Introduction
This technical memorandum has been prepared to summarize Natural Resource Technology’s (NRT) research to establish a bibliography of sediment sites that include site-specific polycyclic aromatic hydrocarbon (PAH) background investigations.

Site-Specific Background Investigation
A summary of the use of background sediment investigations and data from the following sites and sources are included in this technical memorandum:

- Campmarina
- North Branch of the Chicago River
- San Francisco Bay
- Bellingham Bay
- Gowanus Canal
- Former Oneonta MGP
- Former Penn Yan MGP
- Former Newburgh MGP
- Cortland Homer Former MGP
- Former East 21st Street Works

Information from all sites is summarized in the enclosed Table 1.

Campmarina (NRT 2009)
An MGP historically operated at the Sheboygan-Campmarina site in Sheboygan, Wisconsin adjacent to the Sheboygan River. Remedial investigation and remediation is being conducted at the site under the USEPA Superfund Alternative Sites Program. Previous investigations of the adjacent Sheboygan River and Harbor Site, which overlays the footprint of the former MGP site, indicated that elevated
concentrations of PAHs and metals existed upstream of this site and were unrelated to the former MGP activities. Eight sediment samples were collected upstream of the former MPG to evaluate ambient levels of total PAHs (sum of 13) (tPAH-13). Upper tolerance limits (UTLs) were calculated from the eight upstream samples to calculate an ambient tPAH-13 concentration. The selected remedy includes removal of all sediment containing oil-wetted sediment or NAPL in any form and removal of significant sediment that contains tPAH-13 above the ambient concentration of 18 milligrams per kilogram (mg/kg).

**North Branch of the Chicago River (NRT 2013)**

Three former MGPs and their associated adjacent river areas (ARA) are located on the North Branch of the Chicago River and enrolled in the USEPA Superfund Alternative Sites Program. The sites are located in close proximity to each other. An ambient sediment investigation was performed upstream of the former MGPs to establish background concentrations of PAHs and metals and the potential for toxicity in sediments that are outside the influence of the former MGP. During the ambient sediment investigation, 20 locations were sampled for a total of 51 ambient sediment samples. The investigation identified high concentrations of total PAHs and moderate toxicity to invertebrates in the ambient sediment. To evaluate the incremental effect of the MGPs on total PAH concentrations in ARA sediments, UTLs were calculated for the ambient sediment data set. The tPAH-13 UTLs for surface sediment (0-1.5 feet below sediment surface) and subsurface sediment (deeper than 1.5 feet below sediment surface) were calculated as 342 mg/kg and 410 mg/kg, respectively. Total PAH concentrations above these UTLs in the ARAs may be attributable to the MGPs, rather than ambient sediment conditions. Since the ambient sediment itself was found to be moderately toxic to invertebrates, toxicity testing was not used to identify the incremental effect of the MGP on sediments in the ARA.

**San Francisco Bay (San Francisco Bay Regional Water Quality Control Board 2015)**

Since San Francisco Bay sediments are not totally free of anthropogenic and naturally occurring pollutants, the San Francisco Bay Regional Water Quality Control Board defined “ambient” sediment concentrations as the typical range of concentrations that one would expect to find in sediment in the less polluted or “cleaner” portions of the bay. Ambient sediment concentrations for this use refer to the 90% upper confidence limit of the 90th percentile concentrations of typical sediment concentrations from the previous 10 years. The 2002-2012 ambient tPAH-25 concentration is 4.54 mg/kg.
Bellingham Bay (State of Washington 2015)

The State of Washington publishes natural background sediment concentrations as a potential Sediment Cleanup Objective (SCO). However, a 2013 revision to the Sediment Management Standards (SMS) includes both natural and regional background as potential Cleanup Screening Levels (CSL) for sites. Regional background means the concentration of a contaminant within a department of defined geographic area that is primarily attributable to diffuse sources such as atmospheric deposition or storm water, not attributable to a specific source or release. The concept of a regional background was applied at the Bellingham Bay Area of Interest (AOI). Samples for the regional background study were collected from within the AOI but excluded cleanup sites along the shoreline. The Bellingham Bay study looked at the seven carcinogenic PAHs (cPAHs) and toxic effect concentrations (TEC). Twenty-three sediment samples were collected for cPAH analysis as a part of the regional background study. The regional background cPAH 90/90 UTL of 86 µg TEQ/kg was more than five times greater than the natural background of 16 µg TEQ/kg. These values were presented for informational purposes to guide future CSL decision making at sediment cleanup sites located in Bellingham Bay.

