

March 2022 Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee Estuary Area of Concern

Forensic Evaluation and Source Review Technical Memorandum

Prepared for Wisconsin Department of Natural Resources EPA GLRI Grant No. GL-00E02392 March 2022 Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee Estuary Area of Concern

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Prepared for

Wisconsin Department of Natural Resources 1027 West St. Paul Avenue Milwaukee, Wisconsin 53233

Prepared by

Anchor QEA, LLC 290 Elwood David Road, Suite 340 Liverpool, New York 13088-2104

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ABBREVIATIONS

BRRTSBureau for Remediation and Redevelopment Tracking SystemDNRWisconsin Department of Natural ResourcesCSOcombined sewer overflowDMRdischarge monitoring reportEPAU.S. Environmental Protection AgencyERPEnvironmental Repair ProgramFL0/PY0fluoranthene to pyreneGLLAGreat Lakes Legacy ActGLRIGreat Lakes Restoration InitiativeKK RiverKinnickinic RiverMGmillion gallonsmg/kgmilligrams per kilogramMGPmanufactured gas plantMISMilwaukee Interceptor SystemMKE AOCMilwaukee Estuary Area of ConcernMMSDMilwaukee Metropolitan Sewerage DistrictN/TPAH (18)naphthalene to TPAH (18)NPDESNational Pollutant Discharge Elimination SystemPAHpolycyclic aromatic hydrocarbonPCBpolsbe effects concentrationProposalKinnickinic River - Source Review and Forensic Analysis ProposalR2coefficient of determinationTech MemoForensic Evaluation and Source Review Technical MemorandumTetra-CBtetrachlorobiphenylTPAH (18)total PAH (18)TSCAToxic Substances Control ActWVTPwastewater treatment plant	BF-Tot/PY	total benzofluoranthenes to pyrene
CSOcombined sewer overflowDMRdischarge monitoring reportEPAU.S. Environmental Protection AgencyERPEnvironmental Repair ProgramFL0/PYOfluoranthene to pyreneGLLAGreat Lakes Legacy ActGLRIGreat Lakes Restoration InitiativeKK RiverKinnickinnic RiverMGmillion gallonsmg/kgmilligrams per kilogramMKE AOCMilwaukee Interceptor SystemMKE AOCMilwaukee Estuary Area of ConcernMMSDNational Pollutant Discharge Elimination SystemPPESNational Pollutant Discharge Elimination SystemPAHpolycyclic aromatic hydrocarbonPCBcoefficient of determinationR²coefficient of determinationR²coefficient of determinationProposalForensic Evaluation and Source Review Technical MemorandumTetra-CBtetrachlorobiphenylTPAH (18)total PAH (18)TPAH (18)total PAH (18)R²coefficient of determinationR²coefficient of determinationTetra-CBtetrachlorobiphenylTPAH (18)total PAH (18)TPAH (18)total PAH (18)	BRRTS	
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EPAU.S. Environmental Protection AgencyERPEnvironmental Repair ProgramFL0/PY0fluoranthene to pyreneGLLAGreat Lakes Legacy ActGLRIGreat Lakes Restoration InitiativeKK RiverKinnickinnic RiverMGmillion gallonsmg/kgmilligrams per kilogramMGPmanufactured gas plantMISMilwaukee Interceptor SystemMKE AOCMilwaukee Metropolitan Sewerage DistrictN/TPAH (18)naphthalene to TPAH (18)NPDESNational Pollutant Discharge Elimination SystemPAHpolycyclic aromatic hydrocarbonPCBpolychlorinated biphenylPECcoefficient of determinationR ² coefficient of determinationR ² tetrachlorobiphenylTetra-CBtetrachlorobiphenylTPAH (18)total PAH (18)TPAH (18)Source Review Technical MemorandumTetra-CBtetrachlorobiphenylTPAH (18)total PAH (18)TSCAToxic Substances Control ActWPDESWisconsin Pollutant Discharge Elimination System	CSO	combined sewer overflow
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MKE AOCMilwaukee Estuary Area of ConcernMMSDMilwaukee Metropolitan Sewerage DistrictN/TPAH (18)naphthalene to TPAH (18)NPDESNational Pollutant Discharge Elimination SystemPAHpolycyclic aromatic hydrocarbonPCBpolychlorinated biphenylPECprobable effects concentrationProposal <i>Kinnickinnic River – Source Review and Forensic Analysis Proposal</i> R ² coefficient of determinationTech Memo <i>Forensic Evaluation and Source Review Technical Memorandum</i> Tetra-CBtetrachlorobiphenylTSCAToxic Substances Control ActWPDESWisconsin Pollutant Discharge Elimination System	MGP	manufactured gas plant
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TSCAToxic Substances Control ActWPDESWisconsin Pollutant Discharge Elimination System	Tetra-CB	tetrachlorobiphenyl
WPDES Wisconsin Pollutant Discharge Elimination System	TPAH (18)	total PAH (18)
5	TSCA	Toxic Substances Control Act
WWTP wastewater treatment plant	WPDES	Wisconsin Pollutant Discharge Elimination System
	WWTP	wastewater treatment plant

1 Introduction

This *Forensic Evaluation and Source Review Technical Memorandum* (Tech Memo) has been prepared for the Wisconsin Department of Natural Resources (DNR) under the U.S. Environmental Protection Agency (EPA) Great Lakes Restoration Initiative (GLRI) grant (EPA GLRI Grant No. GL-00E02392) and has been completed in accordance with the approved *Kinnickinnic River – Source Review and Forensic Analysis Proposal* (Proposal; Anchor QEA 2021a). This Tech Memo describes the results of a source review and forensic analysis of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the Kinnickinnic River (KK River) within the Milwaukee Estuary Area of Concern (MKE AOC).

Sediment sampling in September 2020 identified sediments with PCB concentrations greater than 50 milligrams per kilogram (mg/kg)¹ and total PAH concentrations greater than 114 mg/kg (five times the probable effects concentration [PEC]) within Reach 1 of the KK River.² These PCB and PAH concentrations observed in 2020 were much greater than sediment PCB and PAH concentrations observed during previous sampling events (Arcadis 2016). Reach 1, defined as KK River beginning downstream of the South Chase Avenue Bridge extending to the West Becher Street Bridge, is the furthest upstream reach within the MKE AOC. Reach 1 is characterized as having the shallowest water depths and most natural shoreline within the KK River of the MKE AOC. Reach 1 is also directly upstream of Reach 2 (defined as KK River beginning at West Becher Street Bridge downstream to the South Kinnickinnic Avenue Bridge), where a remedial action was performed in 2009. Under this remedial action, 170,000 cubic yards of sediment was dredged as part of a Great Lakes Legacy Act (GLLA)-funded project, followed by the placement of a 1- to 4-foot sand cover over most of the remediated area (CH2M Hill 2011).

Results of sediment sampling in 2020 showed surface sediment concentrations exceeded screening criteria for at least one chemical (metals, total PAHs, or total PCB Aroclors) at every location within Reach 2, including above the observed sand cap, where present (Anchor QEA 2021b). The elevated PCB and PAH concentrations (greater than 50 mg/kg for PCBs and five times the PEC for PAHs) in Reach 1 and surface sediment concentrations above the screening levels in Reach 2 have prompted efforts for a desktop study of potential sources through the use of environmental forensics and a source review.

Environmental forensics is the evaluation of chemical, physical, and historical information to identify and differentiate sources of contamination observed in the environment. This approach is most often differentiated from more traditional site investigations by the application of chemical fingerprinting

¹ 50 mg/kg was the highest screening level provided by DNR and represents a PCB threshold where specific materials management and disposal are required under the Toxic Substances Control Act (TSCA).

² Additional detail pertaining to the larger KK River and Milwaukee Bay Project can be found in the *Site Investigation Report* for KK River and Milwaukee Bay (Anchor QEA 2021b).

as a central line of evidence. Environmental forensics investigations combine chemical fingerprinting with other site information, such as facility operations, chemical concentration patterns, and chemical fate and transport evaluations, to develop a multiple-lines-of-evidence determination of likely contaminant sources at an environmental investigation site.

This Tech Memo first presents a chemical fingerprinting analysis of PAH and PCB samples collected during the 2020 sediment sampling event in the MKE AOC (Section 2) and then presents a summary of investigations regarding current and historical facilities that could have used PAHs and PCBs and potentially discharged into the MKE AOC (Section 3). Results of this desktop study were then used to inform where additional sampling in 2021 may help to identify the source and/or extent of PCB and PAH concentrations above the screening criteria.

2 Chemical Fingerprinting

Chemical fingerprinting involves the analysis of specific chemical patterns that can be used to differentiate contamination sources (Murphy and Morrison 2007; Murphy and Morrison 2015; Stout and Wang 2016; Sullivan et al. 2001). Chemical fingerprinting can be performed for any group of associated contaminants or for specific classes of chemicals, such as PAHs or PCB congeners (Murphy and Morrison 2007). To try to correlate contaminant sources to environmental samples, Anchor QEA develops site-specific reference fingerprints (fingerprints representing contaminant signatures at that site) from site-specific analysis. In addition, fingerprints from published data for known contamination types are commonly used to confirm and corroborate site-specific fingerprints.

This section is divided into fingerprinting investigations for PAHs (Sections 2.1 and 2.2) and PCBs (Sections 2.3 and 2.4). Chemical correlations are provided in Section 2.5 and chemical fingerprinting conclusions are provided in Section 2.6.

As described in the Proposal, the objectives of this forensic evaluation were as follows:

- Conduct a PAH chemical fingerprint evaluation of samples collected in 2020 in Reaches 1 through 4 to evaluate spatial distribution of PAH fingerprints, whether there is support for distinct PAH signatures observed in Reaches 1 and 2, and what types of sources may be represented by the fingerprints.
- Conduct a PCB chemical fingerprint evaluation of samples collected in 2020 in Reaches 1 through 3 to evaluate spatial distribution of Aroclors, mixtures of Aroclors, and other PCB signatures to determine if there is evidence of specific PCB sources in the project area.
- Conduct a correlation analysis among contaminant types (total PCBs, total PAHs, and metals) to determine the potential for correlated signatures and source markers.

2.1 PAH Forensic Methods

PAHs are aromatic hydrocarbons composed of two or more fused benzene rings. The benzene rings may have only hydrogen atoms attached to the ring structure (parent PAHs) or may have one or more alkyl substituents, such as methyl and ethyl groups, in place of hydrogen atoms (alkylated PAHs).

Anthropogenic PAHs in the environment originate from the following two primary sources (Afanasov et al. 2009; Birak and Miller 2009; Murphy and Morrison 2015; Stogiannidis and Laane 2015; Stout and Graan 2010; Stout and Wang 2016; Baldwin et al. 2017):

1. **Petrogenic PAHs:** These PAHs are derived from fossil fuels such as crude oil and rock coal, as well as from refined petroleum products such as gasoline, diesel, bunker C fuel, motor oil, and asphalt.

2. **Pyrogenic PAHs:** These PAHs are derived from combustion products of organic or petrogenic material, including manufactured gas plant (MGP) tar, coal tar products such as parking lot sealant, creosote and pitch, and airborne combustion waste such as vehicle exhaust from diesel.

The relative abundance of individual PAHs (PAH fingerprints) can provide information about potential sources of PAHs to environmental samples. Histograms showing concentration results for individual PAHs (PAH profiles) are routinely used for this purpose. PAHs in profiles are arranged in a standard left-to-right order of increasing benzene ring number and are further arranged in order of increasing number of alkyl substituents (alkylated series) from zero to four on parent PAHs (Figure 2-1). Table 2-1 lists the full chemical names, abbreviations (used in figures and text), ring numbers, and alkyl group numbers of the PAHs analyzed in this Tech Memo. The relative abundance of pairs of PAHs in a PAH histogram are frequently quantitatively evaluated in forensic analysis using ratios of their concentrations. The diagnostic ratios produced from this practice can be used to identify and distinguish PAH sources from each other if the ratios are consistent within each source, different for different sources, and resistant to changes resulting from weathering (Murphy and Morrison 2015; Stogiannidis and Laane 2015).

The 16 EPA priority pollutant PAHs (PAH [16]) routinely quantified in environmental site investigations are only a subset of a larger group of PAHs (termed "forensic PAHs" for the purposes of this discussion) typically used to evaluate and distinguish PAH sources in forensic investigations. The larger set of PAH results improves the resolution of source-specific PAH fingerprints and, importantly, includes alkylated PAHs, which are useful for distinguishing pyrogenic from petrogenic PAH source types (Murphy and Morrison 2015; Stogiannidis and Laane 2015; Stout and Wang 2016). The sampling program that produced the data analyzed for this Tech Memo reported 18 PAHs (concentration sum reported as total PAH [18] [TPAH (18)])³. TPAH (18) includes PAH (16), an additional parent PAH (benzo[e]pyrene), and one alkylated PAH (2-methyl naphthalene). PAH (18) provides some additional information over PAH (16) but is still limited compared to a larger forensic set of PAHs for fingerprint analysis.

Figure 2-1 shows published examples of forensic PAH profiles for three general PAH source types for a forensic set of PAHs: 1) a pyrogenic source (fresh coal tar; Uhler and Emsbo-Mattingly 2006); 2) a petrogenic source (number 6 fuel oil; EPRI 2000); and 3) a mixed source (urban background, Portland Harbor, Oregon; Stout et al. 2004). The typical pyrogenic PAH profile pattern is dominance of parent PAHs and decreasing abundance of alkylated PAHs within each alkylated series. Petrogenic sources

³ The PAHs included in the TPAH (18) sum are 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene.

are dominated by alkylated PAHs and usually have a hump-shaped abundance pattern (i.e., unweathered) or increasing abundance pattern (i.e., weathered) within each alkylated series.

A pervasive PAH urban background presence in urban and suburban settings results from a mixture of vehicle exhaust, tar-based pavement coatings, fuel and motor oil spills, and industrial combustion, among other sources. Urban background PAH profiles tend to be dominated by high-molecular-weight PAHs, which are distinct from coal tar PAH profiles, except in cases of advanced tar weathering. Urban background PAH profiles also have more variability in alkylated PAH patterns but typically have predominantly pyrogenic features (Stout et al. 2001, 2004).

2.2 PAH Forensic Results

Potential PAH signatures were evaluated by analyzing sediment PAH fingerprints for all sediment samples collected in the KK River during the 2020 sampling program. The PAH profiles for each sediment sample are provided in Appendix A. As a result of this evaluation (described in more detail below), two consistent PAH fingerprint patterns were repeatedly observed in the sediment samples. These two patterns will be referred to as Fingerprint 1 and Fingerprint 2 (Figure 2-2). Both fingerprints have a fluoranthene to pyrene (FL0/PY0) ratio greater than 1.0, which is typical of pyrogenic PAH sources derived from coal tar (EPRI 2000; Uhler and Emsbo-Mattingly 2006; Birak and Miller 2009). Various sources of coal tar signatures include coal tar pitch (roof tar, boat epoxy, and anodes for aluminum smelting are potential sources), parking lot seal coat, MGP tar from coal combustion, and creosote. Alternatively, FL0/PY0 ratios less than 0.5 are often indicative of petrogenic PAH sources (Murphy and Morrison 2015; Stogiannidis and Laane 2015; Stout and Wang 2016).

Two sediment samples were selected to represent each fingerprint—KKR-20-010-C-00-01-200918 for Fingerprint 1 and KKR-20-023-C-00-01-200914 for Fingerprint 2 (Figure 2-2). These were selected because they were sediment samples with TPAH (18) concentrations within the highest range for their respective fingerprints (511 and 105 mg/kg, respectively; Figure 2-3) and appeared during a qualitative review to match many other samples in similar concentration ranges. This observation was confirmed by a cross plot analysis described below. Selecting samples with the highest PAH concentrations as representative fingerprints is done to obtain samples most likely to represent PAH source fingerprints. The PAH profiles for each sediment sample are provided in Appendix A.

Fingerprints 1 and 2 can be differentiated from each other based on several identifying characteristics. Figure 2-3 shows the TPAH (18) concentrations versus the total benzofluoranthenes⁴ to pyrene (BF-Tot/PY) ratio in sediment samples. Fingerprint 1 has higher intermediate-molecular-weight PAH concentrations than Fingerprint 2 and a BF-Tot/PY ratio less than 1. As Figure 2-3 shows,

⁴ Total benzofluoranthenes are the sum benzo(b)fluoranthene and benzo(k)fluoranthene.

samples with the highest TPAH (18) concentrations (often greater than five times the PEC) had BF-Tot/PY less than 1, and all of these within Reach 1 were reliably identified as Fingerprint 1. Alternatively, Fingerprint 2 is characterized by TPAH (18) concentrations that are two to five times the PEC, a predominance of heavy-weight PAHs and a BF-Tot/PY ratio greater than 1. As Figure 2-3 shows, samples with a BF-Tot/PY ratio greater than 1.0 occurred at intermediate TPAH (18) concentrations at two to five times the PEC range. A summary of the characteristics of each fingerprint is provided in Table 2-2.

All sediment samples were compared to Fingerprint 1 and Fingerprint 2 using cross plot analysis and categorized as matching Fingerprint 1, Fingerprint 2, or Other (a different profile). Cross plot analysis compared individual PAH concentrations for all 18 PAHs in each sediment sample on the y-axis to the percent weight of each PAH in the Fingerprint 1 and Fingerprint 2 reference samples on the x-axis. High coefficient of determination (R^2) values and scatter-free diagonal line patterns indicate a strong correlation and high goodness of fit between a sediment sample's PAH concentration and a particular fingerprint. Samples with high R² values (>0.95), in conjunction with a visual check of goodness of fit with either fingerprint, can be gualified as having the same PAH fingerprint. In addition, visual observation of the cross plots provided additional insight in determining if a particular sediment sample resembled a mixture of the two fingerprints, another PAH fingerprint, or a weathered version of either fingerprint.⁵ In general, mixtures of these fingerprints were only rarely apparent, indicating a relatively discrete distribution of the source type representing each of the fingerprints. An example of cross plot comparison is shown in Figure 2-4 with four panels on one page—two panels on the top and two panels on the bottom. Sample KKR-20-021-C-01-2.1-200917 in the top row of panels is compared to both Fingerprint 1 (left) and Fingerprint 2 (right) and can be seen to be a strong match for Fingerprint 2. Sample KKR-20-021-C-2.1-3.2-200917 in the bottom row of panels, conversely, is a strong match to Fingerprint 1, on the left. The cross plots of each sample against Fingerprints 1 and 2 are provided in Appendix B.

Spatial distributions, by reach and by depth (summarized in Table 2-2), of Fingerprint 1 and Fingerprint 2 were evaluated to try to better understand the origins of these two fingerprints. Figure 2-5 shows the distribution of Fingerprints 1 and 2 and Other by reach. Fingerprint 1 is predominantly found in the most upstream reach, Reach 1, whereas Fingerprint 2 is not found in Reach 1 and is observed most frequently in Reaches 2 and 3. The example cross plots in Figure 2-4 further illustrate the typical depth distributions of Fingerprints 1 and 2 where they were observed in the same core. The two samples in Figure 2-4 are from the same core—the top row sample is for the 1- to 2.1-foot depth and the bottom row sample is for the 2.1- to 3.2-foot depth. Typically, as demonstrated in Figure 2-4, matches to Fingerprint 2 in Reaches 2 and 3 were found in surface or, occasionally,

⁵ High R² values can artificially suggest a correlation, such as in the case of a single PAH having an extremely high concentration in the sample being evaluated and corresponding relative percent weight in the reference sample. The regression correlation coefficient will then be artificially high and could be erroneously interpreted.

shallow subsurface samples, whereas matches to Fingerprint 1 were found in subsurface samples. These spatial patterns suggest the following:

- An upstream source or Reach 1 source with Fingerprint 1 PAH profiles
- A source in Reaches 2 and/or 3 with Fingerprint 2 PAH profiles
- The surface distribution of Fingerprint 2 indicates it potentially originates from a more recent source than Fingerprint 1

There were no observed localized areas with a predominance of either Fingerprint 1 or Fingerprint 2, suggesting that it is unlikely there is a single specific point source as the source of Fingerprint 1 or Fingerprint 2 PAHs.

Two less prevalent PAH signatures were identified—small defined areas in both Reaches 3 and 4 were identified with a naphthalene-dominant signature (Fingerprint 3) and a small defined area with a petrogenic signature was identified in Reach 4. Figure 2-6 shows the ratio of naphthalene to TPAH (18) (N/TPAH [18]) versus the identification number of each core⁶. The cores with a naphthalene-dominant signature are KKR-20-033 (Reach 3; Figures A-138 to A-142 in Appendix A), KKR-20-034 (Reach 3; Figures A-143 to A-148 in Appendix A), and KKR-20-046 (Reach 4; Figures A-184 to A-189 in Appendix A). Based on cores with a naphthalene-dominant signature being from small defined areas adjacent to and downstream of the Solvay Coke and Gas Superfund Alternative Site and not widespread throughout the river, the source of the naphthalene-dominant signature (Fingerprint 3) is likely separate from the source of Fingerprints 1 and 2.

A potential petrogenic PAH signature is observed in the samples from KKR-20-067 (Figures A-251 to A-254 in Appendix A). The TPAH (18) concentrations in samples from this core are five times the PEC (highest TPAH [18] concentrations in the sampling event). Figure 2-7 shows the PAH profile from one sample from this core alongside Fingerprint 1 (top panel) and Fingerprint 2 (bottom panel). The location from which this core was collected is adjacent to two combined sewer overflow (CSO) outfalls and one sanitary sewer outfall. Lines of evidence for a petrogenic signature often include FL0/PY0 ratios less than 1 (0.55 to 0.61 in samples from this core, and shown by example with the arrows in Figure 2-7), a 2-methylnaphthalene concentration greater than naphthalene, and lower-molecular-weight distribution of PAHs (high 2- and 3-ring PAHs relative to higher-molecular-weight PAHs). However, it is difficult to confirm petrogenic signatures without a more complete list of alkylated PAHs included in the laboratory analysis.

