GTI Project Number: 40453-01

COMPARATIVE ANALYSIS OF TEN SEDIMENT SAMPLES FROM CHEQUAMEGON BAY, ASHLAND, WISCONSIN

THIRD ADDENDUM TO THE REPORT: COMPARATIVE ANALYSIS OF NAPL RESIDUES FROM THE NSP ASHLAND FORMER MGP SITE AND THE ASHLAND LAKEFRONT PROPERTY (KREHER PARK)

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EXECUTIVE SUMMARY

The Gas Technology Institute (GTI) has conducted laboratory analysis of ten sediment samples retrieved from the Chequamegon Bay near the Kreher Park shoreline in Ashland, Wisconsin. Samples were tested using identical methods described in the report, *Comparative Analysis Of NAPL Residues From The NSP Ashland Former MGP Site And The Ashland Lakefront Property (Kreher Park)* (NAPL Report, March, 2000), and evaluated against results of that report and associated Addendum reports. An initial Addendum Report, *Comparative Analysis Of Sediment Samples From The Chequamegon Bay Near The Kreher Park Shoreline, Ashland, Wisconsin*, was prepared in May, 2000. A second Addendum report, *Comparative Analysis Of Two Samples From Kreher Park, Ashland, Wisconsin*, was prepared in April, 2001. This document serves as a Third Addendum to the NAPL Report.

Using GC/FID fingerprinting techniques, results concluded that all ten sediment samples tested are very similar to each other in tar composition and appear to be from the same source. They are very similar to the tar contained in previously tested sediment samples AS-2 and AS-4 (Initial Addendum), very similar to the tar contained in the samples "12" Clay Pipe" and "NAPL/Water" (Second Addendum) and very similar to the tar contained in the NAPL sample from MW-7, previously described in the NAPL Report. The tar from all ten sediment samples described in this report is dissimilar to NAPL samples from wells MW-15 and EW-1, from the NSP Property.

The 10 sediment samples each possess a middle weight petroleum (oil) fraction, ranging 8.3 to 15 percent aliphatic hydrocarbon. The percentages of oil fraction in the 10 sediment samples are similar to those found in previously analyzed sediment samples AS-2 and AS-4 (6.8 and 16 percent, respectively).

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INTRODUCTION

Northern States Power Company (NSP) has contracted the Gas Technology Institute (GTI) to determine whether 10 sediment samples retrieved from the Chequamegon Bay near the Kreher Park shoreline in Ashland, Wisconsin are chemically similar or dissimilar to NAPL residues found in wells located at the NSP former MGP site (MW-15 and EW-1) and in an area of former wood treatment operations in Kreher Park (MW-7). The ten sediment samples were also compared to previously examined sediment samples (AS-2 and AS-4) and additional samples retrieved from Kreher Park (samples "12" Clay Pipe" and NAPL/Water). The results of these sediment analyses serve as the Third Addendum to the report, *Comparative Analysis of NAPL Residues From The NSP Ashland Former MGP Site And The Ashland Lakefront Property (Kreher Park)* (NAPL Report).

GTI and its subcontractor (META Environmental, Inc.) have completed forensic analysis of ten sediment samples. Analyses of these samples have included identification and/or quantification of: 1) monocyclic hydrocarbons (MAHs), 2) polycyclic aromatic hydrocarbons (PAHs), and, 3) aliphatic hydrocarbons and polar hydrocarbons. Analyses and hydrocarbon fingerprinting were performed using gas chromatography with flame ionization detection (GC/FID). These analyses are described in detail in the NAPL Report. Results of all sediment analyses are included in this Third Addendum Report, with expanded analytical data detailed in Appendix A.

SITE BACKGROUND

Historically, Chequamegon Bay has been utilized as a vital transportation route for the shipment of various materials to and from the town of Ashland, Wisconsin, including iron ore, lumber, pulp and coal. During the 19th century, Ashland was one of the busiest ports on the Great Lakes (1).

