SEDIMENT CPAH LEVELS IN TRIBUTARIES OF THE LITTLE MENOMONEE RIVER

MOSS-AMERICAN SITE
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EXECUTIVE SUMMARY

The Moss-American Milwaukee facility is comprised of a former wood preserving plant and approximately 5 miles of the Little Menomonee River (LMR) in Milwaukee, Wisconsin. Byproducts of the former wood treating processes include carcinogenic polycyclic aromatic hydrocarbons (CPAHs), which have affected a portion of the LMR that flows south from the site. In order to demonstrate that the site is not the sole source of CPAHs in the LMR, a tributary sediment sampling event was performed in November and December of 2002.

A total of 135 investigative samples were collected from 40 tributaries to Reaches 2 through 5 (approximately 2-5 miles south of the former wood preserving plant). These tributaries included streams and dry ditches, as well as select storm sewer catch basins that ultimately contribute to the LMR. Each sample was analyzed for CPAHs in the field, and sent for laboratory confirmation if the field-determined CPAH concentration exceeded 15 mg/kg.

Of the 135 investigative samples, 28 (21 percent) contained CPAH concentrations greater than 15 mg/kg, and 3 (2 percent) of those contained CPAH concentrations in excess of 100 mg/kg. The value of 15 mg/kg is noteworthy because it has been identified as the cleanup level for LMR sediments based upon previous investigations of background CPAH levels. The results reported in this study are not uncommon for urban soils and sediments affected by typical industry, developments, and automobiles. These samples indicate off-site non-point sources of CPAHs that contribute to the CPAH levels in the sediment of the LMR.

SECTION 1
INTRODUCTION

The Moss-American Milwaukee facility, as defined by the Consent Decree, includes the former Moss-American wood preserving plant property and approximately 5 miles of the Little Menomonee River (LMR). The LMR flows through the eastern portion of the former wood preserving plant, continuing on through the Milwaukee County Parkway, to its confluence with the Menomonee River about 5 miles south. Operations at the former wood preserving plant included using creosote to treat wood. Creosote contains, among other chemicals, polycyclic aromatic hydrocarbons (PAHs), a group of compounds composed of two or more fused aromatic rings. Eight of the PAHs are considered to be probable human carcinogens at the site. PAHs may be introduced into the environment via natural or anthropogenic processes, including wood treating as well as incomplete combustion of petroleum, oil, coal, and wood.

1.1 PURPOSE AND OBJECTIVES

The purpose of this report is to present current concentrations of carcinogenic polycyclic aromatic hydrocarbons (CPAHs) in sediments from tributaries contributing to Reaches 2 through 5 of the LMR. These results are intended to evaluate the presence of off-site sources of CPAHs contributing to the LMR in areas proposed for future remediation.

In addition, literature reports on CPAH levels in urban sediments are also discussed with an emphasis on results obtained from Milwaukee, Wisconsin.

1.2 PREVIOUS INVESTIGATIONS

1.2.1 1994 Investigation

Samples from tributaries to Reaches 1 through 5 of the LMR were collected and analyzed during a sampling event in August of 1994 (Predesign Task 2b, WESTON, 1994). Background concentrations in downstream tributaries were determined by collecting several sediment samples from each of eleven tributaries, for a total of 46 samples. The conclusion of this investigation was that the maximum probably background concentration was 48 mg/kg of CPAHs.

1.2.2 2002 Investigations

Several site-related investigations have taken place in the recent past with the objectives of determining concentrations of CPAH in the field and determining the implementability and reliability of a new field procedure. These investigations include a Phase I Testing of Reach 1 Floodplain Soil (WESTON 2002b), Phase II Testing of Reach 1 Floodplain Soil (WESTON 2002c), and confirmation sampling of the soils excavated during Reach 1 construction.