As is discussed in Section 3, no specific facilities could be directly tied to the PAH Fingerprints 1 and 2. The potential for these fingerprints to have originated from coal tar-based asphalt sealant is

⁶ The core identifications were sequentially numbered from the most upstream sample location in Reach 1 (001) to the most downstream sample location in Reach 4 (069). Therefore, the numbers can be used as a surrogate for river mile and spatial patterns can be evaluated.

evaluated here. Coal tar-based sealants that are commonly applied to asphalt driveways and parking lots throughout the United States can contain a high percentage of coal tar and, therefore, have extremely high PAH concentrations (Van Metre and Mahler 2014; Baldwin et al. 2017). They have recently (2017) been banned in Milwaukee (City of Milwaukee 2019). These seal coats can form a dust from repeated vehicle traffic and the dust can become entrained into runoff. Recent research has determined that coal tar-based sealants can be a major source of PAHs to freshwater sediments (Van Metre and Mahler 2014), including specifically to the KK River in Milwaukee (Baldwin et al. 2017; USGS 2020). Fingerprint 1 and Fingerprint 2 are both consistent with expectations of a coal tar sealant, based on their FL0/PY0 ratio greater than 1 and dominance of high-molecular-weight PAHs. Specific PAH fingerprints of coal tar sealants are variable depending on the commercial mixture used. Figure 2-8 demonstrates that Fingerprint 1 resembles parking lot dust samples collected from two Milwaukee parking lots treated with coal tar sealant (data from Baldwin et al. 2017) and that Fingerprint 2 resembles an average of coal tar sealant PAH fingerprint dust from six cities (data from Van Metre and Mahler 2014), providing some support for coal tar-based sealants as a source for Fingerprints 1 and 2. The widespread nature of the concentration patterns of Fingerprints 1 and 2, as opposed to a more centralized "bullseye" pattern indicating a specific point source facility, is also consistent with a PAH source coming from overland runoff discharging through multiple outfalls. Specific linkage and pathways from local sealant applications to the KK River sediments in Reaches 1 and 2 cannot be confidently identified due to the lack of available information regarding coal tarbased sealant applications.

Potential sources of PAHs and PCBs to Reach 1 and Reach 2 are further evaluated in Section 3 of this Tech Memo.

2.3 PCB Forensic Methods

PCBs are a class of nonpolar, synthetic, halogenated hydrocarbons composed of a biphenyl backbone with 1 to 10 chlorine atoms substituted at one or more of the 10 available positions. There are 209 possible configurations of chlorine atoms around the biphenyl, and the molecules corresponding to each of these configurations are referred to as PCB congeners. A sequential numbering system (from 1 to 209) has been assigned to each congener and is used to refer to individual congeners. Congeners with the same number of chlorine atoms, but in different positions, are called homologs. For example, the homolog tetrachlorobiphenyl (Tetra-CB) comprises all PCB congeners that contain four chlorine substitutions. There are a total of 10 PCB homologs, ranging from chlorobiphenyl (one chlorine substitution) to decachlorobiphenyl (10 chlorine substitutions).

Commercial mixtures of PCBs were produced by Monsanto and sold under the trade name Aroclor. Aroclors were designated by overall chlorine content by weight percent, which determines oil viscosity and, consequently, industrial applications (Murphy and Morrison 2007). Aroclors were identified by a four-digit number. The first two digits refer to the product series as designated by Monsanto, and the last two digits indicate the chlorine content of the mixture (e.g., Aroclor 1254 contains 54% chlorine by weight).

Each Aroclor contains a distinct array of congeners, which create a unique pattern, or fingerprint (Frame et al. 1996). The relative congener distributions in Aroclors 1242, 1248, 1254, and 1260, with homologs indicated by color, are shown in Figure 2-9. Higher congener numbers correspond to a higher number of chlorines on that congener; therefore, with congeners arranged in increasing order, from 1 to 209, the distribution of congeners shifts to the right as percent weight of chlorine in the Aroclor increases (Figure 2-9). Because the variety of Aroclor products used can vary by facility based on manufacturing processes and facility operations, samples collected from nearby environmental media can have unique congener fingerprints.

Only samples with individual congener results from EPA Method 1668 were relied upon for source evaluation in this Tech Memo. Due to lower precision, the total Aroclor method (EPA Method 8082) can lead to misidentification of Aroclor composition, particularly in cases where Aroclors occur as mixtures or have undergone weathering, which would be expected in most environmental settings (Alford-Stevens 1986; Safe et al. 1987). Consequently, use of total Aroclor data from EPA Method 8082 is not recommended for forensic PCB source investigations (Douglas et al. 2007; Uhler et al. 2010).

2.4 PCB Forensic Results

To evaluate potential sources of PCBs to the river, PCB congener profiles were assessed in five cores (total of 19 samples) where congeners were measured via EPA Method 1668. Evaluations consisted of graphical comparison of congener results from sediment samples to Aroclor congener profiles. These are provided for all sediment samples, with congener results in Appendix C. The evaluation included qualifying the types and mixtures of Aroclors in samples based on visual comparison with Aroclor profiles and evaluating the vertical and horizontal spatial trends with respect to Aroclor types observed in the samples.

The five cores with congener results were collected in Reach 1 (KKR-20-010; Table 2-3), Reach 2 (KKR-20-015, KKR-20-022, and KKR-20-025; Table 2-4), and Reach 3 (KKR-20-027; Table 2-5). Table 2-3 shows the PCB results for KKR-20-010, located in Reach 1. The congener results suggest a mixture comprising predominantly Aroclors 1242/1248 in the sediments from 0 to 1 foot below the sediment surface (Figure 2-10, top panel) and transitioning to a mixture comprising predominantly Aroclors 1248/1254 in the deeper sediment of 5 to 7 feet below the sediment surface (Figure 2-10, bottom panel). This shows that there is a shift from lower-molecular-weight Aroclors (1242/1248) to higher-molecular-weight Aroclors (1248/1254) with increasing depth. This suggests that there was a change in PCB source over time in Reach 1 or potentially an ongoing source. Section 3.5 of this

memorandum summarizes a review of potential sources. In addition, further sediment sampling was completed in 2021 to aid in further potential source evaluations.

Also shown in Table 2-3 is that EPA Method 8082 for Aroclor concentrations does not correlate with an evaluation of the PCB congener profiles. In many cases, the laboratory reported a much higher frequency of Aroclor 1260 than what can be ascertained from a qualitative evaluation of the PCB congener profiles. Therefore, EPA Method 8082 Aroclor designations cannot be reliably used to determine PCB Aroclor mixtures for source assessment. This is consistent with publications recommending that EPA Method 8082 is unreliable for forensic Aroclor source assessment (Douglas et al. 2007; Uhler et al. 2010). Similar mismatched results between visual observation of congener profiles and EPA Method 8082 results occurred in Reaches 2 and 3 (Tables 2-4 and 2-5).

Table 2-4 shows the PCB congener summary results for the three cores collected in Reach 2. All but one sample have a mixture of Aroclors 1242/1248/1254 skewed more heavily toward the less chlorinated Aroclors 1242/1248. Most samples also appeared to contain a minor amount of Aroclor 1260 (Figure 2-11, top panel). The only exception to this pattern occurred in KKR-20-022 (Figure 2-11, bottom panel), where in the 1- to 3-foot sample, the prevalence of nona- and deca-PCB homologs, which would be consistent with a potential paint pigment source. These particular congeners are not prevalent in Aroclor mixtures (see Figure 2-9) but are found in certain pigments and dyes (Anezaki and Nakano 2014), potentially indicating a distinct PCB source to this area of the river. However, these concentrations are low relative to other PCB results, and should not be indicative of a major PCB source to the sediments in Reach 3.

Table 2-5 shows the PCB congener summary results for KKR-20-027 located in Reach 3. Consistent with Reach 2 results (Table 2-4, Figure 2-11), the surface sediments from 0 to 3 feet below the sediment surface have a mixture of Aroclors 1242/1248/1254 with a minor amount of Aroclor 1260. The deepest sample (3 to 4.3 feet) had a slightly higher-molecular-weight congener distribution skewed slightly toward a mixture of Aroclors 1248/1254. This is also the highest concentration sample in the core. Similar to the PCB congener results in the core from Reach 1, this supports the possibility of a change in PCB source over time.

This evaluation shows that most PCB profiles for samples where congener data were available indicate a broad mixture of Aroclors, which is consistent with mixed urban sources. The Aroclor signatures of the highest PCB concentrations identified in the sampling program were not evaluated because they only had results for EPA Method 8082. Future PCB source investigation may be aided by analysis of PCBs using EPA Method 1668 and was included in the 2021 sediment sampling program.

2.5 Chemical Correlations

Contaminants that correlate with each other spatially may provide information to potentially refine sediment source evaluations. Correlation in sediment samples of concentrations of different chemical groups (total PCBs, total PAHs, and the trace metals [arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc]) was evaluated to determine if a common source was indicated for any of these groups. Concentration cross plots, with one chemical or chemical group on the x-axis and another on the y-axis, were evaluated using R^2 and a visual observation of the results. Figure 2-12 shows the TPAH (18) concentrations versus total PCBs by EPA Method 8082 (Aroclor) concentrations in sediment samples from Reaches 1 and 2. There is a significant amount of scatter in this cross plot, where much of the data do not fall in a straight line ($R^2 = 0.11$), suggesting that PAHs and PCBs are not well correlated and are likely from different sources.

Figure 2-13 shows arsenic and cadmium concentrations plotted against the chromium concentrations measured in sediment samples from Reaches 1 and 2. Most of the chromium samples fall along the local urban background relationship versus other metals (the red line). Urban background metals contamination often correlates with other metals (Thorbjornsen and Myers 2007). However, some of the highest chromium concentrations (circled) deviate from the urban background pattern, indicating a potential for a local chromium source. This group of samples is from two reaches—KKR-20-023 and KKR-20-024 (Reach 2) and KKR-20-032 and KKR-20-034 (Reach 3). Cross plots of other chemicals showed little to no correlation and are not presented further in this Tech Memo.

2.6 Chemical Fingerprinting Conclusions

Two primary PAH fingerprints were identified from the 2020 KK River sediment sampling program. Both fingerprints have TPAH (18) concentrations multiple times greater than the PEC. These fingerprints are consistent with a coal tar source, with a higher concentration source potentially originating in or upstream of Reach 1 (Fingerprint 1). The second fingerprint is located more frequently in Reaches 2 and 3, suggesting that there is more than one source of PAHs to the river. There are no clear points of origin (i.e., localized areas where either Fingerprint 1 or Fingerprint 2 dominate). In addition, two more localized fingerprints, a naphthalene-dominant (Fingerprint 3) and a potential petrogenic signature, were identified in downstream reaches, suggesting distinct, localized PAH sources in these areas. Figures 2-14 through 2-17 show the PAH fingerprint assignments for surface and subsurface sediment sampling locations in Reaches 1 through 4, respectively, of the KK River.

PCB congener profiles indicate a mixture of low-molecular-weight and high-molecular-weight Aroclors, skewing toward a greater abundance of low-molecular-weight Aroclors (1242 and 1248). A change in Aroclor mixtures in the Reach 1 core with increasing depth below the sediment surface suggests the potential for a change in PCB sources over time. Aroclor mixtures in the highest PCB concentration samples cannot be determined due to a lack of congener data and not unexpected inconsistencies between the Aroclor designations reported by the laboratory and an evaluation of PCB congener profiles.

PAHs and PCBs do not covary with each other, nor with trace metals. This suggests independent sources for these chemicals.

3 Potential Sources Review

A source review was completed to identify potential sources of the two primary PAH fingerprints (Fingerprints 1 and 2) identified by the forensic analysis and described in Section 2 and to identify any obvious PCB sources to Reaches 1 and 2—the forensic analysis had insufficient data to identify a specific type of PCB source to Reaches 1 and 2. The source review area extended from the downstream boundary of Reach 2 at the South Kinnickinnic Avenue Bridge upstream through Reach 1 to the 29th Street Bridge.

The source review focused on the following items:

- Current property owners (Section 3.1; Table 3-1; Figures 3-0 through 3-22) and historical land use (Section 3.1; Appendix D)
- Sites identified in environmental databases (e.g., spill records; Section 3.2; Table 3-2; Figures 3-0 through 3-22)
- Identification and review of CSOs (Section 3.3; Table 3-3; Figures 3-0 through 3-22)
- Identification of other National Pollutant Discharge Elimination System (NPDES)-permitted discharges (Section 3.4; Table 3-4; Figures 3-0 through 3-22)

As discussed in Section 2.2, analyses of the PAH data indicated the presence of two primary fingerprints—an upstream PAH profile (Fingerprint 1) and a different PAH profile in Reaches 2 and/or 3 (Fingerprint 2). Both fingerprints are consistent with a coal tar source type, which could be a coal tar creosote (oily liquid), a coal tar (viscous liquid, semisolid), and/or a coal tar pitch (shiny solid residue). Products made from these three substances include roof tar, boat epoxy, and anodes for aluminum smelting, parking lot seal coat, MGP tar from coal combustion, and creosote (widely used for treating lumber, utility poles, and railroad ties; tox profile coal tar [ATSDR 1995]).

The PCB profiles indicate a mixture of Aroclors consistent with mixed sources. In Reach 1, a mixture of Aroclors 1242 and 1248 are prevalent in the surface sediment and a mixture of Aroclors 1248 and 1254 are prevalent in the subsurface sediment (see detailed discussion in Section 2.3). One sample, KKR-20-022 (see Figure 3-21), contained PCBs consistent with a potential pigment source. PCBs were produced commercially in the United States between 1929 and 1977 (tox profile PCBs [ATSDR 2000]). Before 1974, PCBs were manufactured for use in a wide variety of products and applications. Historical uses associated with the three Aroclors identified in the forensic analysis (1242, 1248, 1254) include the following (ATSTR 2000):

- Aroclor 1242: transformers, heat transfer, hydraulic fluids, vacuum pumps, gas-transmission turbines, rubbers, carbonless paper, adhesives, and wax extenders
- Aroclor 1248: hydraulic fluids, vacuum pumps, rubbers, synthetic resins, and adhesives

• Aroclor 1254: capacitors, transformers, heat transfer, hydraulic fluids, vacuum pumps, rubbers, synthetic resins, adhesives, wax extenders, dedusting agents, inks, cutting oils, pesticide extenders, sealant, and caulking compounds

After 1974, use of PCBs was restricted to the production of capacitors and transformers; and after 1979, PCBs were no longer used in the production of capacitors and transformers (EPA 2000).

The forensic analysis did not identify a specific location or point in time from which the PAH and PCB fingerprints originated. As discussed in the following subsections, many types of industrial activities have occurred in the areas adjacent to the KK River for more than a century. Given these historical industrial uses, and the variety of materials that are consistent with the fingerprints identified by the forensic analysis, additional data are needed to more conclusively identify the sources of PCB and PAH contamination in the sediment, if it is even possible. Conclusions from this source review highlight potential sources that were used to identify locations for additional data collection in the 2021 sediment sampling program.

3.1 Current Property Ownership and Historical Land Use

Current property ownership for parcels along the shoreline of the source review area were obtained from Milwaukee County Land Information Office to understand current land and property use in the source review area and how the current property owners compare with historical uses. This information is presented in Figures 3-0 through 3-22 and discussed in this subsection.

Sanborn Fire Insurance Maps and historical aerial photographs were reviewed to understand historical land use and industrial activities in the source review area. Sanborn Fire Insurance Maps were initially developed in the late 19th century to assist fire insurance agents in the identification and assessment of hazards associated with a property. Sanborn maps include notations indicating site occupants, operational activities (e.g., stone cutting, coal storage), and locations and quantities of storage tanks. Sanborn maps also show building footprints and construction materials, street names, and property boundaries (Library of Congress 2021).

Sanborn maps adjacent to the source review area were obtained and reviewed to identify historical activities that may have resulted in sources of PAHs and PCBs consistent with the fingerprints identified through the forensic analysis discussed in Section 2. Sanborn maps from 1894 were obtained from the University of Milwaukee library. Maps from 1910 (61 maps) and 1969 (48 maps) were purchased from EDR Lightbox.⁷ Additional maps available from EDR Lightbox are 1968 (2 maps), 1967 (16 maps), 1951 (48 maps), 1950 (18 maps), and 1937 (18 maps). Georeferenced Sanborn maps from 1894 and 1910 and historical aerial photographs for 1937, 1951, 1956, 1963, 1967, 1970, 1975, 1976, 1980, 1985, 1990, 2007, 2010, 2013, 2015, 2018, and 2020 are available on Milwaukee County's GIS and Land Information Interactive Map (Milwaukee County 2021). These photographs were reviewed as an additional line of evidence to confirm the spatial footprint and duration of activities documented in Sanborn maps (Library of Congress 2021).

Review of the Sanborn maps and aerial photographs indicates that large portions of the source review area have been in industrial uses for more than a century, with two exceptions. Areas on both sides of the river in the upstream reach between South 16th Street and South 6th Street have remained primarily in residential use (Figures 3-9 through 3-14). The areas on the left bank (facing downstream) of Reach 2—present-day Lincoln playfield and Baran Park (Figures 3-16 through 3-20)—have been occupied by parks since at least the 1930s. In the upstream reach (which was not sampled during the 2020 field effort), historical industrial use was concentrated along the right bank between South 20th Street and South 16th Street (Figures 3-6 through 3-8). Adjacent properties in Reach 1 and Reach 2 have also remained in industrial use since the early 1900s, with the exception of the area near Baran Park. Historical occupants documented in the Sanborn maps adjacent to the river in the source review area are listed in Table 3-1.

The subset of historical industries/uses that are known to produce or use substances consistent with the results of the forensic analysis (i.e., coal tar or PCBs) are indicated in Table 3-1. Activities likely to use products consistent with the forensic evaluation were identified in all three reaches (upstream, 1, and 2). These historical uses included multiple foundries, coal storage yards, lumber storage yards, and railroads. Facilities that produced or used paints, dyes, and pigments in the manufacturing process included the following:

• O'Neil-Duro Co. Lacquer & Enamel Manufacturing (see Appendix D, 1969, V.5, P.500), presentday owner is Milwaukee Metropolitan Sewer District (see Figure 3-20)

⁷ Sanborn maps were updated over time. As the pace of urban development increased in the 1920s, Sanborn began issuing paste-on correction slips on a sheet-by-sheet basis. For example, in the event that an older building underwent extensive renovations and Sanborn was asked to reassess the property, a correction sheet and revision date was assigned to the volume containing that particular building. Thus, the entire volume would hold the new revision date, even if updates were only made to one sheet within the volume. The dates of activities at a specific property should be verified through additional historical resources (e.g., historical deeds).

- National Knitting Works (see Appendix D, 1894, V.4, P.351; 1910, V.5, P. 524; 1969, V.5, P.523), present-day owner is Becher Street Development (see Figure 3-20)
- Hat Factory (knitting, dying, bleaching; see Appendix D, 1969, V5. P.524), present-day owner is Giuffre Properties LLC (see Figure 3-19)

These facilities are considered potential sources due to the type of documented industrial activities; however, it should be noted that many types of facilities used products containing PAHs and PCBs consistent with the findings of the forensic analysis (e.g., burned coal as a source of fuel, maintained on-site transformers, used coal tar sealant to treat parking lots).

3.2 Environmental Database Review

Sites with known contamination were identified using the Bureau for Remediation and Redevelopment Tracking System (BRRTS). The BRRTS database includes sites with ongoing investigations and cleanups of contaminated soil, groundwater, sediment, and indoor air; material management sites; spills and abandoned containers; and Superfund sites (DNR 2021).

Numerous open and closed Environmental Repair Program (ERP) sites, leaking underground storage tanks, and spills exist within the source review area as shown in Figures 3-0 through 3-22 and listed in Table 3-2. Substances (e.g., sulfuric acid, trichlorethylene, lead) associated with each listing in the BRRTS database are included in Table 3-2. Based on the substances identified in the BRRTS database, documented contamination potentially consistent with fingerprints identified in the forensic analysis was identified in all three reaches (upstream, 1, and 2) of the source review area. The following open ERP sites with documented contamination consistent with the forensic analysis were identified—Milwaukee City Engine House (Figure 3-5), Deltrol Control Corp (Figure 3-8), Former Glass Manufacturer (Figure 3-18), Becher Street Development (Figure 3-21), and Former Commercial Heat Treating (Figure 3-21). Detailed review of the records associated with these sites is beyond the scope of this review.

3.3 Combined Sewer Overflows

The areas adjacent to the source review area are served by a combined sewer system in which stormwater and wastewater are conveyed in the same system. Construction of the sewers began in the 1870s, and the majority of the combined sewer infrastructure was constructed prior to 1920 (DNR 1980). The Jones Island wastewater treatment plant (WWTP) began operating in 1925. By the 1970s, the Milwaukee Interceptor System (MIS) had been constructed to convey combined flows to the WWTP. The low-level interceptor conveys flows from the areas near the KK River to the WWTP. When the capacity of MIS is exceeded, combined flows discharge to the KK River (MMSD 2021).

Portions of the KK River drainage area are served by municipal combined sewer systems. In these areas, stormwater and wastewater discharges from private and public sites enter the same pipe and

are conveyed to the WWTP. When the hydraulic capacity of the combined sewer infrastructure is exceeded, combined sewage will discharge directly to the KK River through a CSO outfall. The occurrence of a CSO at a particular outfall is a function of multiple factors, including the amount and intensity of precipitation, hydraulic conditions in regulators and the interceptor sewers, and the water level in the river.