Sanborn Fire Insurance Maps of the vicinity indicate that the jetty currently used by the Ellis Avenue Marina was constructed prior to 1895, and was initially used as a loading dock and to support a rail spur. Two large docks or jetties separated by a slip were constructed prior to 1901 in the vicinity of the present Prentice Avenue Boat Ramp. The shoreline between Ellis Avenue and Prentice Avenue was filled to its approximate present configuration by 1901. A log boom historically extended offshore in the proximity of the present wastewater treatment plant structure. The historic configuration of the sediment investigation area shoreline remained largely unchanged between 1901 and 1951 (2)

In recent times, the shipping industry through the bay has declined because of the decline in the mining and lumber industries in the region. (1)

Previously conducted sampling and analysis of bay sediments is detailed in the Short Elliot Hendrickson Inc. (SEH) Report, *Sediment Investigation Report, Chequamegon Bay- Ashland, Wisconsin*, July, 1996 (Bay Sediment Report). The reported purpose of the Bay Sediment Report was to, "identify the degree and extent of offshore sediment contamination adjacent to the Ashland Lakefront Property." Sampling and analysis of sediments was again conducted in February, 2001, by URS Corporation, on the behalf of Northern States Power Company.

METHODS

The results of the analyses of the ten sediment samples are included in this Third Addendum report, with expanded analytical data detailed in the Appendix of this Addendum report. Sediment samples were collected from Chequamegon Bay near the Kreher Park shoreline in Ashland, Wisconsin between February 28 and March 8, 2001 . These samples were collected by URS Corporation, on behalf of the Northern States Power Company. This work was completed to further characterize sediment contamination previously identified and delineated by SEH on behalf of the WDNR.

Sediment samples were collected from borings advanced through the ice at the pre-determined locations with a track mounted Geoprobe. After cutting a hole in the ice and measuring the water depth, this direct push drilling method was used to hydraulically advance a drill rod attached to a piston-sampling device at two-foot intervals. Each boring was extended a minimum of eight feet into the underlying sediments. For each sample collected, a clear plastic liner was placed in the piston sampler. Recovered sediment samples were withdrawn from the piston sampler in the plastic liners. The liners were cut open, and the length of the sample interval recovered and a description of the sediment was recorded on field boring logs.

The 10 samples selected for fingerprint laboratory analysis were placed in 4-ounce glass jars, filled to the top with zero headspace, and sealed with screw-cap tops. The samples were packed in ice, and shipped overnight with the completed chain-of-custody forms to the laboratory (META Environmental, Inc.,Watertown, MA) for immediate analysis. The results of laboratory testing were sent to GTI for interpretation.

Analyses of the samples included: 1) gas chromatography with flame ionization detection (GC/FID), and, 2) simulated distillation. A chromatographic fingerprint was obtained from each sample using GC/FID, identifying and/or quantifying each of the compound classes: 1) monocyclic hydrocarbons (MAHs), 2) polycyclic aromatic hydrocarbons (PAHs), and, 3) aliphatic hydrocarbons and polar hydrocarbons.

RESULTS

The GC/FID fingerprint data from the ten sediment samples shows that the whole extracts of all samples is highly similar and likely from the same source. The aromatic fraction in the ten sediment samples are also very similar to the aromatic component in the previously examined sediment samples AS-2 and AS-4, the samples "12" Clay Pipe" and NAPL/Water from Kreher Park and the NAPL sample from well MW-7, located near the former wood treatment operations in Kreher Park (refer to NAPL Report and First and Second Addendums). Particular observations drawn from the results are as follows:

- The GC/FID fingerprints of the whole extracts of the 10 sediment samples are very similar, exhibiting a tar-like pattern. The results strongly suggest that they are all from the same source.

- The GC/FID fingerprints of the aromatic fractions (tar) of the 10 sediment samples are different from the aromatic fractions in NAPL samples from wells MW-15 and EW-1 (on or below the Ashland NSP former MGP property).

- The GC/FID fingerprinting of the tar fraction of the 10 sediment samples are highly similar to the tar component of the NAPL sample from well MW-7, in Kreher Park. The data strongly suggests that tar from the 10 sediment samples and the sample from MW-7 share the same source.