The first phase of immunoassay testing was performed during May 2002 to determine the effectiveness and implementability of the RaPID Assay® immunoassay test (distributed by Strategic Diagnostics, Inc. [SDI], of Newark, Delaware) for field analysis of total CPAH concentrations. Soil samples were collected from the upper 1 foot (ft) interval below ground surface (bgs) at stations located approximately every 200 ft along the new alignment for Reach 1 of the LMR proposed in the 90% Design Report (WESTON 2002a). A total of 30 floodplain soil samples were field-analyzed for total CPAHs and moisture content using the RaPID Assay immunoassay and the Speedy Moisture Meter, respectively. A random selection consisting of 10 of the 30 samples collected was sent to the lab for analysis of total CPAHs and moisture content to facilitate an evaluation of the field results. Overall, excellent correlation was observed between field and laboratory measurements of moisture content, with results varying by no more than 8%. The correlation between field- and laboratory-measured total CPAH concentrations was also very good. Variance occurred only at the very low concentrations (i.e., 1 to 3 milligrams per kilogram [mg/kg] range), where the RaPID Assay tended to overestimate the total CPAH concentration by approximately 1 to 2 mg/kg. Thus, the results of the first stage of immunoassay testing were deemed reliable and were used to guide the second stage of sampling.

Based on the first stage of immunoassay soil sampling, total CPAH concentrations of 3 of the 30 soil samples exceeded the 6.1 mg/kg soil cleanup objective, and 2 of these samples exceeded the 15 mg/kg soil excavation standard. The objective of the second stage of immunoassay field analysis was to delineate the extent of soil containing total CPAH concentrations exceeding the excavation standards in these three areas. The immunoassay sampling for this investigation revealed that occasionally, the results revealed false positives, i.e., the RaPID assay suggested the soil exceeded the applicable cleanup standard when, in fact, the laboratory reported that samples met the criterion. However, in no instance did the immunoassay provide a false

negative. Discussion with SDI regarding the discrepancies in the data have led us to conclude that the disparity between the data in these instances is a combination of two major factors: nonhomogenous nature of soil producing data that has variability, and interferences with other constituents (i.e., noncarcinogenic PAHs) that elevate the immunoassay result.

Based on the first two rounds of immunoassay soil sampling, the RaPID Assay field testing method was deemed reliable enough to use for field confirmation sampling during the construction of the new route in Reach 1.

The use of the new field assay technology as a screening tool made a large-scale tributary sampling event cost-effective. In this report, a total of 40 tributaries over 4 river miles and 135 samples was analyzed, compared to the 9 tributaries over 5 river miles and 46 samples analyzed in 1994.

1.3 2002 TRIBUTARY SAMPLING INITIAL ACTIVITIES

A site-scoping visit was performed on 26 and 27 September 2002, prior to mobilization of personnel and equipment for these sampling activities. Maps were prepared for this visit with tributaries identified from depressions in the topography and storm sewer network diagrams. During this initial visit, each tributary was examined for sampling potential.

In general, most manholes inspected during the site-scoping visit contained little or no sediment. In many instances, tributaries consisted of a stormwater sewer, with several manholes along its run, which discharged directly to the LMR. In these instances, since there was no sediment within the manholes and the sewer outfall was directly to the LMR, sampling of these was determined to be infeasible. Of the few catch basins that had sufficient sediment present to sample, several were relatively dry and several others had standing water present.

Natural drainage features located ranges from swales to open flow channels that contained up to several feet of water. All of these features were sampled.

SECTION 2
SAMPLING COLLECTION, ANALYSIS, AND RESULTS

Tributary sample collection activities were performed 4 through 19 November 2002, and field and sample preparation for laboratory analysis was performed within 6 days of sample collection.

2.1 SEDIMENT SAMPLING LOCATIONS

Sediment sampling locations were selected based on the results of the site scoping visit (Section 1.3) and were adjusted as needed in the field. In general, relatively large tributaries with flowing water were sampled at 3 to 6 locations, with the locations more concentrated at the beginning of the tributary (i.e., storm sewer outlet, roadside, etc.). Smaller tributaries and dry ditches were sampled proportionally fewer times, and manholes were sampled once. These locations were marked in the field and the GPS coordinates were recorded. All sampling locations and CPAH levels are depicted in Figures 2-1 through 2-4.

2.2 SEDIMENT SAMPLING, HANDLING, AND ANLYSIS

Each soil sample was collected using a stainless-steel bucket auger. The auger was decontaminated between sampling intervals at each sampling location using an Alconox wash followed by a distilled water rinse. The sample media removed from the auger was placed into plastic bags and stored in an iced cooler until all soil samples from the sampling phase were collected. Free product was not observed in any of the media. Strict chain-of-custody procedures were employed during storage of the samples.