With the operation of the Inline Storage System in 1994, CSO discharges to the KK River were greatly reduced (from 8,000 million gallons [MG] in 1993 to 176 MG in 1994). Sewers are connected to the deep tunnels by diversion structures, backed up with bypasses to rivers. When CSO discharges do occur, Milwaukee Metropolitan Sewerage District (MMSD) reports the location, duration, and volume of the discharge to DNR. In total, 20 CSO outfalls are located in the source review area. CSO discharges in the source review area in 2018, 2019, 2020, and 2021 are summarized in Table 3-3. These CSO discharge events occurred in spring and late summer and ranged from 1 to 4 days in duration. In the past 4 years, approximately 225 MG were discharged from 13 of these outfalls. Of this 225 MG, approximately 216 MG discharged near South 6th Street and West Cleveland Avenue (see Figure 3-14) at Outfall 260 (170 MG) and Outfalls 165, 166, or 166A (46 MG). GIS data from MMSD indicate that Outfall 260 is located approximately 2,000 feet from the KK River at the intersection of South 6th Street and Oklahoma Avenue, therefore, it is not visible in Figure 3-14. However, notifications to DNR show the outfall located adjacent to Outfalls 165, 166, and 166A on the downstream side.

3.4 Other NPDES-Permitted Discharges

Individual permits are issued by DNR under the Wisconsin Pollutant Discharge Elimination System (WPDES), Wisconsin's regulatory program approved by EPA. Individually permitted facilities are required to monitor the discharge for parameters identified in each facility's permit and to report the monitoring data to regulatory agencies in discharge monitoring reports (DMRs). Individual permits are written for each specific facility, and the requirements of each permit vary.

Individual permits are specifically developed for the needs of a single facility. General permits are written to apply to multiple discharges within a type of activity or geographic area that have similar environmental impacts. A general permit is designed to cover multiple facilities under one permit when they perform similar operations, produce the same type of wastewater streams, employ similar wastewater treatment operations, or are subject to similar effluent limitations and monitoring requirements.

In Wisconsin, Tier 1 and Tier 2 permits for stormwater discharges associated with industrial activity have been issued by DNR. Tier 1 permits are issued to sites engaged in "heavy" industries such as paper manufacturing, chemical manufacturing, petroleum refining, shipbuilding/repair, and bulk storage of coal, minerals, and ores. Tier 2 permits are issued to sites engaged in "light" industry, such

as food processing, transportation, vehicle maintenance facilities, and non-metallic mining (e.g., gravel). Facilities that fall within one of these categories may apply for coverage under the permit. In addition to facilities with permitted discharges, a facility that has been identified by regulatory agencies as a candidate for permit coverage may be assigned an NPDES number.

Facilities presented in Table 3-4 and Figures 3-1 through 3-22 were identified using EPA's Envirofacts database. The 2020 Facilities Plan Report (MMSD 2021) lists WPDES-permitted wastewater and stormwater facilities in the Kinnickinnic River Watershed by permit type (e.g., Industrial Stormwater Tier 1). The report indicates that the information presented in the tables reflects permit status in 2003. There are several facilities identified as WPDES-permitted facilities in the 2020 Facilities Plan Report that were not listed as NPDES sites in the Envirofacts database. It is assumed that these sites are no longer permitted.

Sites with NPDES-permitted discharges and sites that have been assigned an NPDES number are presented in Table 3-4 and listed in the following:

- Maynard Steel Casting (Figure 3-2)
- Acme Galvanizing (Figure 3-8)
- WIS DOT-2060-00-06 (roadway improvement on South Chase Avenue; Figure 3-16)
- Cimco Resources (facility is located at 2929 Chase Avenue, which is beyond the extent of the source review area)
- St. Mary's Cement (unpermitted⁸, Figure 3-22)

The current permit types were not available on Envirofacts. However, the 2020 Facilities Plan Report indicates that in 2003 Maynard Steel had both an individual permit and a Tier 1 Industrial Stormwater permit and Acme Galvanizing was permitted to discharge both non-contact cooling water and Tier 2 Industrial Stormwater. Review of site-specific permit documentation and DMRs was beyond the scope of the source review.

3.5 Source Review Conclusions

The source review identified three areas of interest for additional data collection due to historical industrial activities, known contamination, recent documented discharges from CSOs and other NPDES-permitted discharges. Historical activities in the upstream reach were concentrated near the former Acme Galvanizing, Pelton Steel, and Deltrol Controls sites (see Figures 3-6 through 3-8), as well as near CSO Outfalls 165, 166, and 166A, and 260 (Figure 3-14). In Reach 1, areas of interest for additional data collection were identified near the former O'Neil-Duro Company Lacquer and Enamel

⁸ Although this site does not have a current NPDES permit, it is tracked as an unpermitted NPDES site on Envirofacts and has been assigned an NPDES number WIU000029.

(see Figure 3-20). Additional data collected through the 2021 sampling events may be helpful to inform and focus future source evaluations.

4 Conclusions

This Tech Memo presents a desktop study comprising a forensic analysis and source review of PAHs and PCBs in the KK River. Findings and recommendations from the forensic analysis and source review are provided as follows:

- Four distinct PAH fingerprints were identified; of these, three are identified as pyrogenic and one as likely to be petrogenic.
 - The likely petrogenic signature is in Reach 4 at the confluence of the Milwaukee River and coincides with a localized area of high PAH concentrations. Further resolution of the type of PAH source or sources in this signature requires samples where alkylated PAH analysis is performed.
 - Of the pyrogenic signatures:
 - Fingerprint 1 has the highest concentrations and is the most predominant signal in Reaches 1 through 3, particularly in Reach 1 where more than 85% of the samples identify as Fingerprint 1. Fingerprint 1 resembles published sources of coal tar sealant, particularly parking lot dust.
 - Fingerprint 2 does not appear in Reach 1 and begins and peaks in Reach 2, and is also identified in Reach 4. Fingerprint 2 resembles published average coal tar sealant PAH fingerprint dust from six cities.
 - Fingerprint 3 is a naphthalene-dominated signature that occurs in two distinct locations—one in Reach 3 and one in Reach 4. Both locations are in the vicinity of the former Solvay Coke and Gas Superfund Alterative Site, a former MGP.
 - Although PAH Fingerprints 1 and 2 resemble coal tar-based sealants, their origin is uncertain because specific information regarding the application of sealants in the area is unavailable. The City of Milwaukee banned coal tar-based sealants in 2017, which should eventually attenuate coal tar sealants as a potential future source.
- PCB data were not optimal for identifying sources but indicated different sources are likely. These different sources may vary across reaches and/or discharge at different times. Laboratory analysis of PCB congeners and alkylated PAHs in samples collected in any future investigations may provide additional insight on PCB and PAH sources.
- The source review identified two areas of interest upstream of Reach 1 and one area of interest within Reach 1 to target for additional sediment sampling.
- A web map was developed to facilitate our source review work and can be an excellent tool going forward to assist in identifying linkages between data and upland sources. This web map can be made available to DNR and others for a modest fee to maintain and update the site.

Additional sediment sampling was performed in August 2021 within the KK River in areas upstream of Reach 1, as well as targeted areas within Reaches 1 through 4. All sediment samples were analyzed for PAHs (TPAH 18), PCB Aroclors, and metals, and select samples near 2020 locations with PCB concentrations above the screening criteria (i.e., 1 mg/kg, 5 mg/kg, and 50 mg/kg) were analyzed for PCB congeners. Results of these analyses were reported in the 2021 Sediment Sampling Technical Memorandum (Anchor QEA 2022).

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Tables

Table 2-1Summary of PAHs Used for Forensic Fingerprinting

Chemical Name	РАН Туре	Plot Codes: Chemical Name Abbreviations	Number of Benzene Rings	Number of Alkyl Groups
Naphthalene	Priority Pollutant/PAH (18)	N0	2	0
2-Methyl Naphthalene	PAH (18)	2MeN	2	1
C1-Naphthalenes	Forensic	N1	2	1
C2-Naphthalenes	Forensic	N2	2	2
C3-Naphthalenes	Forensic	N3	2	3
C4-Naphthalenes	Forensic	N4	2	4
Acenaphthylene	Priority Pollutant/PAH (18)	AY	3	0
Acenaphthene	Priority Pollutant/PAH (18)	AE	3	0
Fluorene	Priority Pollutant/PAH (18)	FO	3	0
C1-Fluorenes	Forensic	F1	3	1
C2-Fluorenes	Forensic	F2	3	2
C3-Fluorenes	Forensic	F3	3	3
Dibenzothiophene	Forensic	DBTO	3	0
C1-Dibenzothiophenes	Forensic	DBT1	3	1
C2-Dibenzothiophenes	Forensic	DBT2	3	2
C3-Dibenzothiophenes	Forensic	DBT3	3	3
C4-Dibenzothiophenes	Forensic	DBT4	3	4
Anthracene	Priority Pollutant/PAH (18)	A0	3	0
Phenanthrene	Priority Pollutant/PAH (18)	PO	3	0
C1-Phenanthrenes/Anthracenes	Forensic	PA1	3	1
C2-Phenanthrenes/Anthracenes	Forensic	PA2	3	2
C3-Phenanthrenes/Anthracenes	Forensic	PA3	3	3
C4-Phenanthrenes/Anthracenes	Forensic	PA4	3	4
Fluoranthene	Priority Pollutant/PAH (18)	FLO	4	0
Pyrene	Priority Pollutant/PAH (18)	PYO	4	0
C1-Fluoranthenes/Pyrenes	Forensic	FP1	4	1

Table 2-1Summary of PAHs Used for Forensic Fingerprinting

Chemical Name	РАН Туре	Plot Codes: Chemical Name Abbreviations	Number of Benzene Rings	Number of Alkyl Groups
C2-Fluoranthenes/Pyrenes	Forensic	FP2	4	2
C3-Fluoranthenes/Pyrenes	Forensic	FP3	4	3
Benz[a]anthracene	Priority Pollutant/PAH (18)	BAO	4	0
Chrysene/Triphenylene	Priority Pollutant/PAH (18)	CO	4	0
C1-Chrysenes	Forensic	BC1	4	1
C2-Chrysenes	Forensic	BC2	4	2
C3-Chrysenes	Forensic	BC3	4	3
C4-Chrysenes	Forensic	BC4	4	4
Total Benzofluoranthenes ¹	Priority Pollutant/PAH (18)	BF-Tot	5	0
Benzo[e]pyrene	PAH (18)/Forensic	BEP	5	0
Benzo[a]pyrene	Priority Pollutant/PAH (18)	ВАР	5	0
Perylene	Forensic	PER	5	0
Dibenz[a,h]anthracene/Dibenz[a,c]anthracene	Priority Pollutant/PAH (18)	DA	5	0
Indeno[1,2,3-cd]pyrene	Priority Pollutant/PAH (18)	IND	6	0
Benzo[g,h,i]perylene	Priority Pollutant/PAH (18)	GHI	6	0

Note:

1. Total benzofluoranthenes are the sum of benzo(b)fluoranthene and benzo(k)fluoranthene.

Abbreviation:

PAH: polycyclic aromatic hydrocarbon

Table 2-2

Summary of PAH Fingerprint 1 and Fingerprint 2 Characteristics

Observation	Fingerprint 1	Fingerprint 2	Conclusion
PAH Concentration	Often > 5x PEC	Often 2 to 5x PEC	Highest concentrations are associated with Fingerprint 1
Spatial Distribution	Dominates Reach 1, least common in Reach 4	Reach 4 Reaches 2 and 3 Fingerprint 1 may originate in or upstream	
Vertical Distribution	Mainly subsurface, also surface in Reach 1	Mainly surface	may be a legacy source Fingerprint 2 originates downstream of Reach 1 and may be a potential ongoing source
Fluoranthene/Pyrene	> 1	> 1	Ratio greater than 1 suggests both profiles are pyrogenic and derived from coal tar
Benzofluoranthenes/ Pyrene	> 1	< 1	Diagnostic ratio can differentiate between the two most common profiles

Abbreviations:

PAH: polycyclic aromatic hydrocarbon PEC: probable effects concentration

Forensic Evaluation and Source Review Memorandum Characterization of Sediments in KK River and Milwaukee Bay

Table 2-3 Reach 1 PCB Results

		Total PCB Aroclors	Total PCB Congeners	Congener Profile	
	Depth	(EPA Method 8082;	(EPA Method 1668;	Primary Aroclor	EPA Method 8082
Core ID	Interval	mg/kg)	mg/kg)	Match	Aroclor Designation
	0 – 1 feet	0.28	0.99	1242/1248	1254
	1 – 3 feet	5.5	9.7	1242/1248	1248/1260
KKR-20-010	3 – 5 feet	3.8	7.5	1248/1254	1248/1260
	5 – 7 feet	3.4	14.4	1248/1254	1248/1260
	7 – 8 feet	0.0023	0.0005	NA	NA

Abbreviations:

EPA: U.S. Environmental Protection Agency

mg/kg: milligrams per kilogram

NA: not applicable - concentrations too low for pattern evaluation

PCB: polychlorinated biphenyl

Table 2-4 Reach 2 PCB Results

	Depth	Total PCB Aroclors (EPA Method 8082;	Total PCB Congeners (EPA Method 1668;	Congener Profile Primary Aroclor	EPA Method 8082
Core ID	Interval	mg/kg)	mg/kg)	Match	Aroclor Designation
	0 – 1 feet	0.601	1.41	1242/1248/1254	1248/1260
KKR-20-015	1 – 2.8 feet	0.93	1.92	1242/1248/1254	1248/1260
KKR-20-015	2.8 – 3.3 feet	0.0031	0.00143	NA	NA
	3.3 – 4.7 feet	0.0046	0.00138	NA	NA
	0 – 1 feet	0.343	1.73	1242/1248/1254	1248/1260
KKR-20-022	1 – 3 feet	0.0047	0.013	Nona-CB/Deca-CB	NA
	3 – 5 feet	0.0047	0.00003	NA	NA
	0 – 1.2 feet	1.12	2.04	1242/1248/1254	1248/1260
KKR-20-025	1.2 – 2.6 feet	0.0064	0.037	1242/1248/1254	NA
KKK-20-025	2.6 – 5 feet	0.0047	0.0021	NA	NA
	5 – 5.9 feet	0.0047	0.0012	NA	NA

Abbreviations:

EPA: U.S. Environmental Protection Agency

PCB: polychlorinated biphenyl

mg/kg: milligrams per kilogram

NA: not applicable – concentrations too low for pattern evaluation

Table 2-5 Reach 3 PCB Results

	Depth	Total PCB Aroclors (EPA Method 8082;	Total PCB Congeners (EPA Method 1668;	Congener Profile Primary Aroclor	EPA Method 8082
Core ID	Interval	mg/kg)	mg/kg)	Match	Aroclor Designation
	0 – 1 feet	1.75	1.44	1242/1248/1254	1248/1260
KKR-20-027	1 – 3 feet	0.95	3.28	1242/1248/1254	1248/1260
	3 – 4.3 feet	1.58	7.01	1248/1254	1248/1260

Abbreviations:

EPA: U.S. Environmental Protection Agency mg/kg: milligrams per kilogram NA: not applicable PCB: polychlorinated biphenyl

Table 3-1Historical Occupants Documented in Sanborn Maps

Upstream (South 29th Street Bridge to South Chase Avenue Bridge) – Left	Ban	k ¹				
1894			1910	1		
Vol. Pg. Occupants	Vol.	Pg.	Occupants	Vol.	Pg.	Occupants
Area not included in Sanborn map coverage	6	605	-Cream City Foundry Co.* -St. Joseph's Orphanage -South Side Steel & Malleable Casting Co.* -American Granite Co. -Railway*		<u>.</u>	Area not inclu
		502	Peridential	5		-Pulaski Public Park -Forest Home Cemetery -Subdivision
3 330 -Milwaukee Brewing Co. -Residential	5	508	-Milwaukee Brewing Co. -Residential	5	508	-Residential -Residential
3 324 -Residential			-Residential	5		-Residential
3 322 -Residential			 -Residential -C & M.E.R.R. Co. Car Barn -Subdivided land -Subdivision 	5		-Residential -Motor Freight Stations -Subdivision -Generators
Area not included in Sanborn map coverage	5	521	-City Flushing Station* -Railways* -Subdivided land -Empty reserved lot	5	521	-City Flushing Station* -Subdivision -Freeway
Upstream (South 29th Street Bridge to South Chase Avenue Bridge) – Rigl	nt Ba	nk ¹		-		
1894		1	1910		-	
Area not included in Sanborn map coverage	5 5 5 5	518 517 519 520	Occupants -Residential -The Independent Milwaukee Brewery -Residential -Residential	Vol. 5 5 5 5	518 517 519	Occupants -Public Park & Recreation Building -Residential -Residential -Residential
Reach 1 (South Chase Avenue Bridge to West Becher Street Bridge) – Left 1894	Bani	K	1910	Т		
Vol. Pg. Occupants	Vol	Pa	Occupants	Vol.	Pa	Occupants
		516	Recidential	5		-Baran Park -Residential -Freeway
Area not included in Sanborn map coverage	5	515	-Crushed stone shed -Ruins of brick yard -Residential	5	515	-Baran Park -James Whitcomb Riley Public Scho -Police Station -Residential
3 318 - Residential	5	500	-Residential	5	500	-O'Neil-Duro Co. Lacquer & Ename -Oil tank farm* -Freeway -Residential

1969
included in Sanborn map coverage
1969
ding
1969
1505
School
301001
namel Mfg*

		South Chase Avenue Bridge to West Becher Street Bridge) – Rig 1894	1		1910			
Vol	Pa	Occupants	Vol	Pa	Occupants	Vol	Pg.	Occupants
4 368 -Residential				-Milwaukee Metal Bed Co. -Chas Zepnick Greenhouse -Wine Cellar -Subdivision -Railway*	5		-J Kaiser Buildings - General Stage & Light Mfg (powe -Wood posts* -Tile from exposed steel columns a -Subdivision	
4	367	-Railway* -Residential	5	538	-Northern Glass Works Co. Bottle Factory Warehouses -Residential -Railway*	5	538	-Milwaukee Valve Co.* -Railway* -Residential
4	366	-Wisconsin Glass Company -Northern Glass Company -Railway* -C.H. Munzinger Weis Brewing and Mineral Water	5	537	-Petrel Motor Car Co. -C&N.W.R.R. Freight House -Northern Glass Works Bottle Factory -Railway*	5	537	-Milwaukie Valve Co (brass foundry -Residential
		Area not included in Sanborn map coverage	5	524	-The Viltner Manufacturer - Ice Machine Engines and Brewery Machinery -National Knitting Company (w/ coal dock, wood yard)*	5	524	-The Vilter Mfg Company (ice mach -Foran Spice Co -Hat factory (knitting, dying, bleach -Electric Sales and Engineering Con
Rea	:h 2 (West Becher Street Bridge to Kinnickinnic Avenue Bridge) – Le	t Ban	k ¹		-		
		1894			1910		-	1
Vol.	Pg.	Occupants	Vol	. Pg.	Occupants		Pg.	
3	317	-Residential	5	499	-Southside Lumber Co. (coal and wood)* -Residential	5	499	- Banner Lumber Co.* - Freeway
3	314	-Bayley and Sons - Architectural Iron Works and Foundry* -Residential	5	482	-Harsh & Edmond Shoe Co. -Vulcan Iron & Steel Co.* -Milwaukee Stove Co. -Residential -Railway* -Bayley Manufacturing Co Structural Iron and Machine Shop* -Robinson's Slip	5	482	-Tanning & Inprocess Material -Appliance & Sporting Goods -Inland Steel Products* -Aelco Foundry Inc* -Banner Lumber Co* -Brass & Aluminum Foundry* -Motor Freight Station
3	315	-Seamless Structural Co. -E.R. Stillman and Co Cooperage Mfy -Simonson, Claason and Co. (lumber yard)* -J. Christensen - Coal and Wood* -Shulz and Raster Stair Builders -Residential	5	483	-Meyward Steel Casting Co. (foundry)* -Cudany Bros Co. South Side Branch -Residential -Carl Miller Lumber Co.* -Clear Ice Co. -Sand's Lumber Co.*	5	483	-Inland Steel Products Co.* -Heat Treating -Painting Contractors -Fish processing plant -Pioneer Foundry Corporation* -Machy & Pipe Fittings Material -Stage w/ wood posts* -Sheet metal works* -Motor Frt Stage (iron)* -Archery tin shop -Milwaukee Mfrs of sanding -Welding N.C. steel trusses

1969
power and light, electric heat, steam, fuel and fuel oil)*
nns and beams
undry)*
machines, engines and brewery equipment)
leaching)
g Company
1969
Occupants
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1
*
* al

Table 3-1Historical Occupants Documented in Sanborn Maps

Rea	ch 2	(West Becher Street Bridge to Kinnickinnic Avenue Bridge) – Rigl	nt Ba	nk ¹					
	1894				1910				
Vol	. Pg.	Occupants	Vol.	Pg.	Occupants	Vol. Pg.		Occupants	
4	351	-M Sanderson and Company Lumberyard* -The National Knitting Works* -The Vilter Manufacturing Co - Corliss Engines and Ice Machines -Railway*	5	523	-The Vilter Manufacturing Co. -Ellis Lumber Co. Planning Mill & Lumber Yard* -Steel bridge over KK River	5	523	-Frabill Mfg Co (recreational equi -The Vilter Mfg Co (makers of ice -Motor freight station, fish and n -Edward Gillen Co. -Boat shop* -Private garage -City storage yard (salt, sand)	
4	352	-John Schroder Lumber Co* -Hoffman and Billings Mfg Co (iron, brass and pipe foundry, machine shop)* -The Filer Stowell Co. (foundry, machine shop, coal storage)* -Railway*	5	525	-Painting -Lumber and iron storage -Cement and brick storage -Residential -Repository -Hoffman Billings Manufacturing Co. (operations unclear)* -The Filer & Stowell Co. (operations unclear)*	5	525	-The Filer & Stowell Co (steel fab -Luetzow laundry & cleaners, sou -Stores & Restaurants	

Notes:

* Historical use indicates that materials consistent with the forensic evaluation were likely present at this site.