- The GC/FID fingerprints of the aromatic fractions (tar) of the 10 sediment samples are very similar to previously tested sediments samples AS-2 and AS-4. The data strongly suggests that tar from the 10 sediment samples and the samples AS-2 and AS-4 share the same source.

- The GC/FID fingerprints of the aromatic fractions (tar) of the 10 sediment samples are very similar to previously tested Kreher Park samples "12" Clay Pipe" and NAPL/Water. The data strongly suggests that tar from the 10 sediment samples and the samples "12" Clay Pipe" and NAPL/Water share the same source.

- The percentage of total aliphatic hydrocarbons (middle petroleum distillates) and total aromatic hydrocarbons (tar fraction) varies among the 10 sediment samples. The percent aliphatic ranged from 8.3 to 15 percent. This range of aliphatic hydrocarbon correlates with that found in samples AS-2 and AS-4.

The actual GC/FID scans or fingerprints for each sample are shown in Appendix A of the Addendum report.

DISCUSSION OF RESULTS

Results of all testing indicated the following:

1) The aromatic component (tar) from all 10 sediment samples are highly similar to each other and to the tar component in the NAPL sample from well MW-7, sediment samples AS-2 and AS-4 and "12" Clay Pipe" and NAPL/Water samples. These results are consistent with the fact these samples were retrieved from locations proximal to each other (Kreher Park and the Chequamegon Bay. They all most likely originate from the same source.

2) The aromatic (tar) component in the 10 sediment samples is different from the aromatic component in NAPL from wells MW-15 and EW-1. It has been previously shown that the tar from well MW-7 is different from that found in wells MW-15 and EW-1 (refer to NAPL Report).

3) The quantity (percentage) of aliphatic compounds in the 10 sediment samples varies between 8.3 and 15 percent. This percentage of aliphatic fraction is similar to that found in sediment samples AS-2 and AS-4. These results are consistent with the fact that these samples all originate from the Bay Area.

CONCLUSIONS

Results of testing and analysis of the 10 sediment samples retrieved from the Chequamegon Bay in Ashland, Wisconsin are revealing. The tar contamination present in the sediment material from the Bay is highly similar in composition to the tar found in the NAPL material from other areas previously tested: Kreher Park (MW-7 sample, "12" Clay Pipe" sample and NAPL/Water sample) and the Chequamegon Bay (sediment samples AS-2 and AS-4.) Tars associated with the 10 sediment samples, as well as the NAPL sample MW-7, appear to be derived from the same source. This result is highly consistent with the fact that the Chequamegon Bay is directly adjacent to Kreher Park and was most likely affected by operations on this property.

Testing and analysis of the 10 sediment samples retrieved from the Bay also indicate that the tar is from a separate source from NAPL samples retrieved from wells MW-15 and EW-1. The tar component in the well samples from MW-15 and EW-1 is dissimilar to the tar component in 10 sediment samples.

Laboratory analysis of the aliphatic (oil fraction) and aromatic (tar) fractions of the ten sediment samples reveal a range of values in terms of percent fractions of each. The differences in percent fraction of oil versus tar in each sample may be due to effects of the environment on the sample, condition of the sample upon deposit in the sampling area, or other explanations not elucidated through this laboratory work. However, this range is consistent with the range between previously tested sediment samples AS-2 and AS-4. Most of the aliphatic fraction associated with the 10 sediment samples were mildly to moderately weathered.

Based on the results of analyses performed and in comparison with reference standards, GTI concludes that the tar component in the sediment samples from the Chequamegon Bay and the tar component in the NAPL material from well MW-7, the "12" Clay Pipe" sample, the NAPL/Water sample and the sediment samples AS-2 and AS-4 are highly similar and from the same source. The tar contained in the sediment samples is dissimilar to the tar component in the NAPL samples from wells on the NSP Ashland Property, MW-15 and EW-1. As concluded in the NAPL Report, the NAPL material from well MW-7 is consistent with wood treatment activities reportedly conducted at Kreher Park.