Gowanus Canal (USEPA 2013)

The Gowanus Canal is located in Brooklyn, New York. The Record of Decision (ROD) issued by USEPA for this site compares contaminant concentrations in the Gowanus Canal to reference area sediments in the Gowanus Bay and Upper New York Bay. The tPAH-17 (priority pollutant compounds and 2-methylnaphthalene) concentration ranged from 1 to 14 mg/kg with an average of 6 mg/kg in the reference areas. The reference area concentrations were not used as a specific cleanup criterion but were used to evaluate which canal areas should be included in the remedial footprint. Either the Wilcoxon rank-sum test or Gehan’s test was applied to determine with 95 percent confidence whether contaminant concentrations in the canal were greater than those at the reference locations.

Former Oneonta MGP (NYSDEC 2005a)

The former Oneonta MGP is located in Oneonta, New York adjacent to the Mill Race Creek on the Susquehanna River. Seven background sediment samples were collected from “the tailrace” which is an artificial waterway that ties into the Susquehanna River at both ends. Several hundred feet upstream of the site, the tailrace flows over a small dam, which creates a stilling basin that greatly limits the amount of natural sediment transported through the reach that passes the MGP site. TPAH-16 concentrations in the background samples ranged from 0.01 to 3,782 mg/kg organic carbon. The removal footprint was based on a combination of visible tar, sheen, and tPAH concentrations above background.
Former Penn Yan MGP (NYSDEC 2012)

A former MGP operated in the Village of Penn Yan, Town of Milo, New York. The MGP was located between Water Street and the Keuka Lake Outlet (Outlet). Finger Lake, upstream of the former MPG, serves as an impoundment that limits the amount of natural sediment carried into the Outlet. Thus, most sediment in the Outlet is from anthropogenic sources. Sediment in the Outlet which contained PAHs at levels above the site-specific background concentration of 43 mg/kg tPAHs-17 (includes 2-methylnaphthalene) were removed to a maximum of two feet below sediment surface. The site-specific background is the 90th percentile value calculated from 16 upstream shallow sediment samples.

Former Newburgh MGP (NYSDEC 2005b)

The former MPG is located in Newburgh, New York near the Hudson River. MGP residual material historically migrated off site beneath Water Street, two sets of railroad tracks, and the city sewage treatment plant, and into Hudson River sediment. The selected remedy includes removal of all tar impacted sediments and installation of a sediment cap in the Hudson River in areas where the tPAH-17 concentration exceeds the local background level of 20 mg/kg. Background sediment samples were taken from approximately 37 locations to help distinguish MGP-related contamination from contamination which originated elsewhere in the industrialized Newburgh water front. The statistical method used to evaluate the background samples was not described in the documents reviewed. The background sampling locations were upriver of the site, and are assumed to be unaffected by historic or current MPG site operations.

Cortland Homer Former MGP (NYSDEC 2005c)

The former MGP is located in Homer, New York. The selected remedy includes removal of all sediment containing free tar or NAPL in any form and removal of significant sediment deposits containing tPAH-17 concentrations that are attributable to the site in exceedance of background. Background for this remedial action has been defined as 6.2 mg/kg total PAHs, based on 8 background sediment samples. The statistical method used to evaluate the background samples was not described in the documents reviewed.
Former East 21st Street Works (AECOM 2010)

The East 21st Street Works former MGP is located in Manhattan, New York City, New York near the East River. Sediment investigations were performed to evaluate the background quality of surficial sediments within the East River to use as a baseline of comparison with constituent concentrations at locations adjacent to the site. The background data set consisted of 40 surface sediment samples collected from the East River at 13 locations selected from depositional environments (shoal), water depths and sediment assemblages that are similar to areas located adjacent to the site. The 90th percentile was used to define the site-specific background level. The 90th percentile was calculated using USEPA's ProUCL software, and defines a site-specific background value of 71 mg/kg for tPAHs-13. NYSDEC has determined that for purposes of this analysis, 70 mg/kg can be used as the site-specific background value for total PAHs and should be used as the baseline for comparison of MGP-impacted material adjacent to the site.