1. Pages are listed in the reach and bank for which they provide the most coverage. In some cases, pages show portions of multiple reaches (e.g., pages 499 and 523 in 1910 and 1969) or both the right and left banks (e.g., pages 521, 522 in 1910 and 1969).

1969

luipment) ce machines & brewery equipment) net house

abrication, foundry, machine shop)* outh side laundry (laundry and dry cleaners)

Table 3-2Environmental Cleanup Sites Adjacent to the Source Review Area

Reach	Bank (Left/Right)	Site Name	Facility ID	BRRTS No.	Туре	Open/Closed	Substances or COCs	Potentially Consistent with Forensic Analysis? ¹
				Upstream+2:28l12:25l12:252: 292:32l12:252:292:2822:43	ERP	Open	Lead, metals, chlorinated constituents, TCE	No
		241020050	03-41-540712	LUST	Open	Diesel fuel, TCE	No	
Upstream	Lett	eft ACME Galvanizing Inc FMR	241036950	04-41-047877	SPILL	Historic Spill	Petroleum	No
				04-41-563961	SPILL	Closed	Acid (SULFURIC ACID)	No
				04-41-563963	SPILL	Closed	Gas aerosol (LIQUID PROPANE)	No
Upstream	Left	S&J Recycling LLC	341196460	02-41-556367	ERP	Closed	PAHs, petroleum, "unknown substance," chlorinated solvents	Yes (PAHs)
				03-41-151044	LUST	Closed	Diesel fuel	No
Upstream	n Left ST Evenignasiak LLC/2640 S 5TH ST SPILI		241318000	04-41-550283	SPILL	Closed	Engine waste oil	No
				08-41-550484	AC	Closed	Paints, inks, and dyes (LATEX PAINT)	No
Unstroom	Left	Deltrol Control/Corp	241028590	02-41-584513	ERP	Open	PCE, TCE, PAHs, toluene, xylene, ethylbenzene, CVOC daughter product	Yes (PAHs)
Upstream	Leit	Dentor control/corp	241020390	03-41-004136	LUST	Closed	Petroleum (fuel oil)	No
				03-41-001750	LUST	Closed	Diesel fuel	No
Upstream	Left Maynard Steel		241005710	04-41-550958	SPILL	Closed	Hydraulic oil	No
				04-41-552428	SPILL	Closed	Other industrial chemicals (TOXIC CHEMICALS; UNK AMT)	No
			241565170	03-41-001403	LUST	Closed	Diesel fuel, VOC, petroleum, non-chlorinated solvents (NAPHTHA THINNER)	No
Upstream	Left	Aurora (St Lukes) Property		02-41-524386	ERP	Closed	Barium, chlorobenzene compounds	No
opstream	Leit	Autora (St Lukes) Property	241024300	03-41-002409 LUST Closed Diesel fuel		Diesel fuel	No	
				04-41-564136	SPILL	Closed	Mercury	No
Upstream	Left	Pelton Steel/ Former Crucible	241005380	02-41-000933	ERP	Closed	Metals, RCRA wastes	Yes*
opstream	Leit		241005500	04-41-044960	SPILL	Historic Spill	Petroleum	No
Upstream	Right	Milwaukee City Engine House	241495320	03-41-559351	LUST	Open	Gasoline, diesel fuel	No
Opstream	Ngn	Wilwaukee City Lingine House	241493320	02-41-000662	ERP	Open	VOCs, petroleum, engine waste oil, RCRA wastes, metals	Yes*
Upstream	Right	Secrets	241901330	03-41-110008	LUST	Open	Gasoline	No
Upstream	Right	Grace Lutheran Church	241566710	03-41-002748	LUST	Closed	Petroleum (fuel oil)	No
				03-41-001029	LUST	Closed	Petroleum	No
Upstream	Right	TSM/Kinnickinnic River-2828 S 16TH	241220320	04-41-039547	SPILL	Historic Spill	Not listed	Yes*
				04-41-040159	SPILL	Historic Spill	Not listed	Yes*
1	Right	Former Glass Manufacturer	341138270	02-41-548257	ERP	Open	PAHs [benzo(a)pyrene, benzo(a)fluoranthene, chrysene], petroleum, VOCs	Yes (PAHs)
				03-41-250323	LUST	Closed	Petroleum, diesel fuel, gasoline - unleaded and leaded	No
1	Right	Vilter MFG Corp	241025840	04-41-039456	SPILL	Historic Spill	Not listed	Yes*
				04-41-047376	SPILL	Historic Spill	Ammonia	No
1	Left	US Industrial	241328890	02-41-000978	ERP	Closed	Arsenic, chlorinated solvents, PAHs	Yes (PAHs)

Table 3-2Environmental Cleanup Sites Adjacent to the Source Review Area

Reach	Bank (Left/Right)	Site Name	Facility ID	BRRTS No.	Туре	Open/Closed	Substances or COCs	Potentially Consistent with Forensic Analysis? ¹
1	Left	Milwaukee Cty 2nd Dist Pol #2	241406440	03-41-001389	LUST	Closed	Petroleum	No
2	Left	Robinsons Abandoned Boat Slip/M&I 241497960		02-41-000302	ERP	Closed	Not listed	Yes*
2	Leit	Robinsons Abandoned Boat Silp/Mai	241497900	02-41-109522	ERP	Closed	Not listed	Yes*
2	Left	Aelco Foundry	241027820	02-41-547838	ERP	Closed	Arsenic, chromium, lead, PAHs	Yes (PAHs)
2	Leit	Aelco Foundry	241027020	03-41-003479	LUST	Closed	Petroleum (fuel oil)	No
2	Left	Kotovic Marine	241192930	02-41-111090	ERP	Closed	Not listed	Yes*
2	Leit		241192950	04-41-578193	SPILL	Closed	Gasoline - unleaded and leaded	No
2	Left	Former Commercial Heat Treating	341312510	02-41-583644	ERP	Open	PAHs, VOCs, petroleum, PCBs, cyanide	Yes (PAHs, PCB)
2	Right	Watkins Trucking	241534040	03-41-000354	LUST	Closed	Gasoline - unleaded and leaded, diesel fuel, petroleum	No
2	Right	Lincoln Warehouse	241024960	02-41-544664	ERP	Closed	Metals, arsenic, lead, chromium, mercury, petroleum	No
2	Right	Edward E Gillen Co	241706300	02-41-559224	ERP	Closed	Chlorinated solvents, VOCs, PAHs, salt	Yes (PAHs)
2	Kigin	Edward E Gilleri Co	241700300	03-41-003963	LUST	Closed	Gasoline - unleaded and leaded (UNLEADED GAS), petroleum (fuel oil)	No
2	Right	Milwaukee Cty KK Bridge	241814870	02-41-001143	ERP	Closed	Metals, RCRA wastes, VOCs, gasoline - unleaded and leaded, diesel fuel, petroleum, engine waste oil	No
2	Dialat	De cher Ctre et Develement	241207550	02-41-581468	ERP	Open	PAHs, metals, lead, TCE	Yes (PAHs)
2	Right	Becher Street Development	341297550	03-41-585630	LUST	Closed	Naphthalene	Yes (PAHs)
2	Dialat	De cher Ctre et Develement	241207550	02-41-581468	ERP	Open	PAHs, metals, lead, TCE	Yes (PAHs)
2	Right	Becher Street Development	341297550 -	03-41-585630	LUST	Closed	Naphthalene	Yes (PAHs)
2	Dicht	KK Auto Salvara South	341077440	02-41-460770	ERP	Open	Petroleum, "unknown substance," VOCs	Yes*
2	Right	KK Auto Salvage South	541077440	04-41-524758	SPILL	Closed	Petroleum	No

Note:

1. "No" indicates that substances or COCs listed in BRRTS are not consistent with the results of the forensic analysis. "Yes" indicates that the COCs or substances listed in BRRTS are potentially consistent with the forensic analysis. "Yes*" indicates that the substances or COCs are not specified in BRRTS.

Abbreviations:

BRRTS: Bureau for Remediation and Redevelopment Tracking System COC: contaminant of concern CVOC: chlorinated volatile organic compound ERP: Environmental Repair Program LUST: leaking underground storage tank PAH: polycyclic aromatic hydrocarbon PCB: polychlorinated biphenyl PCE: perchloroethylene RCRA: Resource Conservation and Recovery Act TCE: trichloroethylene UNK AMT: unknown amount VOC: volatile organic carbon

Table 3-3 CSO Outfalls in the Source Review Area¹

				2018	CSOs	2019	CSOs	2020	CSOs	2021	CSOs
			Outfall	Volume		Volume		Volume		Volume	
Reach	Bank	Location	Number	(MG)	Dates	(MG)	Dates	(MG)	Dates	(MG)	Dates
Upstream	Left	S. 8th Street	167							3.3	8/8
Upstream	Left	S. 14th Street	168								
Upstream	Left	S. 27th Street	169								
Upstream	Right	S. 6th Street at W. Cleveland Avenue (middle outfall)	165							7.1	8/8
Upstream	Riaht	S. 6th Street at W. Cleveland Avenue (north outfall)	166		8/27	4.0	9/13			8.2	8/8
-	5.			6.9	through	1.0	9/14			0.2	
Linctroom	Diaht	C 6th Street at W/ Claudand Avenue (couth outfall)	166A		8/29 ²	4.0	9/13			15.9	8/8
Upstream	Right	S. 6th Street at W. Cleveland Avenue (south outfall)	100A			1.0	9/14			15.9	0/0
					10/1	44.2	3/14				
Upstream	Right	S. 6th Street at W. Oklahoma Avenue ³	260	119.6	through	48.3	3/15				
•					10/4	47.9	9/13				
1	Left	W. Lincoln Avenue (west bank)	161								
1	Left	S. Chase Avenue (north bank)	163					0.1	5/17		
1	Right	South of E. Lincoln Avenue	160							1.7	8/8
1	Right	W. Lincoln Avenue (east bank)	162								
1	Right	S. Chase Avenue (south bank)	164					1.0	5/17	1.2	8/8
2	Left	S. Kinnickinnic Avenue (north bank)	152								
2	Left	S. 1st Street (north Bank)	154			0.1	9/13				
2	Left	S. 2nd Street	156			0.3	9/13				
2	Left	W. Rogers Street	157			0.4	9/13				
					8/27						
2	Left	W. Becher Street (north outfall)	158	1.1	through	1.0	9/13				
					8/29 ⁴						
2	Right	S. Kinnickinnic Avenue (south bank)	153								
2	Right	S. 1st Street (south Bank)	155			0.1	9/13				
2	Right	W. Becher Street (south outfall)	159			0.6	9/13				

Table 3-3

CSO Outfalls in the Source Review Area¹

Notes:

1. CSOs listed in this table were identified through annual reports and 5-day notifications available on MMSD's website and may not be inclusive of all CSO events. 2. CSO occurred at 166, 166A, or 167.

3. Not tributary to the ISS dropshaft. GIS data from MMSD indicate that Outfall 260 is located approximately 2,000 feet from the KK River at the intersection of South 6th Street and Oklahoma Avenue, therefore, it is not visible in Figure 3-14. However, notifications to DNR show the outfall located adjacent to Outfalls 165, 166, and 166A on the downstream side.

4. CSO occurred at either 158 or 159.

Abbreviations: CSO: combined sewer overflow DNR: Wisconsin Department of Natural Resources ISS: Inline Storage System KK: Kinnickinnic MG: million gallons MMSD: Milwaukee Metropolitan Sewerage District

Table 3-4

Other NPDES-Permitted Discharges to the Source Review Area¹

Reach	Bank	Name	Address	Number
Upstream	Left	Maynard Steel Casting	2856 S 27th Street	WI0000272
Upstream	Left	Acme Galvanizing Inc	2730 S 19th Street	WIP000050
Reach 1	Right	WIS DOT-2060-00-06	E Ohio Avenue to W Lincoln Avenue	WIG003332
Reach 1	Right	Cimco Resources	2929 S Chase Avenue	WIG000130
Reach 2	Right	St. Mary's Cement	2006 S Kinnickinnic Avenue	WIU000029

Note:

1. Facilities were identified using EPA's Envirofacts database.

Abbreviations:

EPA: U.S. Environmental Protection Agency

NPDES: National Pollutant Discharge Elimination System

Figures

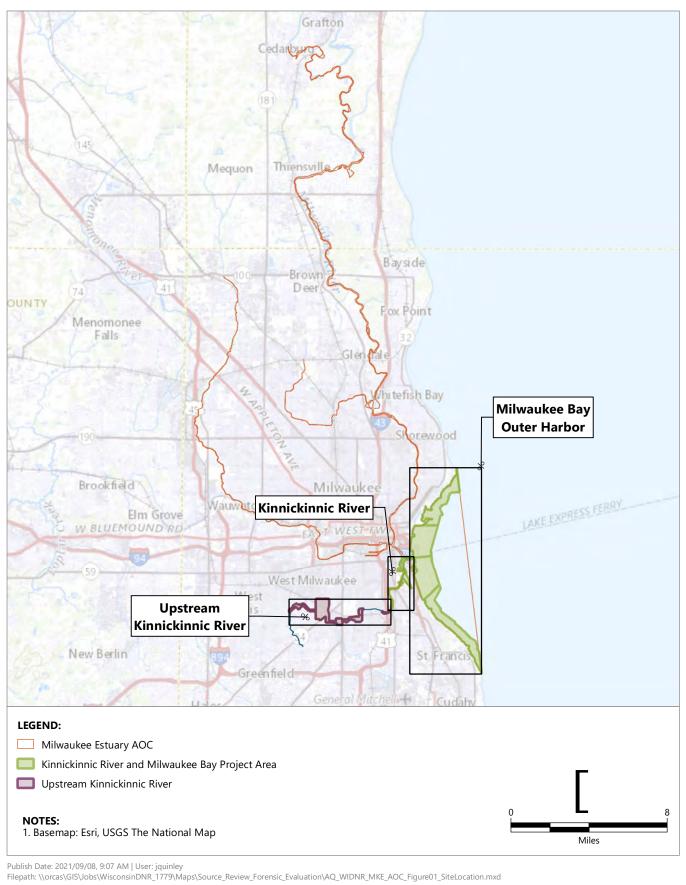
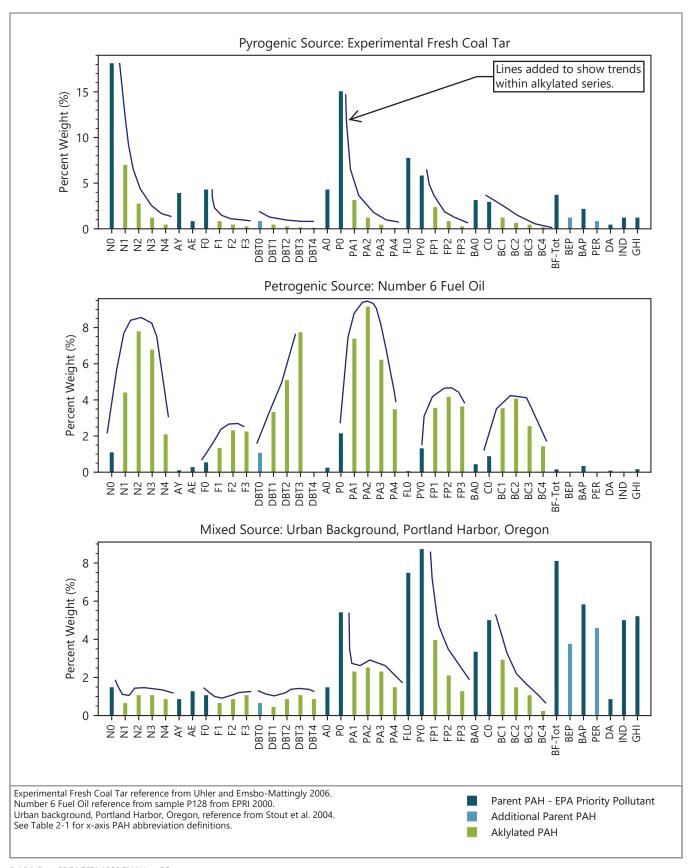




Figure 1-1 **Site Location Map**



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Figure 2-1 Typical PAH Fingerprints from Published Reports

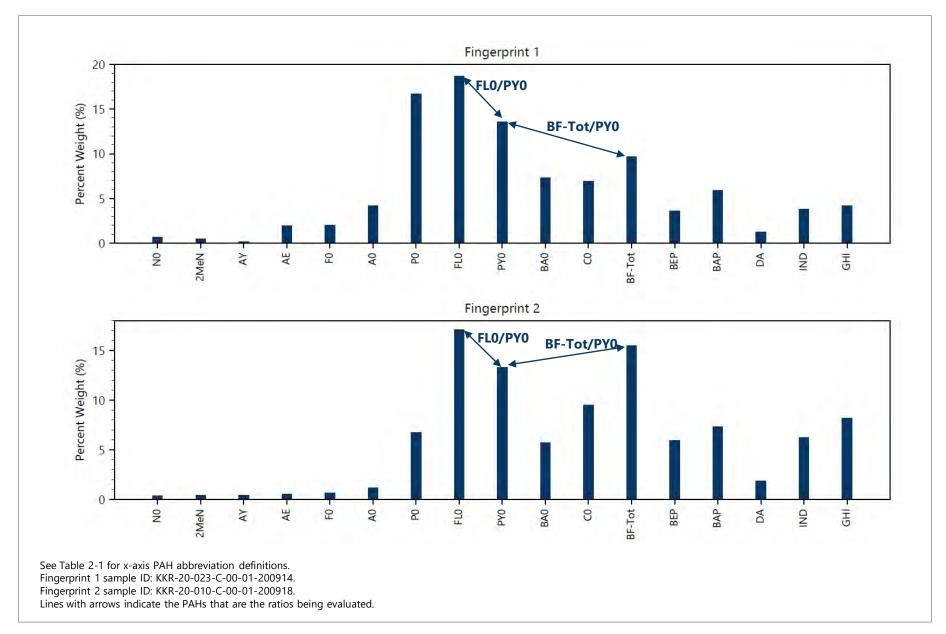




Figure 2-2 PAH Fingerprint 1 and Fingerprint 2

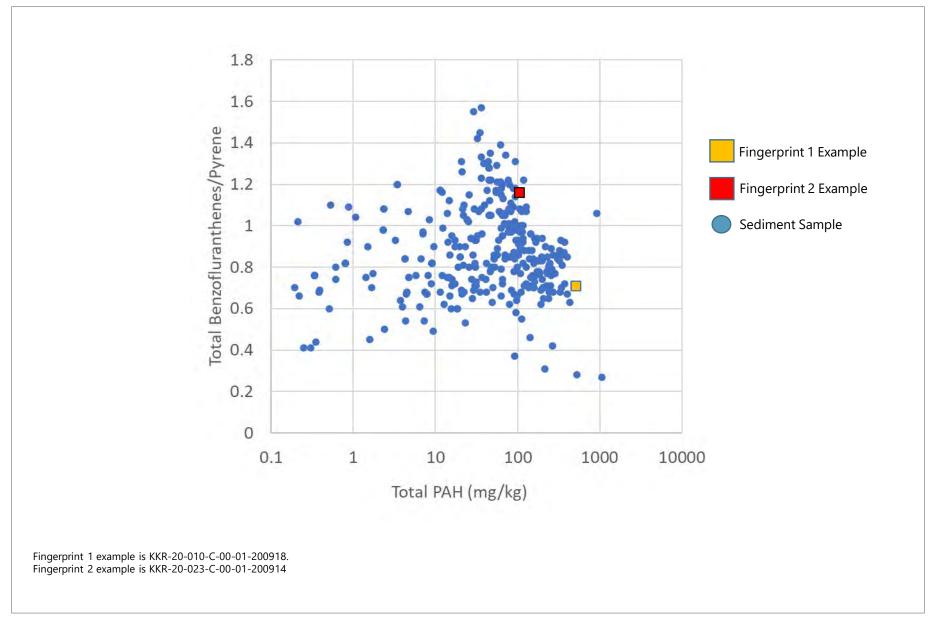
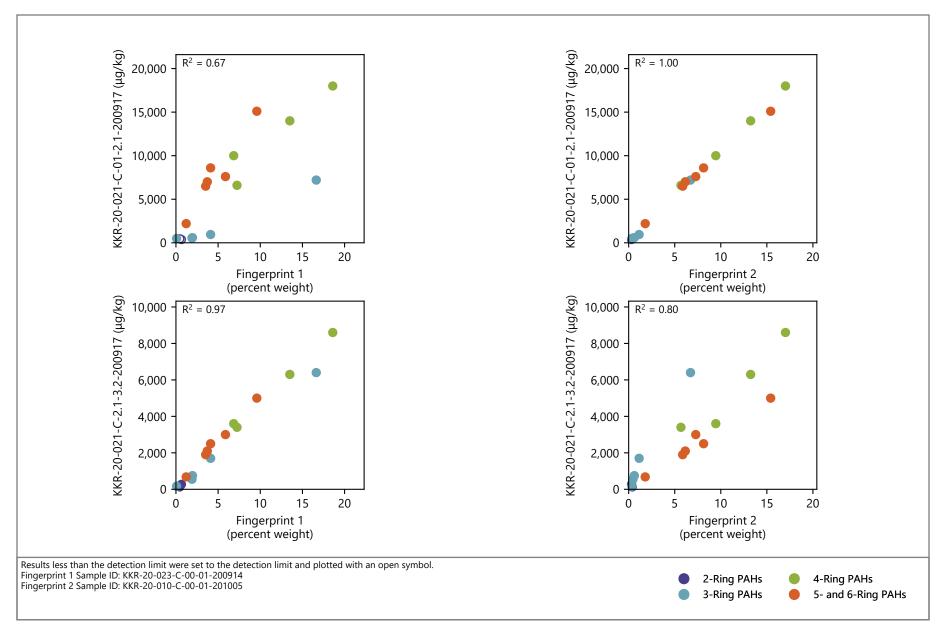




