil were also compared to residential, industrial, and residential busy street site-specific background concentrations. The document concludes that risk from exposure to soil near the Koppers site is similar to risks in other areas of Gainesville. We have the following comments regarding the document:

- 1. Figure 2-3 shows the distribution of background and site arsenic concentrations. Among the background samples, only one sample from a residential area and one sample from an industrial area exceeded the FDEP residential SCTL of 2.1 mg/kg (14.5 and 13.4 mg/kg, respectively). According to the Dixon's Outlier test, both concentrations are outliers at the 1% significance level. These samples likely represent small point source areas and should not be utilized in the background calculations.
- 2. Section 2.1 Arsenic states that off-site concentrations of arsenic that exceed the FDEP soil cleanup target level (SCTL) of 2.1 mg/kg are consistent with background concentrations. The site-specific residential mean background arsenic concentration (excluding the outlier) is 0.9 mg/kg (Table 2-1). The Guidance for Comparing Background and Site Chemical Concentrations in Soil (FDEP, 2008) states that for a non-statistical comparison to background, the lower of the maximum or twice the mean background concentrations should be used. In this case, twice the mean background concentration (1.8 mg/kg) is utilized to represent background. Using this approach, off-site arsenic exceedances (2.5, 3.0, and 3.1 mg/kg) would not be considered background arsenic concentrations.
- 3. Delineation of arsenic contamination does not appear to be refined to the east of the site. Arsenic concentrations along the eastern boundary of the Koppers site exceed

both residential and commercial/industrial cleanup target levels. The closest off-site samples were taken 200-400 feet away from the boundary and are below residential criteria. Off-site soil arsenic concentrations meet the FDEP residential SCTL at some point between Koppers' eastern boundary and the off-site samples. However, it is not possible to extrapolate a concentration gradient from the available data. Therefore, it is unclear how far arsenic contamination above residential criteria extends off-site. We recommend additional arsenic delineation in this area.

- 4. Section 2.2.5 Fingerprinting PAHs and 2.3.2 North and East of Site states that, with the exception of the elevated concentrations in the southwest and southeast corners of the site, PAH and TCDD-TEQ concentrations on the east and south sides of the Koppers facility are either below FDEP criteria or are representative of site-specific background. We have the following comments:
  - a. It appears that commercial/industrial criteria were utilized to screen soil concentrations of contaminants on the south and east sides of the site. Commercial/industrial SCTLs can only be utilized if an institutional control (agreed to by the property owner) is in place preventing future residential reuse. Otherwise, residential (i.e. unrestricted land use) criteria should be used. All of the samples east and south of the site exceed the residential benzo(a)pyrene equivalent (BaP TEQ) criterion of 0.1 mg/kg and the residential TCDD-TEQ criterion of 7 ng/kg.
  - b. Only three industrial background soil samples were taken. The above cited background guidance (FDEP, 2008) suggests a minimum of seven samples for calculating a site-specific background criterion. Therefore, a comparison of the off-site samples to industrial PAH and TCDD-TEQ background concentrations should not be performed with the available data. For PAHs it is especially important that background samples be taken away from roadways, parking lots, ditches, and other areas that may be affected by runoff. It is not clear from the document if these areas were avoided during background sampling.
- 5. Fingerprinting for PAHs was performed using the fluoranthene/pyrene (FI/Py) and benzo(a)anthracene/benzo(a)pyrene (BaA/BaP) ratios. On-site PAH samples have a FI/Py ratio equal to or less than 1.0, while most off-site samples to the east and south have a ratio between 1.1 and 1.3. FI/Py ratios to the west of the site were below 1.0, but PAH exceedances were regarded as isolated and not associated with the Koppers site. The analysis concluded that off-site concentrations of BaP-TEQs exceeding the Florida residential criterion of 0.1 mg/kg did not originate from the Koppers site. We have several concerns regarding this analysis:
  - a. The majority of FI/Py ratios on-site were close to a value of 1. An FI/Py ratio near 1 could result from a mixture of pyrogenic and petrogenic sources (Baumard et al., 1998). The difference between on-site and off-site FI/Py ratios does not necessarily indicate different sources, but could suggest a different percent contribution of each source to the total PAH concentration. Therefore, we do not recommend source determination based on FI/Py ratios alone.
  - b. The FI/Py ratio is utilized to differentiate between petrogenic and pyrogenic origins of PAHs (Baumard et al., 1998; Wang and Fingas, 2003). The most likely sources of PAH contamination at and around the site (e.g., creosote treatment,

auto emissions, and backyard burn barrels) represent pyrogenic sources. This ratio does not appear specific enough to distinguish among the pyrogenic sources. Therefore, it is uncertain how this ratio distinguishes PAH sources at the Koppers site.