During execution of the fieldwork, field identifiers were used to easily label and track samples through the collection, storage, and analysis stages. The basic field identifier implemented consists of a 3-digit code, such as X-Y-Z, where X represents the Reach (2, 3, 4, or 5), Y indicates the tributary number (e.g., 1, 2, 3, 4…), and Z indicates the sample location along the reach (i.e., A, B, C… with A being the furthest from the confluence with the LMR).

Samples were analyzed for moisture content and CPAHs using both field and laboratory methods. A total of 135 investigative samples and 13 duplicate samples were analyzed in the

field for total CPAHs using the RaPID Assay immunoassay test. A total of 135 investigative and 13 duplicate samples were also analyzed in the field for moisture content using a Large Speedy Moisture Meter, manufactured by Ashworth Instrumentation of Lancashire, England. In addition, to confirm the CPAH concentration of any sample that exceeded the screening level of 15 mg/kg using the RaPID Assay, a duplicate sample from that location was submitted to Lancaster Laboratories of Lancaster, Pennsylvania, for analysis of PAHs by SW-846 Method 8310 and moisture content per EPA 160.3 modified. A total of 46 of the 135 samples had RaPID Assay concentrations exceeding the 15 mg/kg screening level, and were sent into Lancaster Laboratories. Four of these were sent in duplicate.

The following subsections provide a brief overview of the RaPID Assay and Speedy Moisture Meter procedures employed during the field analysis, as well as the procedures for sample preparation for field and laboratory analyses.

2.3 SAMPLE PREPARATION

Each sample was homogenized either by manually massaging the material within the plastic bag or using decontaminated, stainless-steel spoons and mixing bowls until the sample appearance (i.e., color and texture) was consistent. For those samples submitted for laboratory analysis, the sample media was placed into 16-ounce glass jars with Teflon-coated lids following homogenization. Upon homogenization of the soil media, aliquots were also collected for analysis using the RaPID Assay and the Speedy Moisture Meter. The samples submitted for laboratory analysis were labeled with identifiers as indicated in Table 2-1, placed in an iced cooler for shipment, and delivered under chain-of-custody via overnight courier to Lancaster Laboratories.

2.4 MOISTURE CONTENT ANALYSIS (SPEEDY MOISTURE METER)

Moisture content of the soil samples was measured in the field using a Speedy Moisture Meter. All 135 of the investigative/replicate soil samples were analyzed using the meter, and an additional 13 duplicate measurements were performed to evaluate the performance of the instrument. Analyses were conducted in accordance with manufacturers specifications.

2.5 TOTAL CPAH ANALYSIS (RAPID ASSAY)

All 135 investigative/replicate soil samples and 13 duplicate soil samples were analyzed for total CPAHs using the RaPID Assay immunoassay. The standard detection range for the RaPID Assay test is 0.01 to 0.5 milligrams per kilogram (mg/kg). The standard test was modified to include a 50-fold serial dilution to increase the detection range maximum level from 0.5 to 25 mg/kg. Analyses were performed in accordance with manufacturers specifications.

The spectrophotometer printout provides both the calibration curve information and prints out the concentration of each sample in micrograms per kilogram (µg/kg). Copies of the spectrophotometer printouts are included as Attachment B (note that the concentrations indicated on the printout are uncorrected for the serial dilution and represent wet weight concentrations). The samples were extracted and analyzed in four batches, each with their own set of CPAH standards for calibration of the standardized curve.

A table containing all tributary sediment sampling results is presented in Table 2-1. This data, along with sample locations are presented in Figures 2-1 through 2-4 on a site map of Reaches 2-5.

2.6 DATA ANALYSIS

All 2002 samples were analyzed in the field for moisture and CPAHs. If the CPAH concentration exceeded 15 mg/kg using the field assay, a duplicate sample was sent to Lancaster Laboratories (see Section 2.2). Table 3-1 compares laboratory data to field data for these samples. In general, moisture content never varied by more than 25% between laboratory and field measurements, and variance was less than 10% in 35 out of 45 samples. The difference between field and laboratory total CPAH measurements was more difficult to quantify. CPAH concentrations frequently measure outside of the calibration range for the field procedure (greater than 25 mg/kg wet weight), and therefore, a field measured CPAH concentration could not be recorded. For those concentrations that were within the calibration range for the field procedure, the field and laboratory measurements varied between less than 1 mg/kg and 94 mg/kg. Based on prior investigations, the sample population sent to the laboratory is expected to have greater variance between field and laboratory measurements than a random selection of samples because of the selection of samples with elevated levels for laboratory analysis.

remainder of the tributaries that were not sampled consists of storm sewer pipelines that contained little or no sediment.