Figure 2-3 Total Benzofluoranthenes/Pyrene Ratio versus Total PAH Concentration



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Example Cross Plot Comparisons of Samples to PAH Fingerprints

Figure 2-4

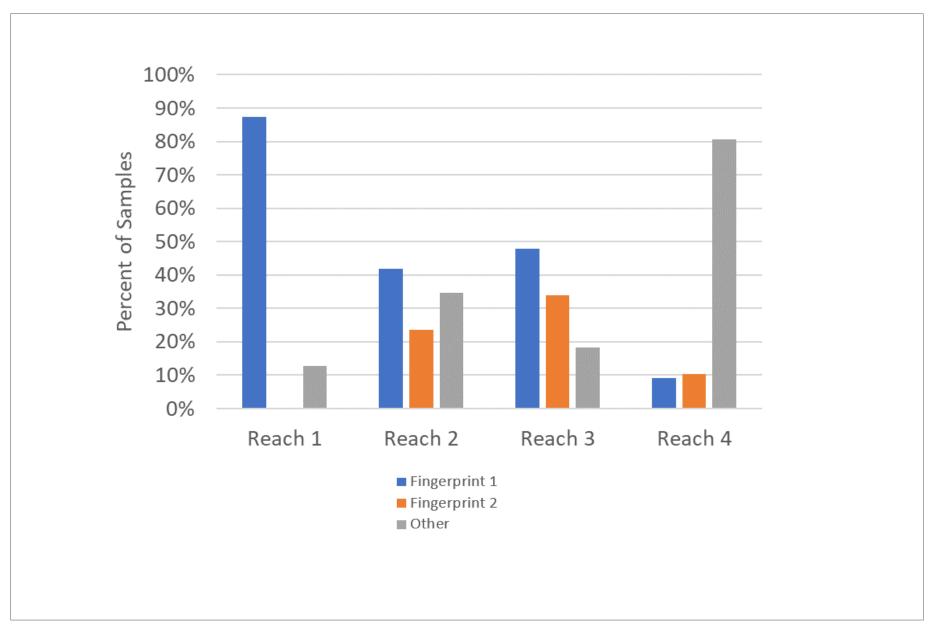




Figure 2-5 Distribution of Fingerprint 1 and Fingerprint 2 by Reach

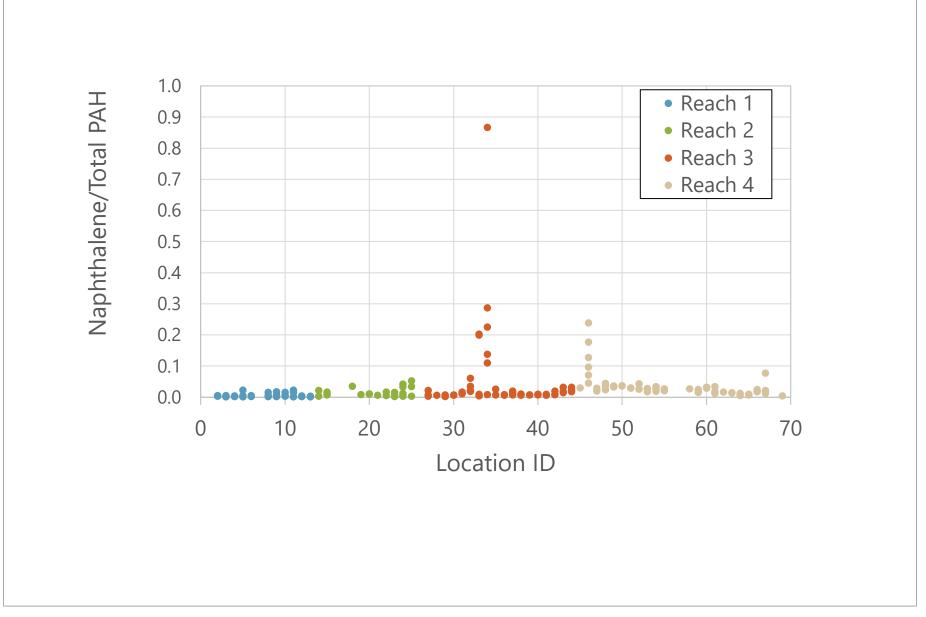




Figure 2-6 Spatial Distribution of Elevated Naphthalene

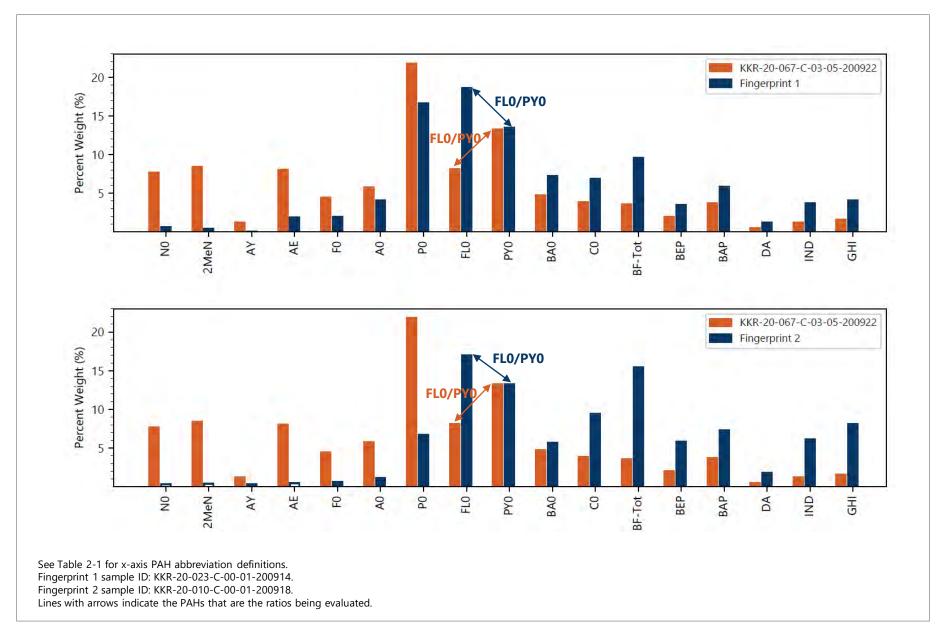
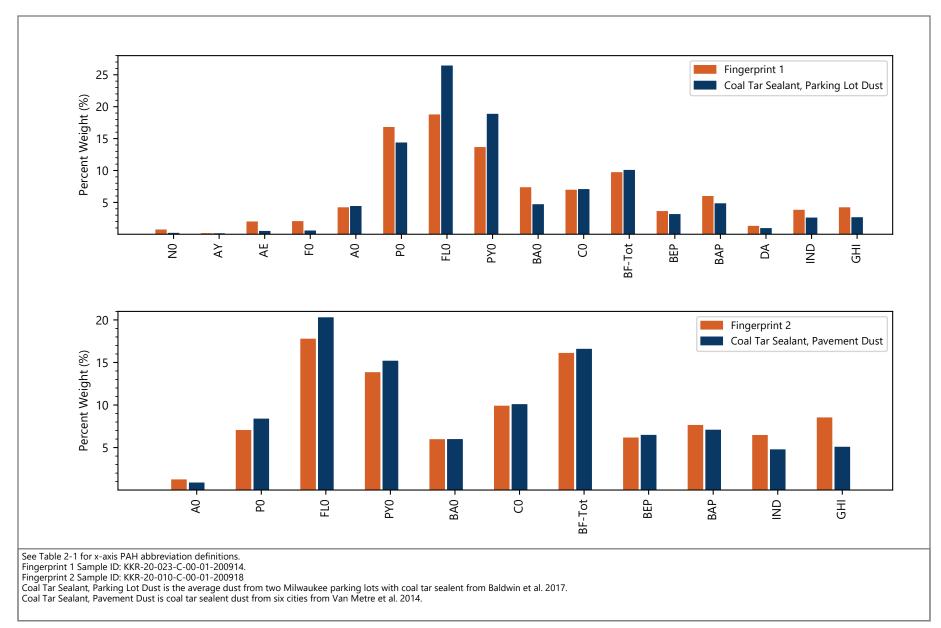




Figure 2-7 Core 67 Potential Petrogenic PAH Profile Compared to Fingerprint 1 and Fingerprint 2



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Figure 2-8 Published Coal Tar Sealant versus Fingerprint 1 and Fingerprint 2

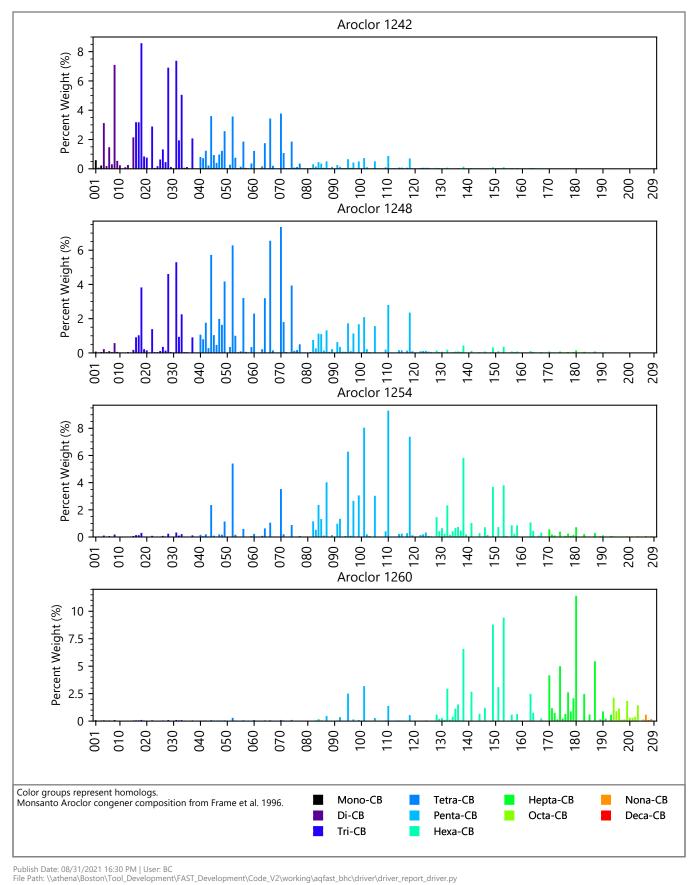
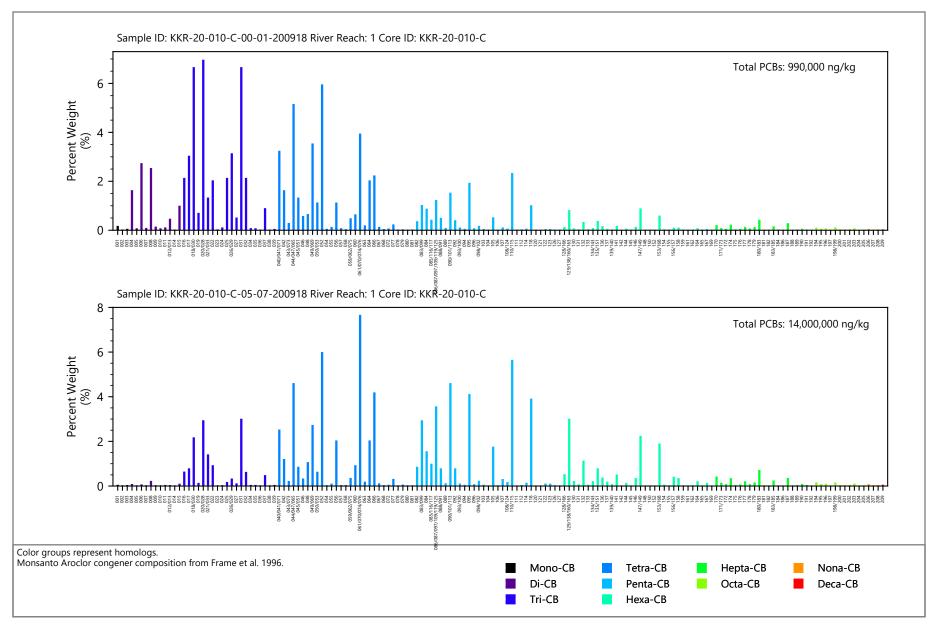




Figure 2-9 **Congener Distribultion in Monsanto PCB Aroclors**



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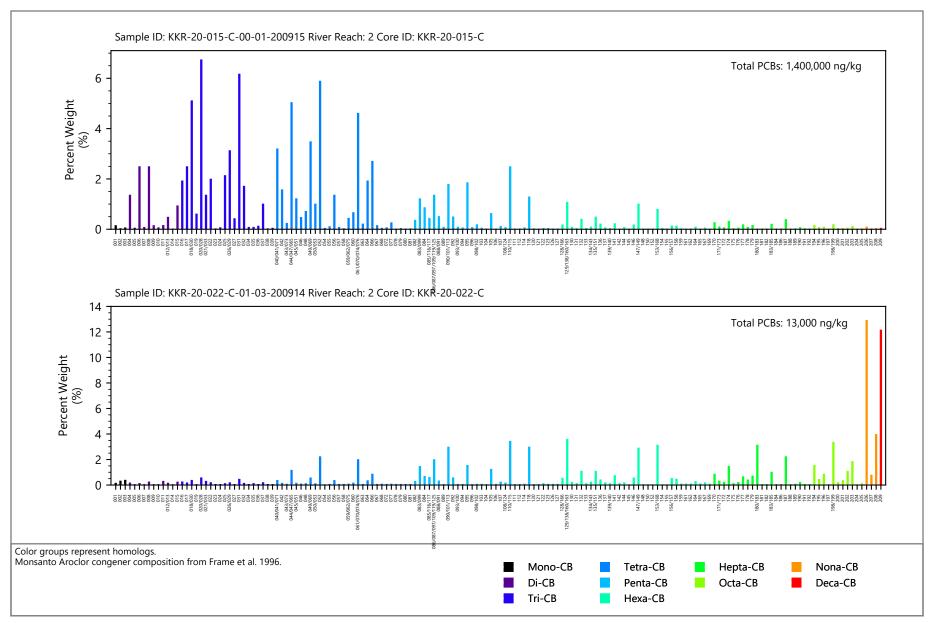
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Figure 2-10 Selected PCB Congener Profile Results for Reach 1

Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee Estuary Area of Concern

Milwaukee, Wisconsin



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Selected PCB Congener Profile Results for Reaches 2 and 3

Figure 2-11

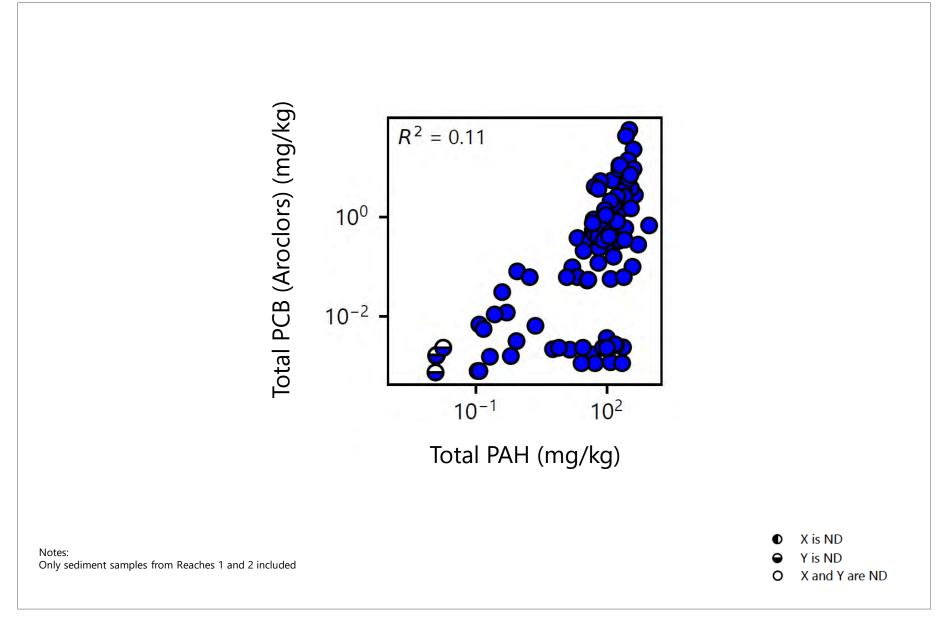




Figure 2-12 Total PAHs versus Total PCBs (Aroclors) in Sediment Samples

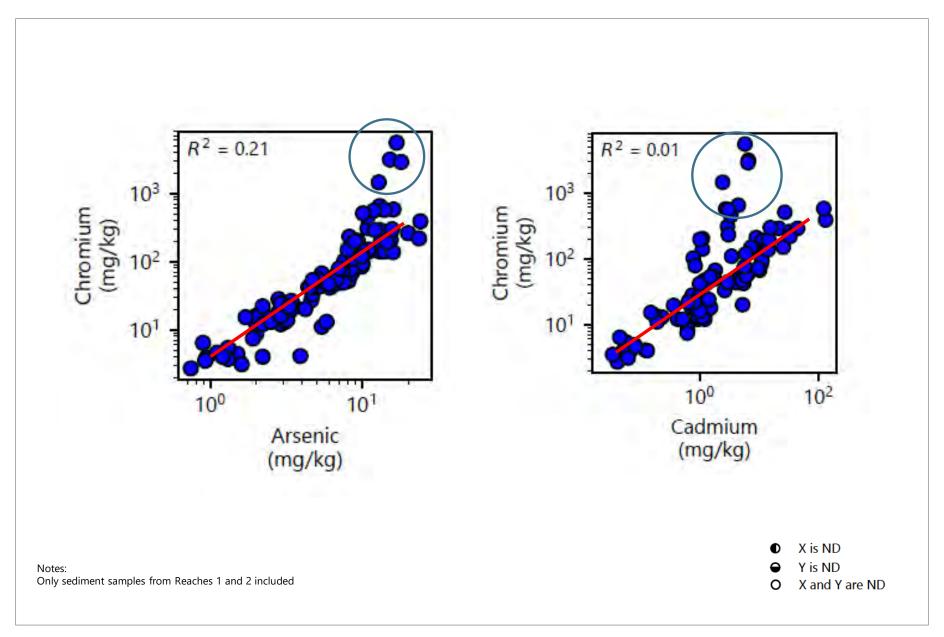
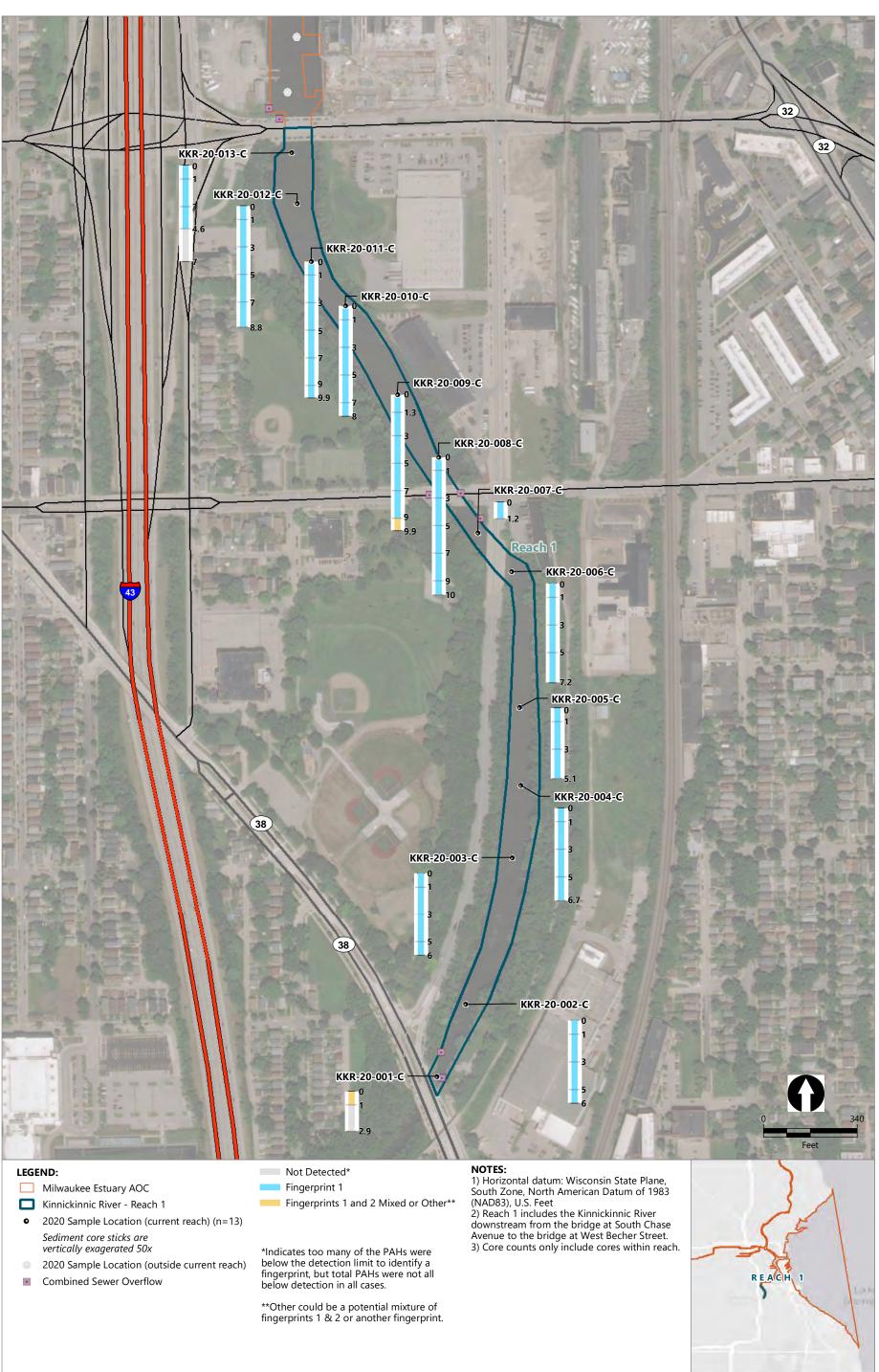