Enclosures
Table 1 - Literature Review for Use of Background PAHs in Sediment
References

http://www.coned.com/publicissues/MGP/E21st_St_Works_RIR_OU2_Final_Tables-092710.pdf


NRT, 2013. Step I Data Evaluation for the North Branch Sediment Sampling. North Branch Chicago River, Willow Street/Hawthorne Avenue Station and Division Street Station Former MGPs. The Peoples Gas Light and Coke Company. February.

http://www.dec.ny.gov/docs/remediation_hudson_pdf/rod439001.pdf


NYSDEC, 2005c. Record of Decision. NYSEG Cortland Homer Former MGP Site, Operable Unit 02 Homer (V), Cortland County, New York. Site Number 7-12-005. March. 
http://www.dec.ny.gov/docs/remediation_hudson_pdf/rod712005.pdf

http://www.dec.ny.gov/docs/remediation_hudson_pdf/862009rod.pdf


https://semspub.epa.gov/work/02/692106.pdf
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<th>Site Name</th>
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<th>Regulatory Agency/Program</th>
<th>Freshwater</th>
<th>Number of PAHs included in Total</th>
<th>Number of Background Samples</th>
<th>Statistical Method</th>
<th>Background Concentration Total PAHs (mg/kg)</th>
<th>Background concentration used for Remedial Planning?</th>
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<td>8</td>
<td>95th Percentile</td>
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<td>342 (0-1.5 ft btos) 410 subsurface (&gt;1.5 ft btos)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>23</td>
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<td>0.086 µg TEQ/kg</td>
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<td>17</td>
<td>10</td>
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<td>1 to 14</td>
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<td>16</td>
<td>7</td>
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<td>0.01 to 3,782²</td>
<td>Yes, either the Wilcoxon rank-sum test or Gehan’s test was applied to determine with 95 percent confidence whether contaminant concentrations in the canal were greater than those at the reference locations</td>
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<td>17</td>
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<td>70</td>
<td>Yes, to be used as the baseline for comparison of MGP-impacted material adjacent to the site</td>
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</table>

Notes:
1 - Likely dry weight, but not specifically stated in each source document
2 - microgram per gram of organic carbon
µg TEQ/kg - microgram Threshold Effect Concentration per kilogram
btons - below top of sediment
ft. - feet
mg/kg - milligram per kilogram
MGP - manufactured gas plant
NA - Not available; information not found in literature reviewed
NYSDEC - New York State Department of Environmental Conservation
PAH - polycyclic aromatic hydrocarbon
SFBRWQCB - San Francisco Bay Regional Water Quality Control Board
SAS - Superfund Alternative Sites Program
USEPA - United States Environmental Protection Agency
UTL - Upper tolerance limit
This technical memorandum has been prepared to summarize Natural Resource Technology's (NRT) research to identify sediment screening levels (SL) beyond those compiled by United States Environmental Protection Agency (USEPA) Region 5 (Ecological Screening Levels [ESL]) and MacDonald et al (Consensus-based Sediment Quality Guidelines, 2002). Identified, published SLs include:

- USEPA Region 5 Resource Conservation and Recovery Act (RCRA) ESLs
- Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems
- National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Table for Organics in Sediment (SQuiRT)
- United States Department of Energy (USDOE) Preliminary Remediation Goals for Ecological Endpoints
  - [https://rais.ornl.gov/documents/tm162r2.pdf](https://rais.ornl.gov/documents/tm162r2.pdf)
- USEPA Office of Solid Waste and Emergency Response Ecotox Thresholds
- Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario
- Washington State Sediment Management Standards
## Sediment Screening Values*

<table>
<thead>
<tr>
<th>Reference</th>
<th>Units</th>
<th>Acenaphthene</th>
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<th>Benzo(a)anthracene</th>
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<td>NR</td>
<td>57.2</td>
<td>16</td>
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* Lowest value reported for freshwater
NR - Not reported
## Sediment Screening Values*

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* Lowest value reported for freshwater
NR - Not reported
## Sediment Screening Values*

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* Lowest value reported for freshwater

NR - Not reported
## Sediment Screening Values*

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* Lowest value reported for freshwater

NR - Not reported
Incorporating Direct Measurements of Bioavailability into Sediment Polycyclic Aromatic Hydrocarbons Assessments at MGP Sites

Environment Brief

Background
Sediments impacted with polycyclic aromatic hydrocarbons (PAHs) represent a challenging site characterization problem. Specifically, it has been difficult to confidently delineate PAH-impacted sediment areas that pose an ecological risk and therefore require management. Traditional characterization methods are overly conservative, and lead to managing large volumes of sediment that do not pose an environmental risk. However, recent advancements in analytical methods coupled with changing regulatory guidance, now allow more accurate sediment assessments. This brief summarizes the evolution of the primary characterization methods, explains a novel method for direct measurement of pore water PAH concentrations, and discusses how this new measurement can be incorporated into the current regulatory frameworks to improve the management of PAH-impacted sediments at manufactured gas plant (MGP) sites.