REFERENCES

1) *Supplemental Facility Site Investigation and Remedial Action Options Evaluation Report.* Dames & Moore. March 1, 1999.

2) *Sediment Investigation Report, Chequamegon Bay – Ashland, Wisconsin.* SEH, July, 1996.

APPENDIX A: Environmental Forensic Report

Environmental Forensic Report

Sediment Analysis: 10 Samples, Ashland, WI

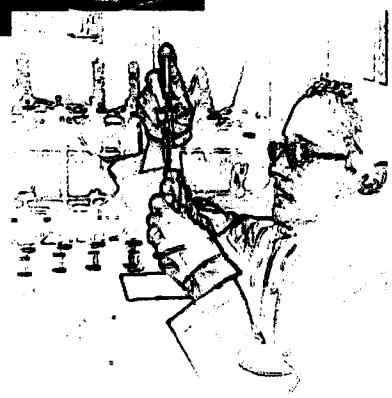
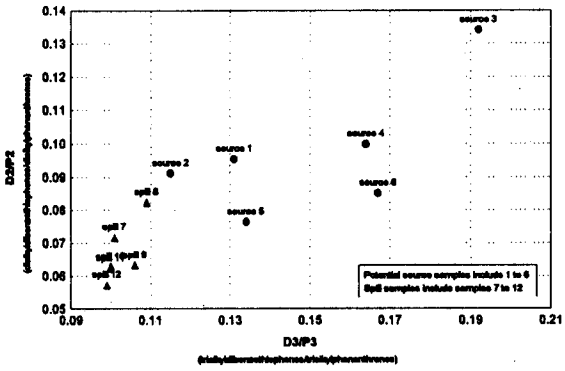


Figure 1. Double Ratio Plot



Report To:

Gas Technology Institute
1700 S. Mt. Prospect Road
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Report By:

META Environmental, Inc.
49 Clarendon Street
Watertown, MA 02472

May 11, 2001

Identifying and allocating sources of pollutants in complex environments.

META Environmental, Inc.
ENGINEERING & CHEMISTRY

Final Laboratory Report

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Certification

This certifies that this package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed herein. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Director and Quality Assurance Officer, as verified by the following signatures.

David R. Craig — Date: 5/11/01
Laboratory Director, META Environmental, Inc.

David M. Mauro — Date: 5/11/01
Quality Assurance Officer, META Environmental, Inc.

Sample Delivery Group Narrative

Project: Ashland MGP Site Sediments Forensic Analyses

Client: Gas Technology Institute
1700 S. Mt. Prospect Road
Des Plains, IL 60018

Report Contact: Dr. Diane Saber

Date of Receipt: 3/9/01

Sample Summary:

The samples received for this project are summarized in the attached sample login forms.

META Project Number: I05001-60

Chain of Custody

Samples were received in good condition. The internal temperatures of the shipment containers were as follows:

Samples received 3/9/2001 4.0°C

Internal chain of custody procedures were followed after sample receipt. Samples were stored in a locked refrigerator. A sample custody logbook contains the record of sample removal from the secure sample storage area to the sample preparation laboratory. The custody record for the sample extracts is present on the sample extraction logbook page.

The disposal of samples and extracts will be authorized 1 month after the release of this data report. Sample disposal will be documented.

Methods

Approximately 2 grams of each sediment sample was extracted with dichloromethane (DCM) (EPA 3570 Draft). Each extract was spiked with internal standard and analyzed by GC/FID (EPA 8100 mod.) and GC/MS/SIM (EPA 8260/8270 mod.).

Subsequently, a portion of each sediment extract was fractionated into aliphatic, aromatic, and polar fractions using silica gel column chromatography (EPA 3630 mod.). Each fraction was analyzed by GC/FID (EPA 8100 mod.).

Results

Sample results were presented in summary forms (CLP Form 1 equivalent) which follow this narrative.