Figure 2-13 Select Trace Metals versus Cadmium in Sediment Samples

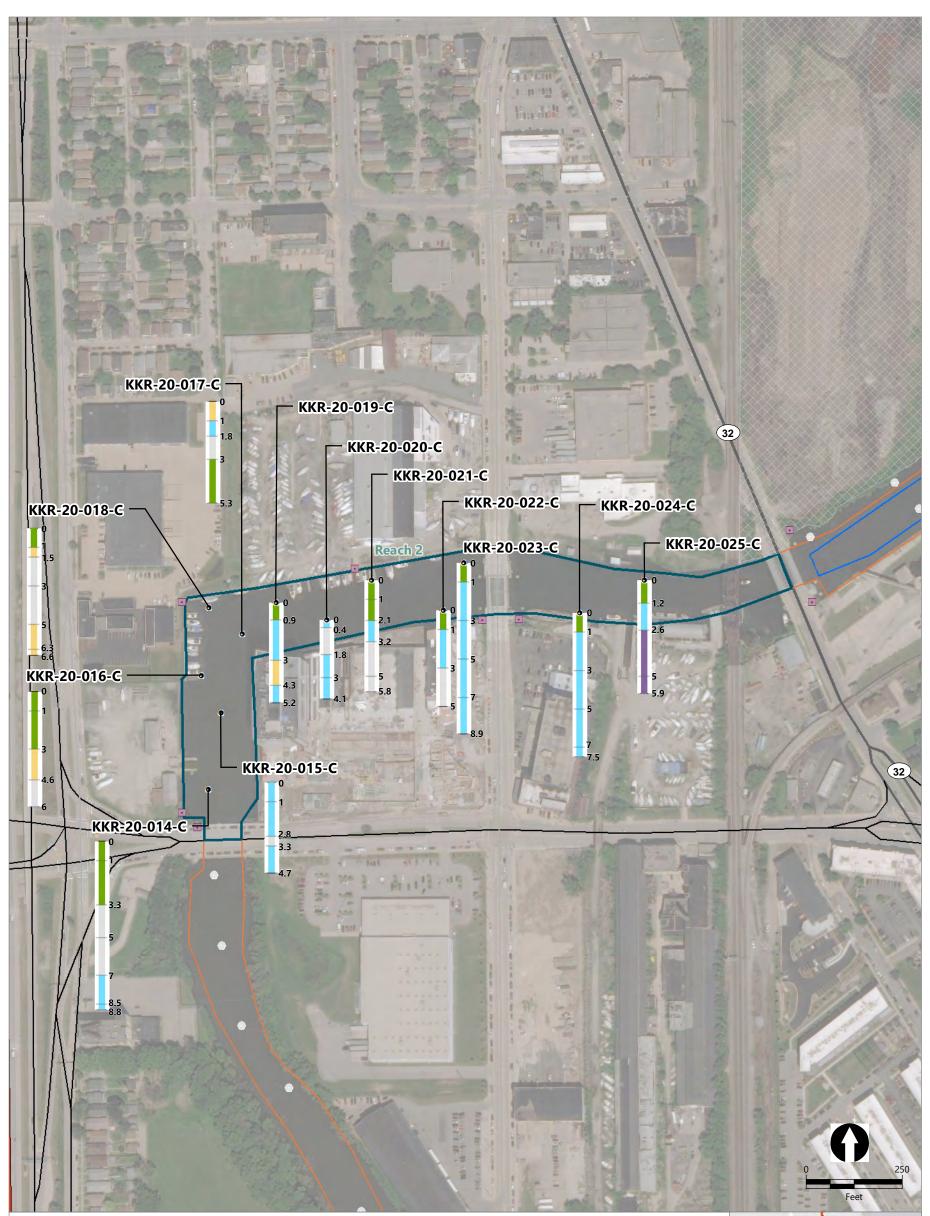


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Figure 2-14

PAH Fingerprints for 2020 Sediment Samples within Reach 1 of the Kinnickinnic River



LEGEND:

Milwaukee Estuary AOC

- Kinnickinnic River Reach 2
- 2020 Sample Location (current reach) (n=12) Sediment core sticks are vertically exagerated 50x
- 2020 Sample Location (outside current reach)
- Combined Sewer Overflow
- Milwaukee Solvay Coke and Gas Site

Not Detected*

Fingerprint 1

- Fingerprint 2
- Fingerprints 1 and 2 Mixed or Other**
- Naphthalene***

*Indicates too many of the PAHs were below the detection limit to identify a fingerprint, but total PAHs were not all below detection in all cases.

**Other could be a potential mixture of fingerprints 1 & 2 or another fingerprint.

***The high Naphthalene fingerprint was accompanied by various other fingerprints.

NOTES:

1) Horizontal datum: Wisconsin State Plane, South Zone, North American Datum of 1983 (NAD83), U.S. Feet

2) Reach 2 includes the Kinnickinnic River from the West Becher Street bridge downstream to the South Kinnickinnic Avenue bridge.3) Core counts only include cores within reach.

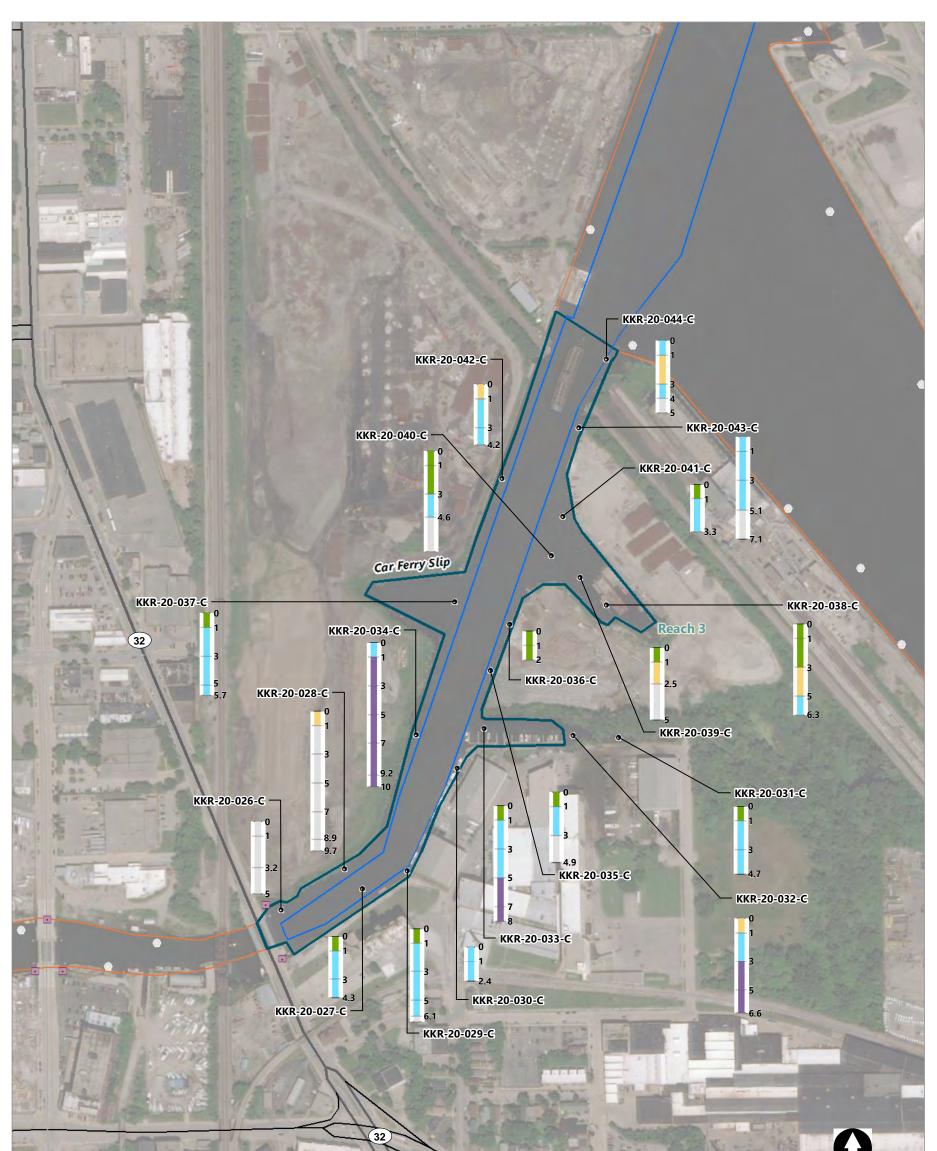


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Figure 2-15

PAH Fingerprints for 2020 Sediment Samples within Reach 2 of the Kinnickinnic River





LEGEND:

Milwaukee Estuary AOC

- Kinnickinnic River Reach 3
- 2020 Sample Location (current reach) (n=19) Sediment core sticks are vertically exagerated 50x
- 2020 Sample Location (outside current reach)
- Combined Sewer Overflow

Not Detected*

- Fingerprint 1
- Fingerprint 2
- Fingerprints 1 and 2 Mixed or Other**
- Naphthalene***

*Indicates too many of the PAHs were below the detection limit to identify a fingerprint, but total PAHs were not all below detection in all cases.

**Other could be a potential mixture of fingerprints 1 & 2 or another fingerprint.

***The high Naphthalene fingerprint was accompanied by various other fingerprints.

NOTES:

1) Horizontal datum: Wisconsin State Plane, South Zone, North American Datum of 1983 (NAD83), U.S. Feet

2) Reach 3 includes the Kinnickinnic River downstream of the South Kinnickinnic Street bridge to the upstream mouth of the Turning Basin.

a) Core counts only include cores within reach.
4) Samples collected as part of this investigation generally targeted locations outside the federal channel. The USACE conducted investigation of the Navigation Channel in 2020 at the request of EPA and DNR (JV 2020).

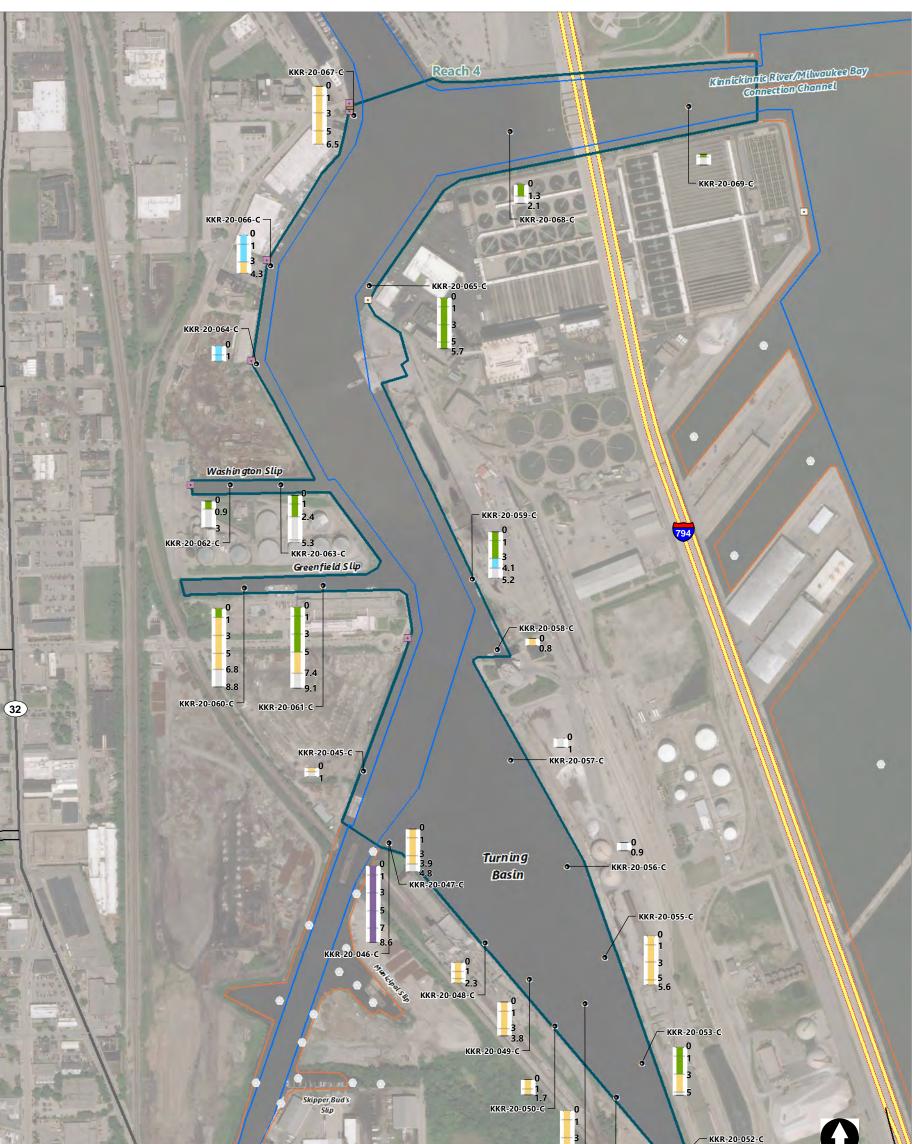


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Figure 2-16

PAH Fingerprints for 2020 Sediment Samples within Reach 3 of the Kinnickinnic River



7. 3 3.5 KKR-20-054-C-KKR-20-051-C Feet

LEGEND:

- Milwaukee Estuary AOC
- Kinnickinnic River Reach 4
- 2020 Sample Location (current reach) (n=25) 0 Sediment core sticks are vertically exagerated 50x
- 2020 Sample Location (outside current reach)
- Unspecified Outfall Location
- Combined Sewer Overflow
- Sanitary Sewer Overflow

- Not Detected*
- Fingerprint 1
- Fingerprint 2
- Fingerprints 1 and 2 Mixed or Other** Naphthalene***

*Indicates too many of the PAHs were below the detection limit to identify a fingerprint, but total PAHs were not all below detection in all cases.

**Other could be a potential mixture of fingerprints 1 & 2 or another fingerprint.

***The high Naphthalene fingerprint was accompanied by various other fingerprints.

NOTES:

1) Horizontal datum: Wisconsin State Plane, South Zone, North American Datum of 1983 (NAD83), U.S. Feet

2) Reach 4 includes the Kinnickinnic River and turning basin from the upstream mouth, Washington and Greenfield slips, downstream to the confluence with the Milwaukee River, and Milwaukee Bay connection channel.3) Core counts only include cores within reach.4) Samples collected as part of this investigation generally targeted locations outside the federal channel. The USACE conducted investigation of the Navigation Channel in 2020 at the request of EPA and DNR (JV 2020).

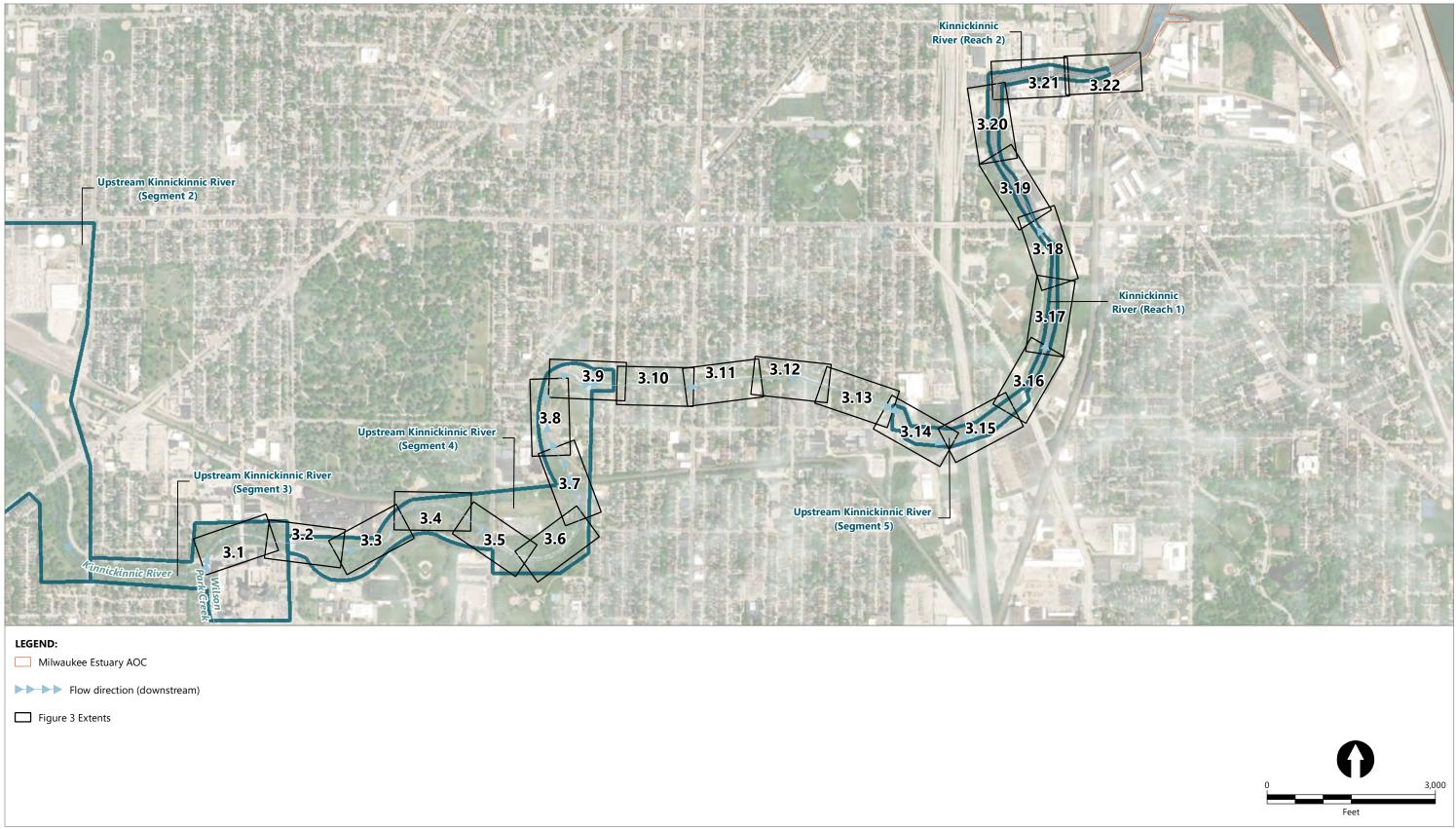


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Figure 2-17

PAH Fingerprints for 2020 Sediment Samples within Reach 4 of the Kinnickinnic River

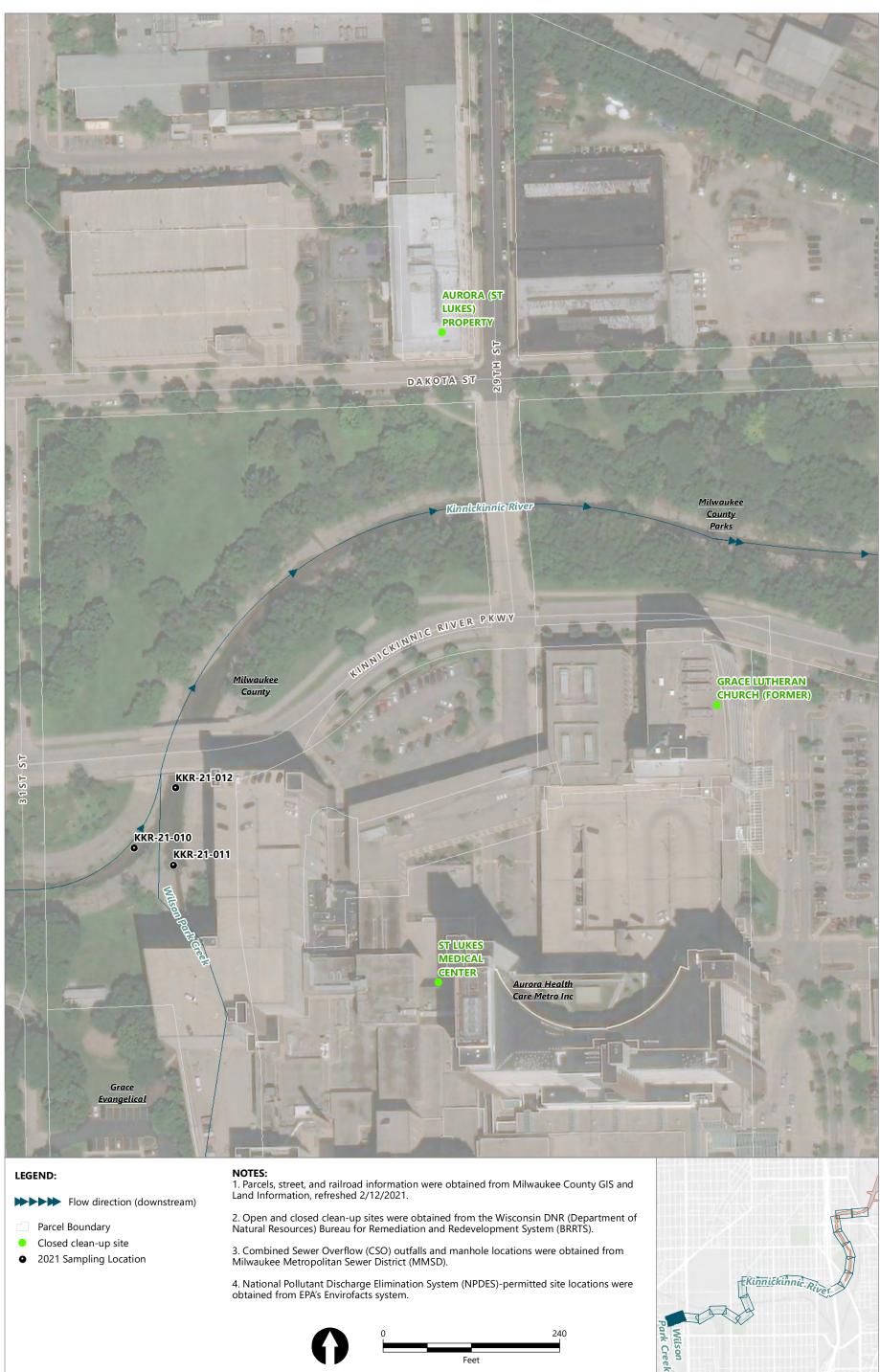


Publish Date: 2022/03/02, 10:01 AM | User: jquinley Filepath: \\orcas\GIS\Jobs\WisconsinDNR_1779\Maps\Source_Review_Forensic_Evaluation\AQ_WIDNR_MKE_AOC_Figure03__MapbookKey.mxd