Summary
Sediment remediation is costly, and the "solid-phase microextraction" (SPME) pore water method and approach provides several direct cost benefits to the utilities.

First, regulatory screening criteria based on total PAH concentrations in sediment, which are not predictive of toxic effects, lead to large volumes of sediment at MGP sites which exceed the criteria. In contrast, the SPME pore water measurement targets only those areas with bioavailable PAHs, which is generally a significantly smaller area. Reductions in the remedial footprint of 50 to 80 percent were derived in many of the case studies used to develop the SPME pore water method.

Second, the SPME pore water measurement is highly sensitive over a range of site conditions, leading to fewer "false positives" (that is, falsely attributing toxicity to MGP site PAHs when they are not the cause). Toxicity testing, often the "gold standard" for sediment characterization, has several confounding factors which could lead to falsely attributing toxicity to site PAHs. Therefore, incorporating the SPME pore water method, either in isolation or in conjunction with toxicity testing, reduces the risk to utilities of false positives and of incurring unnecessary remediation costs.

The implementation of direct pore water PAH measurement through methods such as ASTM Method D7363-07 provides more accurate site characterization data with which site managers can make better, more confident decisions about potential areas of concern and remedial alternatives. Ultimately, these improved decisions will result in the more effective use of both human and financial resources.

Sediment PAH Characterization Methods
Sediment characterization methods have evolved over time and fall into three primary categories: (1) empirical screening values; (2) equilibrium partitioning models; and (3) direct measurement of sediment pore water PAH concentrations.

Empirical Screening Values – Empirical screening values, sometimes referred to as "sediment quality guidelines" (SQGs), originated in the early 1990s when NOAA researchers tried to equate toxicity testing results to sediment total PAH concentrations.
concentrations. These SQGs quickly gained favor due to their simplicity. In less than a decade, total PAH screening values such as the probable effects concentration (PEC) of 22.8 mg/kg for freshwater and the effects range median (ERM) of 44.8 mg/kg for marine sediments evolved into de facto cleanup criteria for delineating sediment areas requiring management. However, this was not the intended function and the original documents cautioned against such an approach.

Equilibrium Partitioning Models – Recognizing the limitations of empirical methods, in 2003 the U.S. Environmental Protection Agency (EPA) published a mechanistic approach to estimate the concentrations of PAHs that may be present in sediment while still protecting benthic organisms from the effects of PAHs. This approach, which is based on equilibrium partitioning of the PAHs from the sediment to the pore water, was viewed as an improvement because it provided a mechanism to explain toxicity (that is, pore water PAHs represent the true exposure concentration). However, a big drawback was the use of generic literature values for the PAH partitioning coefficients used to estimate the amount of PAHs that would go into the sediment pore water given the sediment total PAH concentration and the amount of organic carbon. Field testing of this equilibrium partitioning approach at MGP sites shows that these models over-predict biological effects by orders of magnitude, and are therefore no more predictive than the SQGs they were developed to replace.

A primary reason why the equilibrium partitioning approach fails at MGP sites is that these industrial sediments contain significant fractions of anthropogenic or black carbon. The black carbon fraction more tightly binds PAHs than natural organic matter; therefore, the fraction of PAHs going from the sediment into the pore water is significantly lower than assumed under the equilibrium partitioning models, which are based on natural organic carbon. Attempts to measure the black carbon fraction and estimate the pore water PAH concentration have been shown by EPRI and others to be highly variable and not predictive of biological effects. Therefore, the current paradigm is that direct measurement of the pore water PAH concentration is the preferred approach.

Direct Measurement of Pore Water PAHs – In 2003, a novel approach for measuring low-level dissolved-phase PAH concentration in sediment pore water was developed, incorporating the SPME technique. Over a period of eight years, an extensive international database of case studies including more than 20 MGP and aluminum smelter sites from around the United States and Canada was developed to test the method. The case studies showed excellent correlation between the measured SPME pore water PAH concentrations and laboratory toxicity tests. Across a wide range of site conditions and sediment PAH concentrations, the SPME pore water method was able to accurately predict toxicity (Figure 1). A generic value of 1.0 toxic unit (1.0 TU) was shown to provide sufficient protection of the environment. However, on a site-by-site basis, higher TU thresholds were observed. [A TU is
essentially a hazard quotient created by dividing the pore water concentration of a PAH by its EPA final chronic value. The TU for a PAH mixture is determined by summing the TUs of the individual PAHs.