Quality Control

Analyte Flags

The detection limits were determined as the sample equivalent of the lowest linear initial calibration standard. Analytes measured between 50% and 100% of the lowest standard were reported as "estimated" and flagged with the letter "J." No value was reported above the calibration range. Undetected analytes were flagged with the letter, "U." Analytes marked with a "B" were detected in the associated blank and should be reviewed for a possible positive bias. No deviations were thought significant enough to compromise the integrity of the reported values.

Holding Times

All samples were extracted within holding times. All samples and extracts were stored at 4°C ± 2°C prior to extraction and analysis. All extracts were analyzed within 40 days of sample preparation.

Surrogate Spikes

Extraction surrogates were added to each sample prior to extraction. Fractionation surrogates were added to all extracts prior to fractionation. Recoveries for all surrogates are reported with the sample results. All surrogate recoveries in the unfractionated extracts were within QC limits with the exception of fluorobenzene in samples SD 15-6 and SD 56-4. This low recovery may be indicative of volatile loss, but does not effect the interpretation of the results.

The low recoveries of fluorobenzene in the fractionated extracts are due to loss associated with solvent exchange and fractionation. High recoveries of fractionation surrogates can be attributed to calculation from a single point calibration.

The fractionation surrogate 1-chlorooctadecane was split between pentane and DCM fractions, possibly indicating some carryover of aliphatic compounds into the aromatic fraction However, the fractionation spike shows that this carryover was minor (~1%). These deviations were not thought significant enough to compromise the integrity of the reported values.

Blanks
No target analytes were present above the detection limit in the soil blank

Internal Standards
Internal standards were recovered within acceptable QC limits (50%-200%) relative to the continuing calibration standards.

The extracts had been spiked with internal standards for analysis prior to fractionation. Therefore the resulting fractions were not spiked with internal standards and were quantitated by the external standard method.

Interpretation

Sample SD 54-4
This sample primarily contained a pyrogenic substance. The pattern of PAHs, especially the fluoranthene/pyrene and dibenzofuran/fluorene ratios indicate that this sample is manufactured gas plant (MGP) tar. The low concentrations of MAHs relative to PAHs suggest that this sample has been subject to mild weathering.

Sample SD 9-4
This sample primarily also contained a pyrogenic substance from an MGP source. The low concentrations of MAHs and slightly depleted naphthalene relative to other PAHs suggest that this sample has been subject to mild to moderate weathering.

Sample SD 50-10
This sample also primarily contained a pyrogenic substance from an MGP source. The low concentrations of MAHs relative to PAHs suggest that this sample has also been subject to mild weathering.

Sample SD 51-8
This sample primarily also contained a pyrogenic substance from an MGP source. The low concentrations of MAHs and slightly depleted naphthalene relative to other PAHs suggest that this sample has also been subject to mild to moderate weathering.

Sample SD 37-4
This sample also contained a mildly weathered pyrogenic substance from an MGP source.

Sample SD 15-6
This sample primarily contained a pyrogenic substance from an MGP source, but at a lower concentration than the previous samples. The low concentrations of MAHs and naphthalenes relative to heavier PAHs suggest that this sample has been subject to mild weathering.

Sample SD 47-4
This sample also contained a mildly weathered pyrogenic substance from an MGP source.

Sample SD 56-4
This sample also contained a mildly weathered pyrogenic substance from an MGP source.

Sample SD 34-2
This sample contained pyrogenic substance from an MGP source. This is the least weathered sample of the group.

Sample SD 48-8
This sample also contained a mildly to moderately weathered pyrogenic substance from an MGP source.

Summary – Unfractionated Extracts
All the samples contained MGP tar. The alkyl-PAH patterns and compound ratios in Table 1 show no definitive differences that are not attributable to weathering. These similarities coupled with the FID fingerprints strongly suggest that these samples share a common source. The ranking for least to most weathered, based on the ratio of naphthalene to phenanthrene is as follows: SD 34-2, SD54-4, SD 56-4, SD 47-4, SD-15-6, SD 37-4, SD 48-8, SD 50-10, SD 51-8, and SD 9-4. However, the weathering range is fairly narrow, further supporting the conclusion that the samples are from the same source.