Map Book Key for Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River Figure Set Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee Estuary Area of Concern Milwaukee, Wisconsin

Figure 3



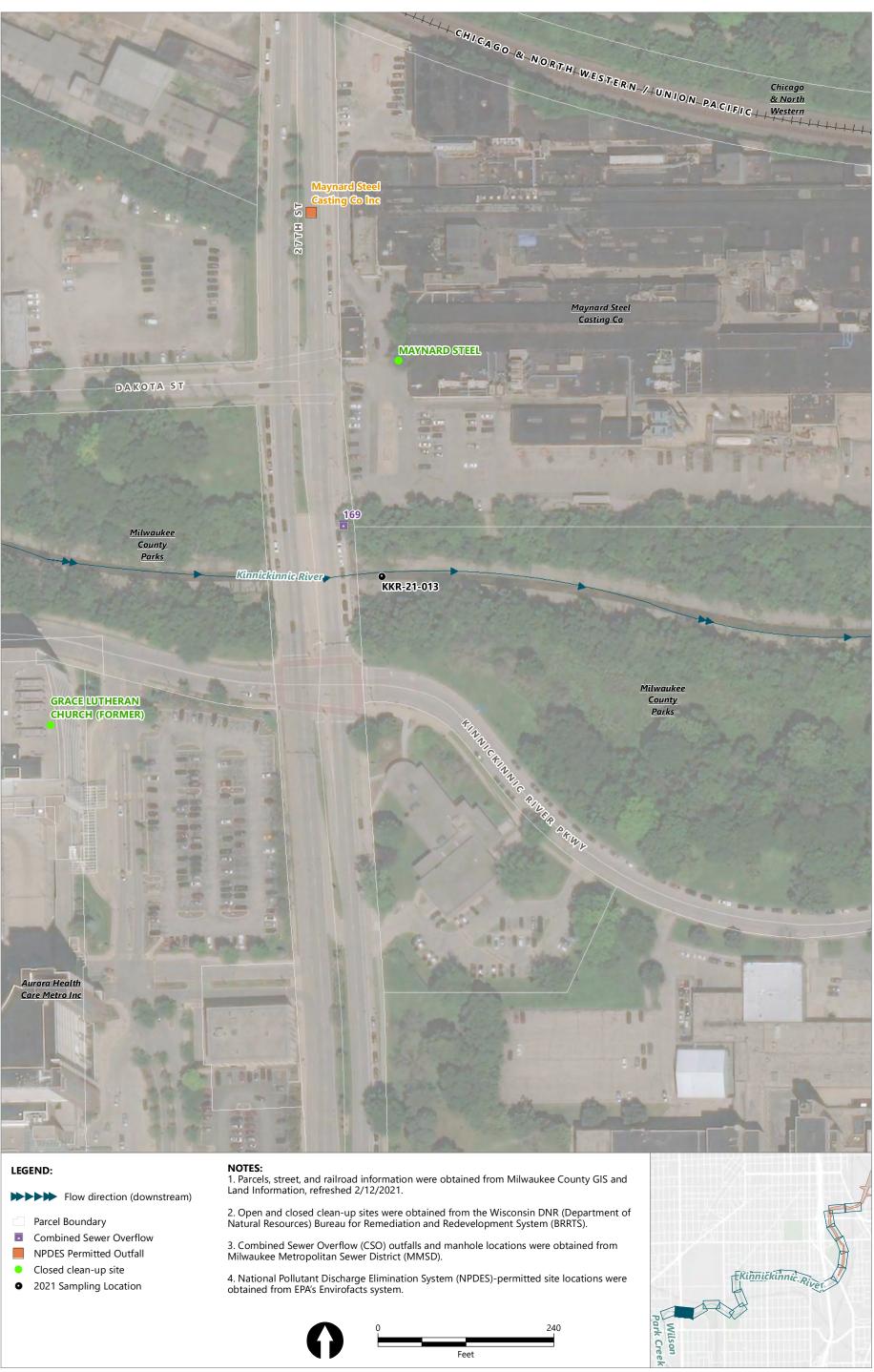


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Figure 3-1

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Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View A





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Figure 3-2 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View B





Parcel Boundary

 Copen and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.





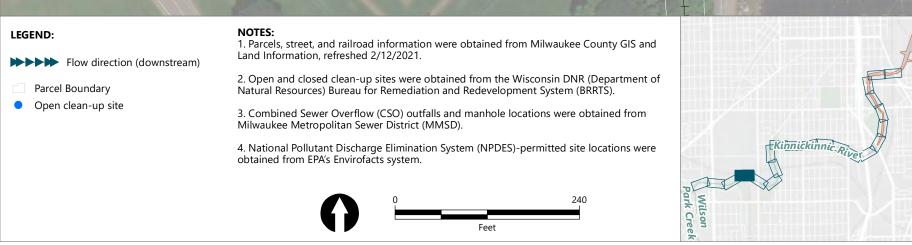
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Figure 3-3



Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View C





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Figure 3-4



Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View D





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Figure 3-5 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View E



LEGEND:

Flow direction (downstream)

Parcel Boundary Closed clean-up site

• 2021 Sampling Location

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.





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Figure 3-6 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View F



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Figure 3-7



Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View G



2021 Sampling Location 0

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



Kinnickinnic Riv Wilson Park Creek

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Figure 3-8 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View H



<u>Milwaukee</u> County Parks

LEGEND:

NOTES:

1011

Flow direction (downstream)

- Parcel Boundary
- Closed clean-up site
- 2021 Sampling Location 0

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



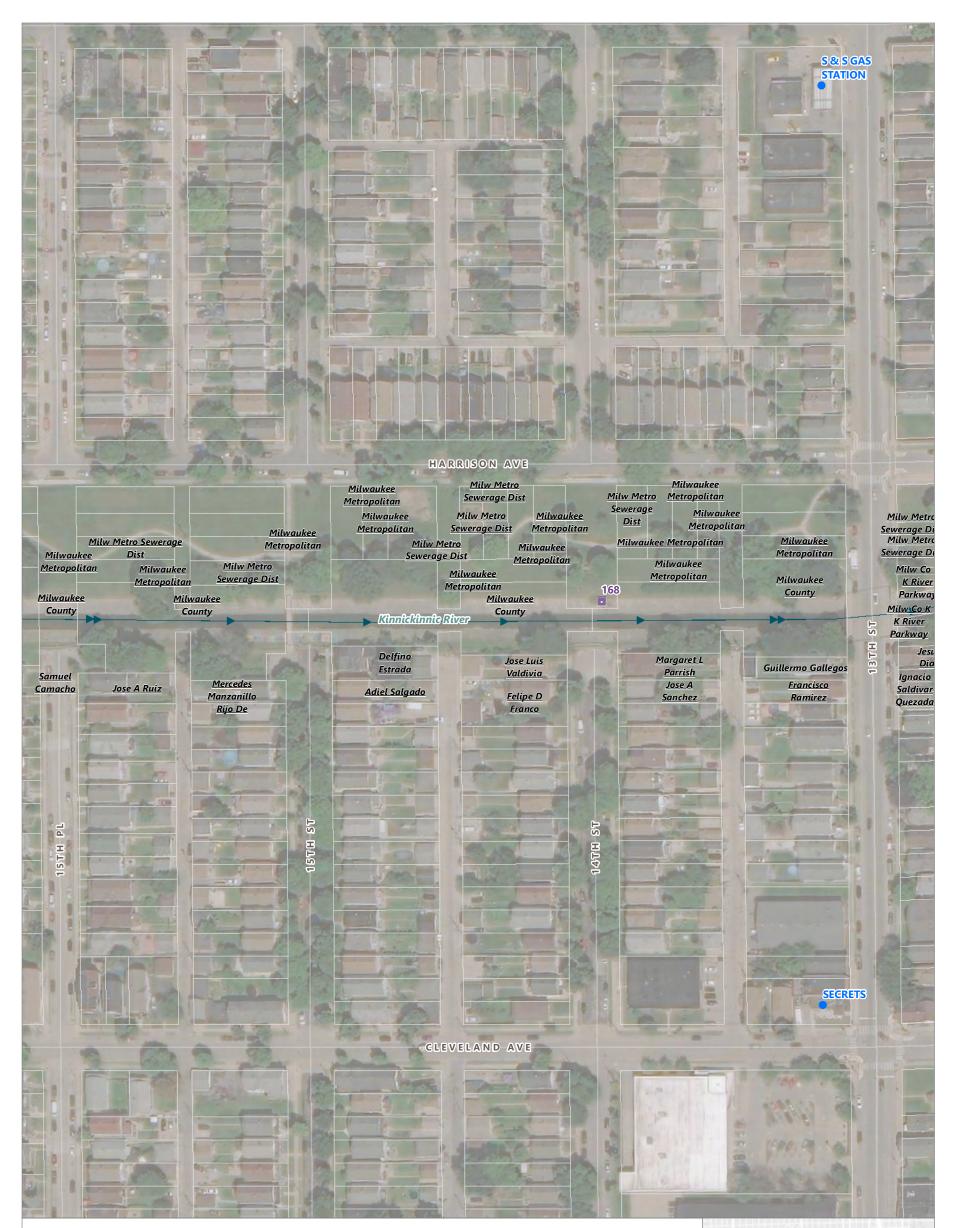


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Figure 3-9

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Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View I



Flow direction (downstream)

Parcel BoundaryCombined Sewer Overflow

Open clean-up site

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.





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Figure 3-10

QEA

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View J





Flow direction (downstream)

Parcel BoundaryOpen clean-up site

▲ Gauge Station

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.





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Figure 3-11

QEA CHOR

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View K



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Figure 3-12

QEA CHOR

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View L



0

Flow direction (downstream)

Parcel Boundary Combined Sewer Overflow

2021 Sampling Location

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



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QEA CHOR

Figure 3-13

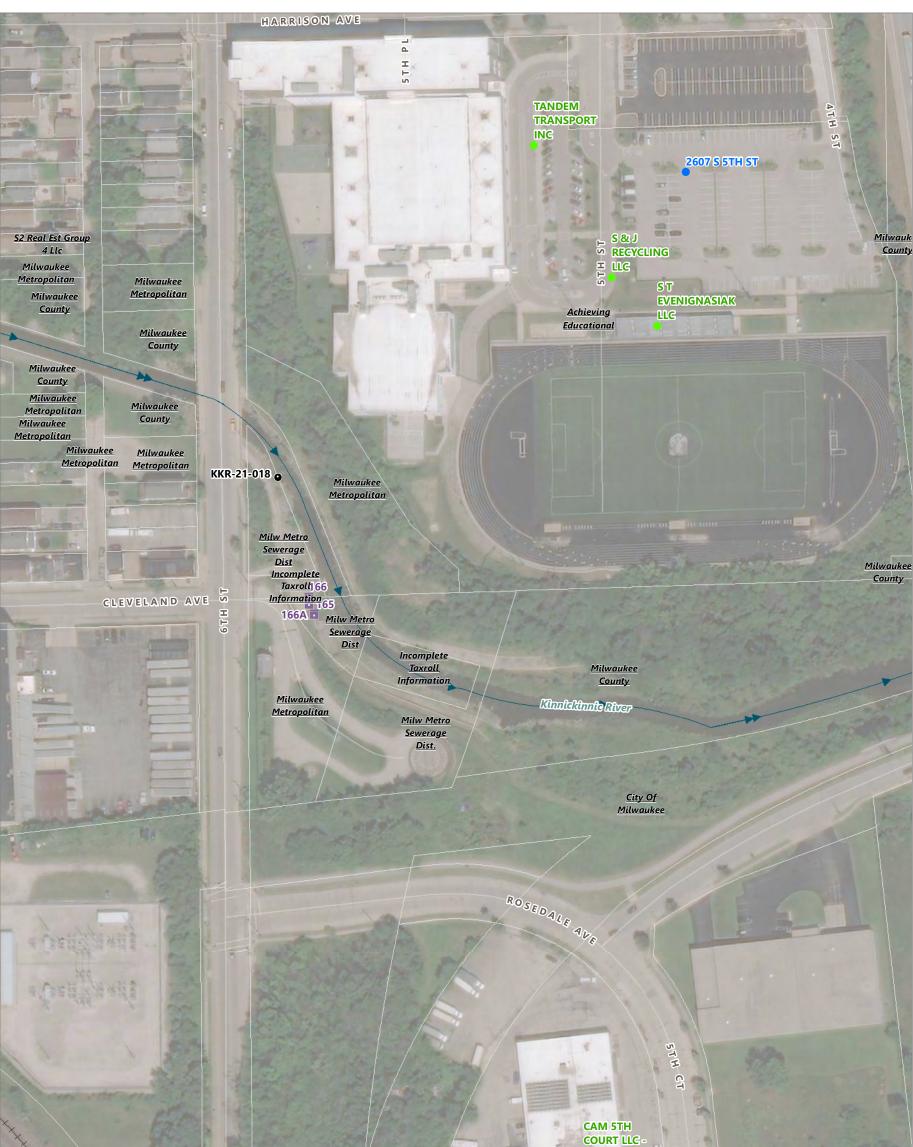
Kinnickinnia

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View M

Characterization of Sediments in Kinnickinnic River and Milwaukee Bay of the Milwaukee Estuary Area of Concern Milwaukee, Wisconsin

park Wilson

Creel



HISTORIC FILL

LEGEND:

Flow direction (downstream)

- Parcel Boundary
- Combined Sewer Overflow
- Closed clean-up site
- Open clean-up site
- 2021 Sampling Location 0

NOTES: 1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.

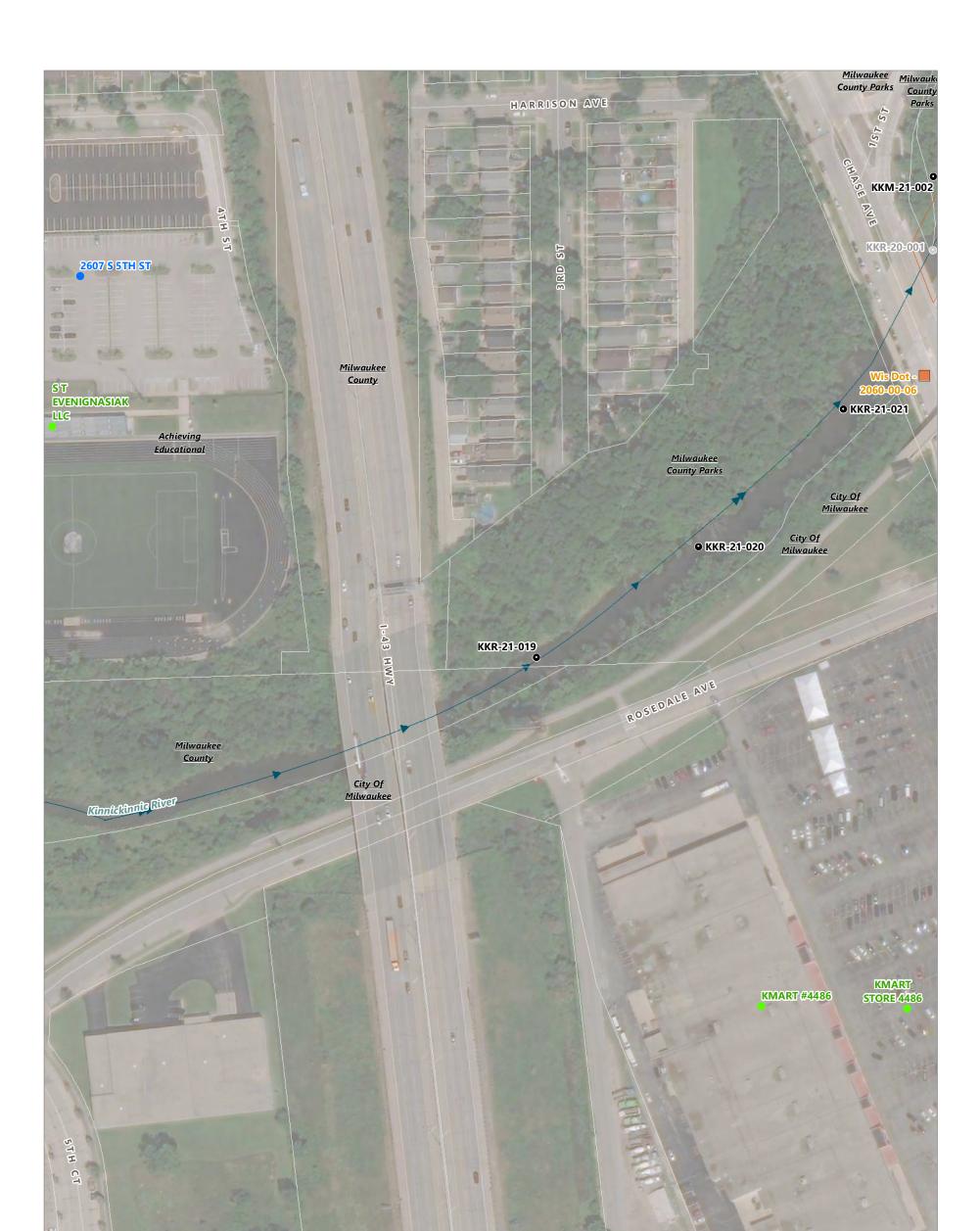


Kinnickinnic Ri Wilson Park Creek

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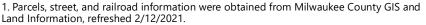
Figure 3-14 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View N



Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- NPDES Permitted Outfall
- Closed clean-up site
- Open clean-up site
- Ô 2020 Sampling Location
- 2021 Sampling Location

NOTES:



2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



Kinnickinnic Rive Wilson Park Cree Creek

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Figure 3-15

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Upstream, View O



Milwaukee

LEGEND:

Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- Combined Sewer Overflow
- NPDES Permitted Outfall
- 2020 Sampling Location 0
- 0 2021 Sampling Location
- ▲ Gauge Station