The concentrations of the samples from tributaries of Reach 4 ranged from non-detect to 253 mg/kg. Four of the twelve tributaries sampled contained sediment with concentrations of CPAH greater than the 15 mg/kg screening level. These include tributaries 4-3, 4-4A, 4-8, and 4-11. Tributaries 4-3 and 4-4A were located near the intersection of Fond Du Lac Avenue and 91st Street; tributary 4-8 was located near a residential area; and tributary 4-11 was not located near any specific feature.

2.6.4 Reach 5

A total of 19 investigative samples were collected from 7 of the 9 identified tributaries to Reach 5. Tributaries 5-2 and 5-3 were not sampled. These were both storm sewer pipelines with little or no sediment.

The concentrations of the samples from tributaries of Reach 5 ranged from non-detect to 35 mg/kg. Three of the 7 tributaries sampled contained sediment with concentrations of CPAH greater than the 15 mg/kg screening level. These include tributaries 5-1, 5-4, and 5-5. Tributary 5-1 is located near the Silver Spring Drive bridge and tributaries 5-4 and 5-5 both stem from residential areas.

2.7 SIMPLIFIED FIGURES

Figures 2-5 and 2-6 were created to focus on the CPAH concentrations in both the tributaries and the river channel and their relative positions. These figures include all CPAH sampling results from tributary sampling and channel sampling events, as well as average concentrations per tributary and per reach. Main channel sampling results come from four separate sampling events, including Remedial Investigation sediment samples (CH2M Hill, 1990), Predesign Task 4 sediment samples (WESTON, 1994), WDNR sediment split samples (WDNR, 1999), and Pilot River Diversion sediment samples (WESTON, 2001).

The laboratory data superceded any field data in any summaries, figures, and the following discussions.

2.6.1 Reach 2

A total of 43 investigative samples were collected from 13 of the 14 identified tributaries to Reach 2. Tributary 2-9 was not sampled because this tributary was identified as a storm sewer line containing little to no sediment. The concentrations ranged from non-detect to 330 mg/kg. Five of the thirteen sampled tributaries contained sediment with concentrations of CPAH greater than the 15 mg/kg screening level. These include tributaries 2-4, 2-5A, 2-5B, 2-6, and 2-7. All five are located relatively close to one another and to West Calumet Road. Two of the samples from these tributaries had CPAH concentrations exceeding 100 mg/kg. The concentration of CPAHs in the channel at these locations is consistently below 100 mg/kg, indicating these tributaries are affected by an off-site source.

2.6.2 Reach 3

A total of 31 investigative samples were collected from 8 of the 12 identified tributaries to Reach 3. Tributaries 3-1, 3-2, 3-8, and 3-10 were not sampled. Tributaries 3-1 and 3-2 are sewer outfalls very near the LMR. Tributary 3-8 was identified on the topographic map as a very slight change in elevation, but was not discernable in the field. Tributary 3-10 was identified as a storm sewer line, but no manholes or outfalls were located in the field.

The concentrations of the samples from tributaries of Reach 3 ranged from non-detect to 84 mg/kg. One of the tributaries sampled contained sediment with concentrations of CPAH greater than the 15 mg/kg screening level. This was tributary 3-6, which included 3 samples exceeding the screening level. These samples were all located along a ditch just behind a residential area.

2.6.3 Reach 4

A total of 42 investigative samples were collected from 12 of the 18 identified tributaries to Reach 4. Tributaries 4-2, 4-5A, 4-5B, 4-7, 4-9, and 4-15 were not sampled. Tributary 4-2 was a concrete median in Highway 45 and contained no accumulation of sediment. Tributary 4-5B was a storm sewer line with an inaccessible manhole (in the middle of an intersection). The

SECTION 3
CPAH CONCENTRATIONS IN TYPICAL URBAN SEDIMENT

The United States Geological Survey (USGS) was contacted in 1992 for information regarding organics in sediment samples from Milwaukee County. Additionally, several publications have been identified that discuss PAH concentrations in urban soil and sediment. The results from these inquires are summarized below.