Fractionated Extracts
The patterns of hydrocarbons in the aliphatic fractions of the ten sediment samples were very similar, resembling a middle weight petroleum distillate. A distillate is indicated by a regular series of normal alkanes from about decane (C10) to triacontane (C30) and an unresolved complex mixture (UCM) centered around 14 minutes. The pattern appears to be the same as was observed in sediment samples AS-2 and AS-4 analyzed in an earlier batch.

Likewise, the patterns of hydrocarbons in the aromatic fractions of the ten sediment samples were very similar and are indicative of an MGP type tar. Also, the PAH patterns appear to be the same as was observed in sediment samples AS-2 and AS-4.

The polar compound fractions of the sediment samples varied somewhat from sample to sample. However, no sample contained tar acids, such as phenol and alkylated phenols, in notable quantities. Numerous other polar compounds were present in most samples. These compounds were unidentified, but could include extracts of natural materials and detritus, hydrocarbon degradation by-products, or other organic inputs to the sediments, such as sewage.

The percent aliphatic and aromatic contents for the ten sediment samples are shown in Table 1. The aliphatic content of the samples ranged from 8.3 to 15 percent of the total extractable hydrocarbons (TEH). The aromatic content ranged from 77 to 95 percent. However, the accuracy of the values for sample SD15-6 was probably low because of the low concentration of TEH in that sample. The aliphatic and aromatic contents of the ten sediment samples were similar to those of samples AS-2 and AS-4.

Table 1
Aliphatic and Aromatic Hydrocarbons in NAPL Samples

Sample	TEH (mg/kg)	Aliphatic (mg/kg)	Aromatic (mg/kg)	% Aliphatic	% Aromatic
SD54-4	5,480	673	4,240	12	77
SD9-4	4,020	517	3,110	13	77
SD50-10	10,100	1,110	8,930	11	88
SD51-8	1,490	179	1,210	12	81
SD37-4	1,620	192	1,460	12	90
SD15-6	682	100	648	15	95
SD47-4	14,400	1,190	11,500	8.3	80
SD56-4	10,500	1,370	7,990	13	76
SD34-2	2,470	219	2,030	8.9	82
SD48-8	1,520	161	1,290	11	85

TEH – total extractable hydrocarbons

References

1 "Chemical Source Attribution at Former MGP Sites," EPRI Report 1000728, December 2000.

Table 1
Source and Weathering Ratios

Sample	Fl/Py	D/F	C17/Pris	C18/Phy	Pris/Phy	C3D/C3PA	C2D/C2PA	N/P
SD 54-4	0.73	0.21	2.21	2.03	1.34	0.64	0.38	2.97
SD 9-4	0.76	0.26	2.18	1.87	1.16	0.67	0.32	1.23
SD 50-10	0.77	0.33	2.65	2.44	1.20	0.72	0.35	1.59
SD 51-8	0.75	0.27	0.46	0.21	1.16	0.77	0.33	1.44
SD 37-4	0.77	0.25	2.03	1.69	1.25	0.78	0.42	1.73
SD 15-6	0.77	0.24	2.46	2.17	1.33	0.60	0.41	1.83
SD 47-4	0.85	0.37	2.38	2.04	1.27	0.83	0.40	2.30
SD 56-4	0.80	0.39	1.26	1.06	1.27	0.80	0.39	2.40
SD 34-2	0.71	0.13	1.35	1.02	1.33	0.64	0.27	3.22
SD 48-8	0.75	0.33	2.45	2.10	1.24	0.53	0.35	1.69

Ratios:

Fl/Py	fluoranthene/pyrene
D/F	dibenzofuran/fluorene
C17/Pris	septadecane/pristane
C18/Phy	octadecane/phytane
Pris/Phy	pristane/phytane
C3D/C3PA	trialkyldibenzothiophenes/trialkylphenanthrenes/anthracenes
C2D/C2PA	dialkyldibenzothiophenes/dialkylphenanthrenes/anthracenes
N/P	Naphthalene/Phenanthrene