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



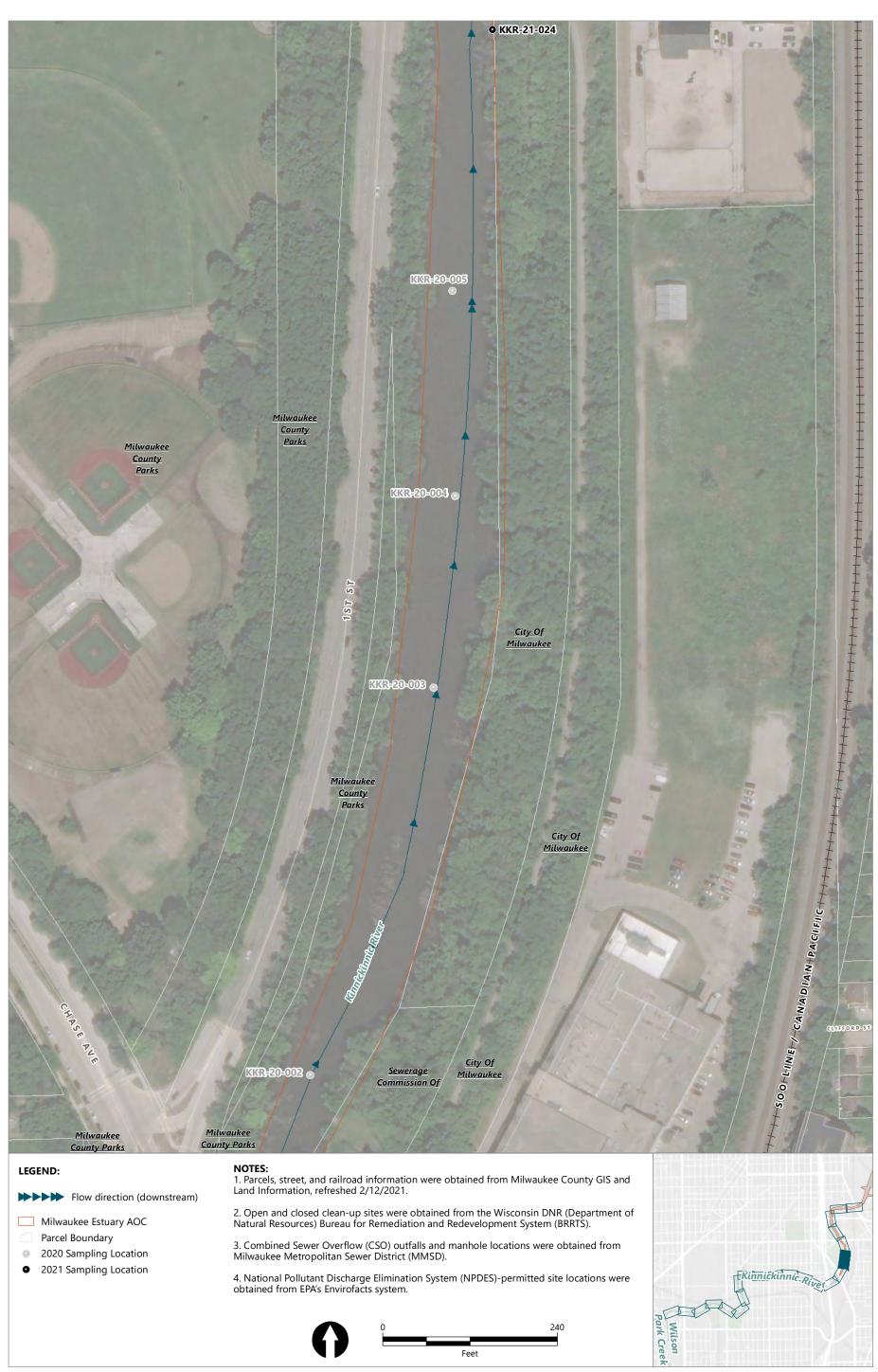
Kinnickinnic Rive Wilson Park Creek

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Figure 3-16

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 1, View A

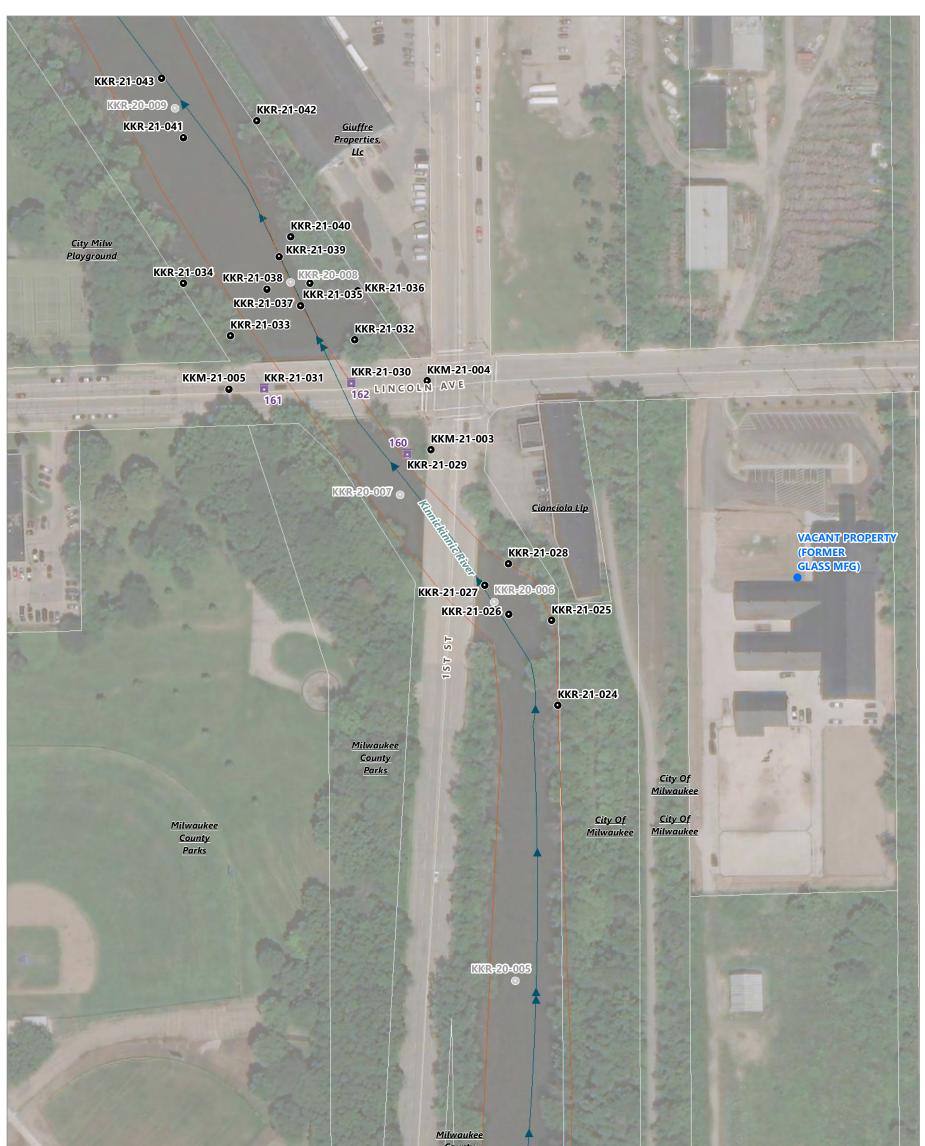


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Figure 3-17

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Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 1, View B





Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- Combined Sewer Overflow
- Open clean-up site
- 2020 Sampling Location 0
- 0 2021 Sampling Location

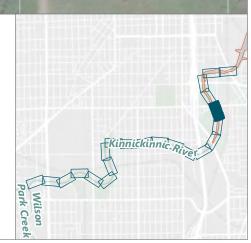
NOTES: 1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

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3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



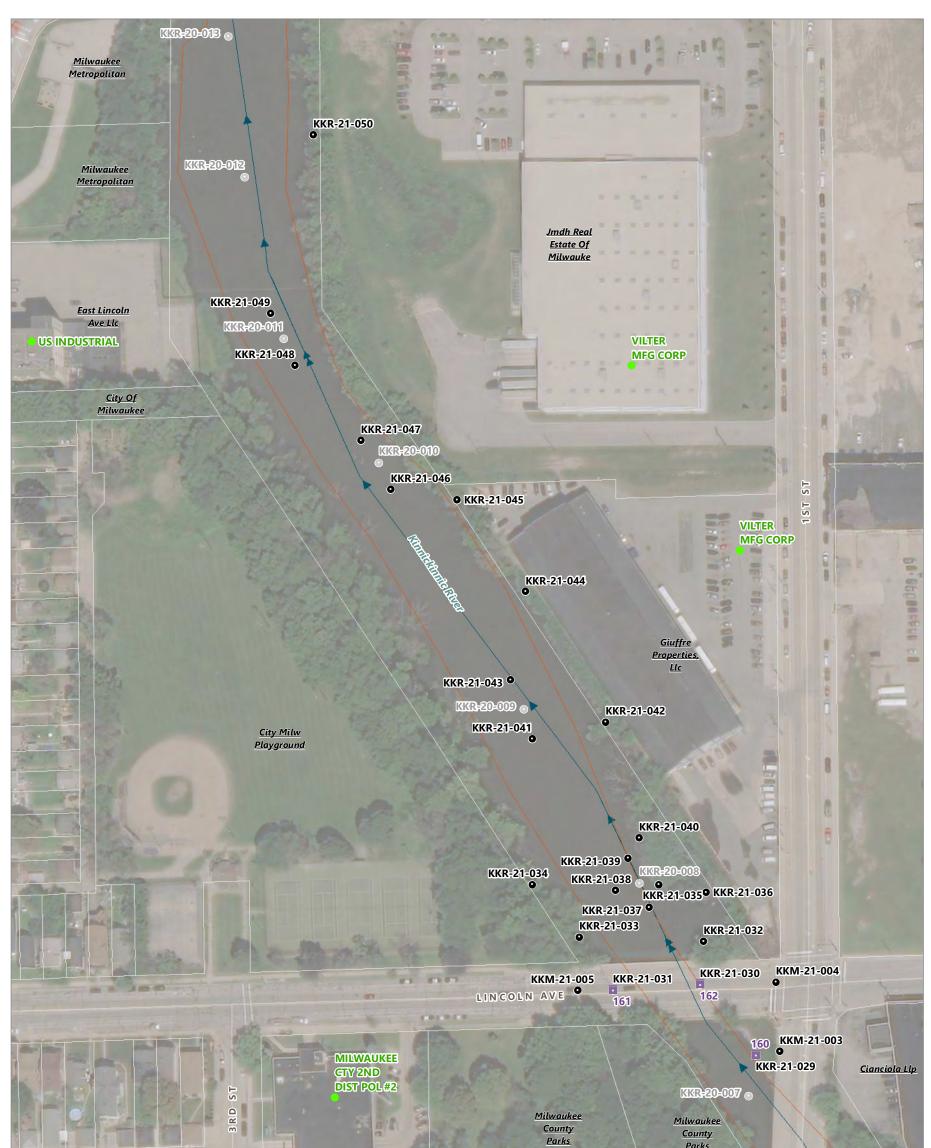


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Figure 3-18

ANCHOR QEA

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 1, View C





Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- Combined Sewer Overflow
- Closed clean-up site
- 0 2020 Sampling Location
- 2021 Sampling Location 0

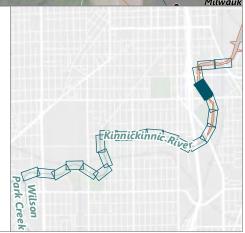
NOTES: 1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.



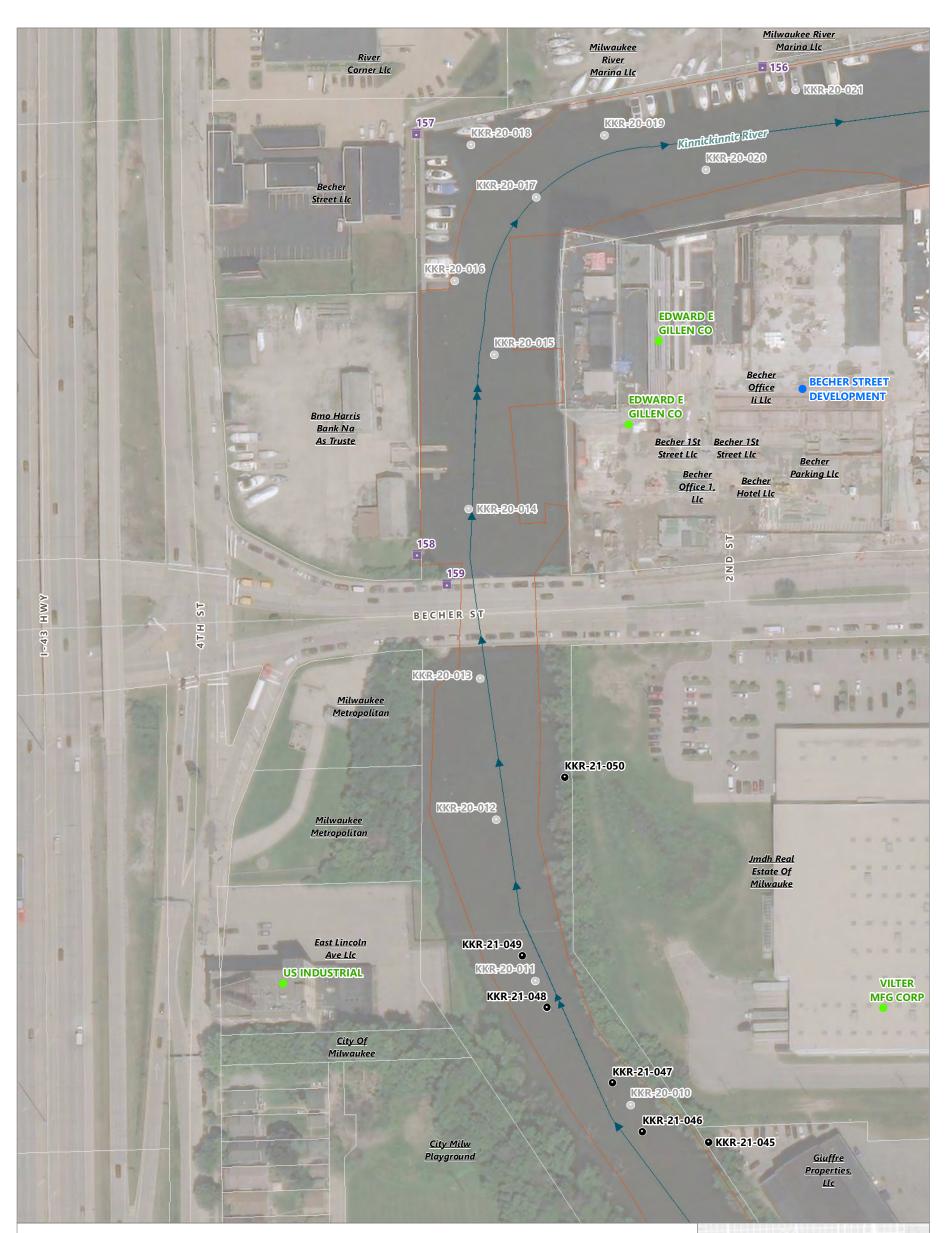


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Figure 3-19

QEA CHOR

Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 1, View D



Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- Combined Sewer Overflow
- Closed clean-up site
- Open clean-up site
- 2020 Sampling Location ٢
- 2021 Sampling Location 0

NOTES:

1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.

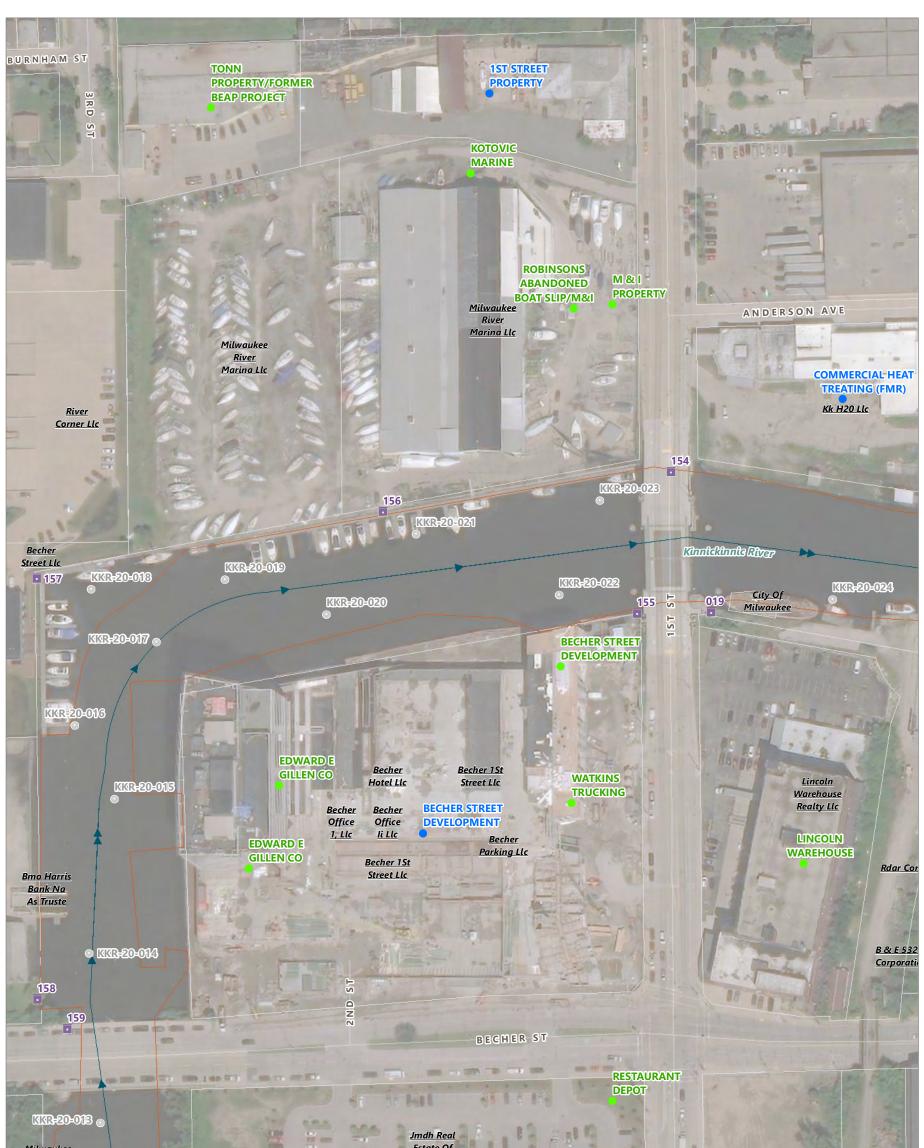


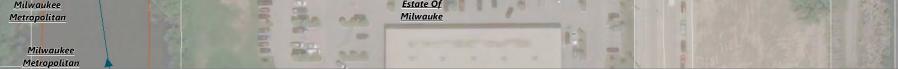
Kinnickinnic Ri Wilson Park Cree Creek

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Figure 3-20 Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 1, View E





Flow direction (downstream)

- Milwaukee Estuary AOC
- Parcel Boundary
- Combined Sewer Overflow
- Closed clean-up site
- Open clean-up site
- 2020 Sampling Location

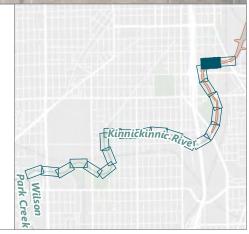
NOTES: 1. Parcels, street, and railroad information were obtained from Milwaukee County GIS and Land Information, refreshed 2/12/2021.

2. Open and closed clean-up sites were obtained from the Wisconsin DNR (Department of Natural Resources) Bureau for Remediation and Redevelopment System (BRRTS).

3. Combined Sewer Overflow (CSO) outfalls and manhole locations were obtained from Milwaukee Metropolitan Sewer District (MMSD).

4. National Pollutant Discharge Elimination System (NPDES)-permitted site locations were obtained from EPA's Envirofacts system.





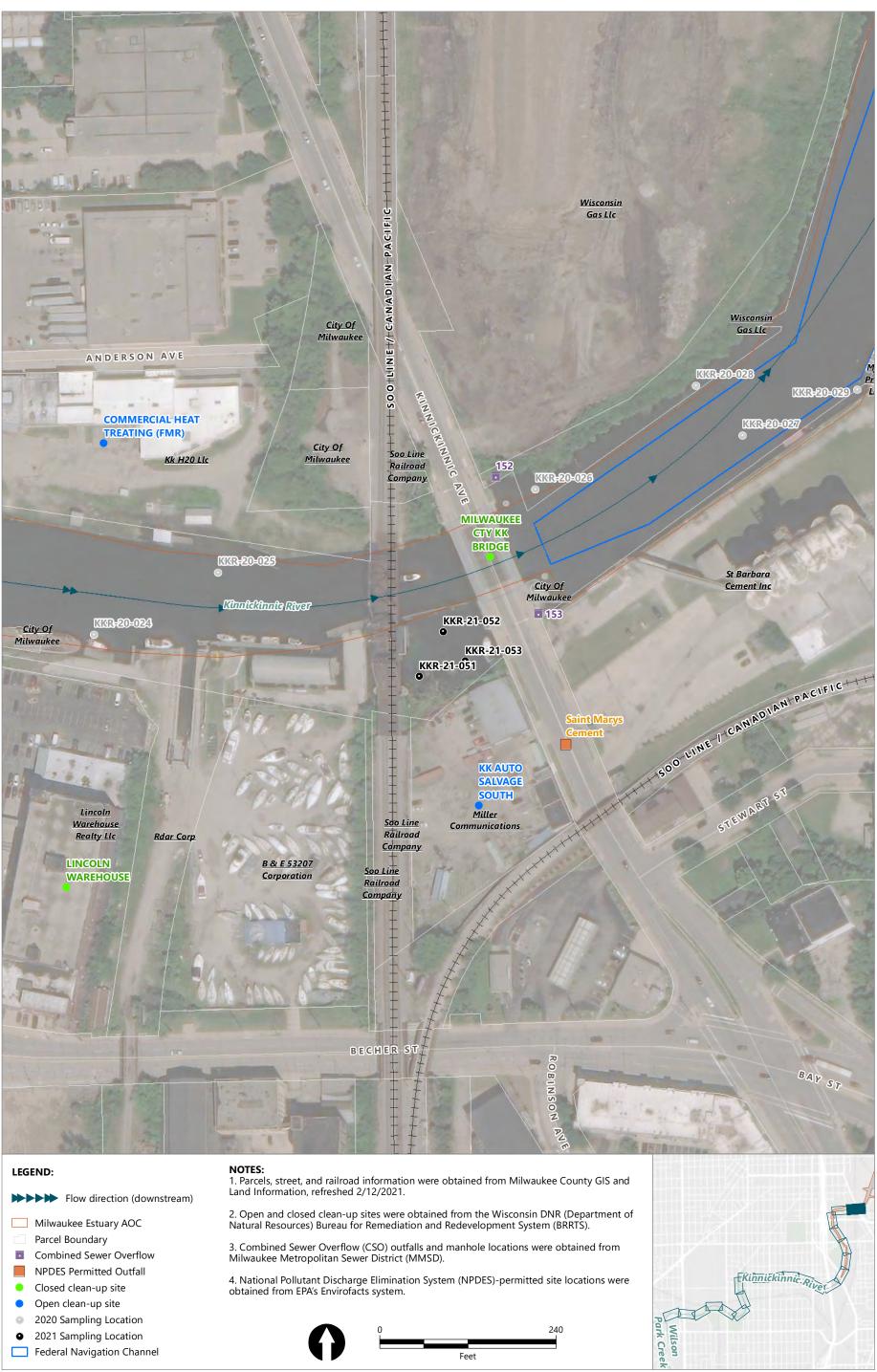
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Figure 3-21

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Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 2, View A





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Figure 3-22

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Property Owners, Permitted Discharges, and Clean-up Sites Adjacent to the Kinnickinnic River — Reach 2, View B