- c. It is unclear what the BaA/BaP ratio is intended to represent. We could not find any precedent for use of this ratio to determine source. The off-site sample SS13 BaA/BaP ratio was compared to an average site BaA/BaP ratio. This is not effective means of determining source. As the FI/Py ratio demonstrates, on-site sample ratios were not identical and sometimes differed greatly (minimum 0.39; maximum 1.39). By averaging the ratios across the site, individual fingerprints are lost and source identification of PAHs at SS13 is not achievable.
- d. The use of only two PAH ratios appears inadequate for source identification. This is especially true for a site that has several probable sources of pyrogenic PAHs in different stages of degradation/weathering. A more detailed analysis of the relationships between on-site and off-site PAH fingerprints appears necessary to determine if the contamination is truly site-related. Further analysis may include the use of additional PAH ratios, alkylated PAHs, or principal component analysis to elucidate probable sources.
- 6. Page 11 states PAH fingerprints at SS06 and SS07 (120-280 ng/kg) were not distinguishable from the site. However, they were assumed to be localized and likely the result of introduction of coal tar-derived or creosote-treated materials in the vicinity of these samples. While we agree a localized source is a possible explanation for the isolated PAH concentrations, no evidence has been presented that the PAHs detected in these areas did not originate from the site. They are located downwind of the site and adjacent to on-site PAH concentrations an order of magnitude higher (3,000 mg/kg). Additional sampling in these areas may be necessary to determine if the source is localized. Otherwise, there does not appear to be substantial evidence that the PAHs in this area originate from a source other than the Koppers site.
- 7. We disagree that the fingerprinting analysis provided "very strong evidence" that the PAH concentrations to the south of the site are not site-related. Although the fluoranthene/pyrene ratios of these samples differ from most of the samples taken on site, they are equivalent to ratios obtained from several site samples located on the southern boundary of the site. Excepting the one southern location with a BaP-TE concentration in excess of 8700  $\mu$ g/kg, there is no substantial evidence that these PAHs did not originate from the site.
- 8. Page 13 states all off-site TCDD-TEQ concentrations were less than the proposed site-specific SCTL of 95 ng/kg. The cleanup target level specified in the Record of Decision is 7 ng/kg, consistent with the Florida cleanup target level for unrestricted land as promulgated in Chapter 62-777, F.A.C.
- 9. Section 2.3.3 South of Site compares the average and maximum TCDD-TEQ concentrations from south of the site to the average and maximum TCDD-TEQ for industrial background and residential busy street background. We have the following concerns with this comparison:

- a. Off-site TCDD-TEQ concentrations should not be averaged. Contamination may be present in only a few sampling areas and averaging effectively dilutes out the areas of higher concentrations. This may result in isolated areas of contamination that could pose a risk to human health. This is especially relevant for samples on different properties such as those near the Koppers site.
- b. Direct comparison of average or maximum concentrations is not a statistically valid method for determining if off-site samples are representative of background. We recommend using the methodology in the above cited background guidance (FDEP, 2008) to determine if off-site samples are indicative of background.
- c. As stated above, only three industrial and residential busy street background samples are available. A minimum of seven background samples is recommended to determine background (FDEP, 2008). Therefore, additional samples are necessary before a comparison should be made with background TCDD-TEQ concentrations.
- 10. Section 2.3.4.3 Multivariate Analysis concludes the cluster of seven samples west of the site in the vicinity of NW 6<sup>th</sup> Street and NW 28<sup>th</sup> Avenue, SS63, SS230, SS238, SS01, SS302, SS303, SS81, SS300, and SS307 have compositions suggesting the PCDDs/PCDFs in these areas originate from sources not related to site activities. While the principal component analysis can support the conclusion that samples were influenced by alternate sources, many of these sample locations have signatures that lie between background and site signatures and cannot easily be categorized as a non-site source. Statistical correlations with background and site samples would help determine source when the signature cannot be readily interpreted by multivariate analysis alone (Bright et al, 1999).
- 11. Additional delineation of TCDD-TEQs appears to be necessary west of NW 6th Street near NW 26th Avenue and NW 29th Avenue. In Section 3.3 Additional Samples West of the Site, Beazer proposes to delay sampling west of NW 6th Street until a larger residential busy street background dataset can be obtained. Beazer suggests a full background dataset will demonstrate dioxin concentrations along NW 6th Street are representative of site-specific residential busy street background. Residential busy street background sampling locations are proposed along Routes 26, 24, and 441. It is unclear if these roadways represent the same traffic patterns as NW 6th Street, and consequently whether they are germane to establishing background TCDD-TEQs due to traffic on NW 6th Street. A more defensible approach, in our opinion, would be to sample along NW 6th Street north and south of the site. This would help establish what dioxin concentrations might be expected along NW 6th Street adjacent to the site absent any site influences. We see no reason to delay sampling residential areas west of NW 6th Street to complete delineation of TCDD-TEQs in this direction. Samples further west will be needed regardless of findings immediately along NW 6th Street in order to evaluate spatial trends and confirm that delineation of site related contamination is complete.
- 12. Additional sampling in industrial areas away from the site is proposed in order to expand the available background data set. The document contends that these data will be helpful in determining the extent to which additional delineation east and south of the site is needed. However, the extent to which the areas proposed for further sampling are representative of commercial activities to the immediate east and south of the site are

questionable. We recommend a more direct approach, sampling commercial areas and right-of-ways moving away from the site to the east and south and evaluating the spatial pattern of contamination to determine when delineation of site-related contamination is complete.

13. Section 4 Conclusions states, cumulative risk from arsenic, PAHs, and PCDDs/PCDFs in the vicinity of the site appear to be similar to or lower than the cumulative risk from these constituents in other areas of Gainesville. This conclusion is out of place — a cumulative risk assessment for areas in the city of Gainesville is well beyond the scope of this report. The document is better served by focusing on its primary function, which is assisting in the design of a sampling program to complete delineation of off-site contamination originating from the Koppers site.

Please let us know if you have any questions regarding this review.

Sincerely,

Leah D. Stuchal, Ph.D.

Lead Steelas

Stephen M. Roberts, Ph.D.

#### References:

Baumard, P, Budzinski, H, Michon, Q, Garrigues, P, Burgeot, T, and Bellocq, J (1998) Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal, and Shelf Science* **47**: 77-90.

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Bureau of Waste Cleanup, Program & Technical Support Section, Tallahassee, Florida.

Wang, Z and Fingas, MF (2003) Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin* **47**: 423-452.