Bioavailability – The Key Metric
The reason that the SPME pore water method works is because of the “bioavailability” of the sediment-bound PAHs. Due to sorption on the organic carbon, not all of the sediment-bound PAHs are available to the benthic invertebrates that inhabit the sediment. The fraction that is available is called the “bioavailable fraction” and represents the true exposure concentration. For PAHs, the pore water concentration is the most accurate indicator of the bioavailable fraction. Therefore, a direct measurement of the sediment pore water provides a measurement of the true exposure concentration. In essence, the SPME pore water method replaces an empirical correlation or an assumed model with a direct measurement.

ASTM D7363-07 and U.S. EPA 8272
Between 2003 and 2011, the SPME pore water method was validated on more than 300 field sediment samples. In 2007, the SPME pore water method was assigned U.S. EPA Method 8272. Later that year, a provisional ASTM standard method was approved, contingent upon successful completion of an inter-laboratory validation (ILV) study. The EPRI-supported ILV study was successfully completed in December 2010. Four independent analytical laboratories participated in the ILV, along with the University of North Dakota Energy and Environmental Research Center (EERC), the custodial lab and method developer. ASTM Standard Method D7363-07 was approved and finalized in July 2011. Both methods are now commercially available.

Field Implementation
A standard set of sediment characterization protocols has been developed since 2003 that is consistent with established practices outlined by EPA and ASTM. In general, the process entails: (1) collection of surface sediment; (2) field homogenization; (3) laboratory analysis of pore water PAHs via ASTM D7363-07; and (4) computation of the pore water TUs using the measured pore water PAH concentrations and EPA published final chronic values. The TU concentration can be compared to a generic value of 1.0 TU, or alternative site-specific thresholds may be developed.

Regulatory Framework
In 2009, EPA published a white paper entitled, “Evaluating Risk to Invertebrate Receptors from PAHs in Sediments at Hazardous Waste Sites” (U.S. EPA, 2009 [EPA/600/R-06/162F]). The document builds upon earlier EPA work, and provides a tiered approach to determine ecological risk from sediment-bound PAHs. The second tier includes an assessment of PAH bioavailability, and references the ASTM Method D7363-07 (that is, SPME pore water method) [Figure 2].

![Diagram](https://via.placeholder.com/150)

Figure 2. Tiered framework to determine the risk of adverse effects due to PAHs in sediments (adapted from U.S. EPA (2009)).
In support of the EPA (2009) framework, in February 2011, the Interstate Technology and Regulatory Council (ITRC) published a sediment guidance document, “Incorporating Bioavailability Considerations into the Evaluation of Contaminated Sediment Sites.” The ITRC guidance is constructed to assist the user in identifying the most relevant places within an exposure assessment that bioavailability can be assessed and which tools and methods are most useful and appropriate. As part of this guidance, the SPME pore water method is included and described in detail. The ITRC guidance, which was reviewed by all of its member states (49/50 states, with South Dakota not currently a member) endorses the use of bioavailability for contaminated sediment management.

Using the EPA (2009) framework as the model, incorporating direct pore water measurement for managing MGP sites with PAH-impacted sediments would entail the following sequence of steps:

**Tier 1** – Determine the total PAH concentrations in the site sediment samples and either (1) compare these concentrations against screening values or (2) use these concentrations and equilibrium partitioning models to estimate pore water TUs. This tier of the analysis is overly conservative and ensures that no toxic sediment samples are classified as non-toxic (that is, minimizes false negatives); however, in doing so, non-toxic sediment samples may be misclassified as toxic (that is, false positives are more likely to exist).

**Tier 2** – If sediment samples exceed Tier 1 values, then evaluate these sediment samples for pore water PAHs and compare the pore water concentrations, expressed in TUs, against the generic value of 1.0 TU.

**Tier 3** – If desired, the prediction of toxicity based on the PAH concentrations in sediment or pore water can be replaced by direct measurements of toxicity (for example, H. azteca 28-day survival) on a subset of site sediment samples. These toxicity measurements can be combined with pore water PAHs to derive a site-specific dose-response. Historical data from past case studies suggests that this approach will yield threshold values greater than the generic 1.0 TU.

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