The USGS, in cooperation with WDNR, conducted an investigation of urban runoff in 1989. Sediment samples were collected in Milwaukee County from areas representing nonpoint sources and analyzed for CPAHs. According to the study, sediment CPAH levels ranged as high as 53.1 mg/kg in these samples (WESTON, 1993).

A study from the New England area (Bradley et. al, 1994) reports on typical CPAH concentrations found in urban soils. Of 60 samples from Boston, MA, Providence, RI, and Springfield, MA, the mean CPAH concentration was 9 mg/kg. The greatest CPAH concentration found was 77.7 mg/kg. Also notable is that the population of samples that were 4-6 feet from pavement was statistically different from those that were further from pavement, indicating that there is a strong correlation between CPAH concentrations and automobile exhaust. Closer to the Moss-American site, a study was performed on the PAHs in the sediments of the Milwaukee Harbor Estuary from 1990 to 1994 (Li et. al, 1998). The focus of the study was to provide a historical overview of the impact of industrialization in the Milwaukee area. To accomplish this, 21 sediment cores and 37 grab sediment samples were collected from the Milwaukee Harbor Estuary and the contributing rivers (Milwaukee, Kinnickinnic, and the Menomonee Rivers). The median total PAH concentration in the surface sediment samples from the different areas of the Estuary ranged from 17.2 mg/kg to 138.3 mg/kg, with a maximum of 390.8 mg/kg. CPAH appears to be 62% of total PAHs, or 25.1 ppm in surface sediment in the area of the Menomonee within 4 kilometers of the Milwaukee Harbor Estuary according to this study. This study also concludes that constant PAH levels over time tend to occur in rivers adjacent to heavy road traffic, again confirming the correlation between CPAH concentrations and automobile exhaust.

Additional studies (Singh et. al, 1993 and Stout et. al, 2001) have suggested that it is possible todetermine non-point sources of PAHs by comparing relative concentrations of specific PAHcompounds to known source "signatures." Known non-point sources of PAHs include coal tar, coal tar air emissions, No. 2 fuel oil, gasoline engine exhaust tar, and highway dust. About halfof the 211 samples analyzed for the Singh et. al Milwaukee area study (including 2 from the Menomonee River) fit well with known source profiles, and of these, 88 percent found highway dust to be a significant source.

These and other studies have confirmed the fact that PAHs are ubiquitous throughout urban areas. Thus, a distinction between soils affected by point sources and those affected by nonpoint sources becomes more difficult to define. CPAH concentrations above 15 mg/kg are common not only in this tributary investigation, but also in soils and sediments throughout Milwaukee County and other urban settings. These levels are easily attributed to non-point sources such as automobile exhaust and highway dust.

SECTION 4
DISCUSSION AND CONCLUSIONS

Three samples from three separate tributaries contained concentrations of CPAH above 100 mg/kg in tributaries to the LMR. All three were found near major roadway intersections. Concentrations of this magnitude are rarely found within the main channel and certainly indicate an off-site source of CPAHs. An additional 25 samples from an additional 10 tributaries revealed CPAH concentrations above the screening criterion of 15 mg/kg, also indicating off-site sources. Literature and other sampling investigations reveal that CPAH concentrations above 15 mg/kg are common in many urban areas, including Milwaukee. These concentrations can be attributed to non-point sources such as automobile exhaust and highway dust. The simplified depiction figures (3-1 and 3-2) reveal that the average CPAH concentration in the channel of Reaches 2 and 3 is more than double the average CPAH concentration the channel of Reaches 4 and 5, and shows a general downward trend with the distance away from the former wood processing plant. The median concentration in each of the tributaries ranges only from 4.3 to 8.0 mg/kg. The median concentrations in the tributaries show no trend with the distance away from the former wood treating facility.

Based on the information presented in this report, the following conclusions can be drawn:There exist off-site non-point sources of CPAHs contributing to the LMR via several tributaries along Reaches 2 through 5. Concentrations of CPAH are elevated within the main channel of the LMR through Reaches 2 and 3, indicating a likely impact from the former wood treating facility, while Reaches 4 and 5 contain CPAH concentrations similar to the CPAH concentrations found in the tributaries.

The elevated levels of CPAHs in tributary sediments indicates that any significant remediation of Reaches 4 and 5 of the LMR is unwarranted.

SECTION 5
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