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B.E.S.T.® BENCH-SCALE TREATABILITY
FINAL REPORT

THUNDER BAY HARBOUR SITE

Lake Superior, Ontario

for

WASTEWATER TECHNOLOGY CENTRE

WTC RFP No. 006

November 1994

Prepared by
RESOURCES CONSERVATION COMPANY
3006 Northup Way
Bellevue, WA 98004-1407

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istered in the U.S. Patent Office

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IONICS

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A Division of Ionics, Incorporated

14 November 1994

Mr. Wayne Randle
Wastewater Technology Centre
867 Lakeshore Road
P.O. Box 5068
Burlington, Ontario Canada L7R 4L7

Subject: **B.E.S.T.® Solvent Extraction Process**
Treatability Study Final Report
Thunder Bay Harbour
WTC RFP # 006

Dear Mr. Randle:

Please find enclosed six copies of the final report for the B.E.S.T.® Bench-Scale Treatability Study on the Thunder Bay Harbour sediment sample.

Two bench tests with the PAH contaminated Thunder Bay sediment were conducted. The first bench test was a trial test to assess performance and allow refinements, if required, before conducting the second bench test. No difficulties were encountered during either test. The mass of contaminated material was reduced almost 300-fold via the B.E.S.T. process.

The key contaminants in this sediment are polynuclear aromatic hydrocarbons (PAHs). The total PAH residual in the feed sediment and the treated solids from the second bench test was 810 and 3.7 mg/kg, respectively, on a dry basis and analyzed per WTC analytical methods. The PAH residual in the treated solids is less than the current Ontario sediment quality guideline for both individual and total PAHs.

Please call me at (206) 828-2400 if you have any questions.

Sincerely,

James C. Nowak

James C. Nowak
Laboratory Manager

JCN/ss

Enclosures

cc: Lanny Weimer, RCC

B.E.S.T.® BENCH-SCALE TREATABILITY
FINAL REPORT

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B.E.S.T.® BENCH-SCALE TREATABILITY TEST
FINAL REPORT

Thunder Bay Harbour Site

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B.E.S.T.® BENCH-SCALE TREATABILITY TEST
FINAL REPORT

WTC
Thunder Bay Harbour Site

I. INTRODUCTION

SUMMARY

Bench-scale treatability tests of the B.E.S.T. solvent extraction process were conducted for the Wastewater Technology Centre under the Contaminated Sediment Treatment Technology Program (COSTTEP) sponsored by Environment Canada, Great Lakes Environment Office. See Attachment 1 for background information on COSTTEP.

Two bench-scale tests of the B.E.S.T. process were conducted on a polynuclear aromatic hydrocarbon (PAH) contaminated sediment sample from the Thunder Bay Harbour site. The first bench test was conducted and the results assessed before conducting the second bench test. The PAH residuals in the treated solids from the first bench test were well below the current, Ontario sediment quality lowest effect level guidelines. (It is currently not known if these guidelines will apply to the remediation of the Thunder Bay site, however, they are the only guidelines available.) In addition, no difficulties were encountered in processing the sample during the first test. Therefore, the second test was conducted in virtually identical fashion to the first. To expedite the bench testing, the PAHs in samples from the first bench test were analyzed per the US EPA method. The WTC PAH analytical method was used for the second bench test. A summary of the bench-scale treatability test results follows:

BENCH-SCALE TREATABILITY TEST RESULTS

	Feed Content (dry basis)	Treated Solids* Residual (dry basis)
Total PAHs, mg/kg		
First Bench Test (US EPA analytical method)	790	1.5**
Second Bench Test (WTC analytical method)	810	3.7

* ninth extraction solids
** 3.3 mg/kg via WTC analytical method for PAHs above detection limit

As can be seen from the data above, the WTC analytical method produced virtually identical PAH results as the US EPA analytical method on the feed. However, the WTC analytical method yielded higher PAH results on the treated solids by a factor of two to three. The PAH removal efficiency of the second bench test after nine extractions was 99.5% and the Ontario sediment quality guideline for total PAHs (4 mg/kg) as well as the guidelines for individual PAHs were achieved using the WTC method results.

RESOURCES CONSERVATION COMPANY'S (RCC) BACKGROUND

Resources Conservation Company (RCC), established in 1971, is a multi-discipline engineering services company that specializes in the design of hazardous waste and wastewater treatment systems. RCC's main office is located in Bellevue, Washington. RCC's treatability laboratory is located near the main office.

THE B.E.S.T. SOLVENT EXTRACTION PROCESS

The B.E.S.T. process is a patented solvent extraction technology using triethylamine as the solvent. Triethylamine is an aliphatic amine that is produced by reacting ethyl alcohol and ammonia.

Triethylamine is an excellent solvent for treating hazardous wastes because it exhibits several characteristics that enhance its use in the solvent extraction system. These characteristics include:

- The ability to treat materials with a wide variety of water content, including high water content sediments, such as that from Thunder Bay, without loss of process performance, i.e., contaminant removal such as PAHs, or loss of throughput. Triethylamine is completely miscible with water below 40 degrees F and is an excellent dewatering agent. It is principally for these reasons that the B.E.S.T. process has been rated number #1 for treating sediments by Research Triangle Institute, North Carolina, USA funded by the US EPA, see Attachment 2.

- The ability to effectively remediate materials contaminated with a wide variety of organic compounds, such as PAHs, PCBs, pesticides, furans and dioxins.

- A high vapor pressure; therefore, the solvent can be easily recovered from the extract solution (oil, water, and solvent) via steam stripping.

- Formation of a low boiling temperature azeotrope with water, allowing the solvent to be recovered from the oil to very low residual levels (typically less than 100 ppm).

- A low heat of vaporization (1/7 of water), allowing solvent to be recovered from the treated solids with very low energy input.

- Triethylamine is alkaline, therefore, some heavy metals are converted to the hydroxide form, precipitate and exit the system with the treated solids. The organic removal efficiency of the process is not negatively affected by the presence of metals. Total metal concentrations in the treated solids, however, generally remain the same as those in the feed, on a dry weight basis.

- Triethylamine readily biodegrades. Data available in EPA document EPA Data ORD USEPA Washington, D.C. 20460, Feb. 1983 (reprint) Manual, Volume 1 600/2-82001a, shows that a level of 200 ppm triethylamine in water was degraded completely within 11 hours by the common soil bacteria *aerobacter*.

A block diagram of the B.E.S.T. process is presented in Figure 1. The first extraction of the contaminated feed is conducted at low temperatures (about 40 degrees F). At this temperature, triethylamine is soluble with water. Therefore, the extract solution contains most of the water in the feed sample. The water is recovered with the solvent by distillation of the extract solutions. The solvent forms a low boiling temperature azeotrope during distillation. The solvent/water azeotrope is condensed and the water is then separated from the solvent by heating the condensed solution above the miscibility point (about 130 degrees F) and decanting the water from the solvent. Residual solvent is then removed from the water via steam stripping. This method produces a very clean water product. A second method which requires less energy but yields a poorer quality water product is an option for water recovery in some cases. The second method is accomplished by heating the extract solution above the miscibility point prior to distillation and decanting the water from the solvent/organic extract phase.

Triethylamine is removed from the treated solids by indirect steam heating. A small amount of steam may be added directly to the dryer vessel to provide the water required to form the low boiling temperature azeotrope. Residual solvent biodegrades readily, sometimes allowing the treated solids to be used as backfill at the site. However, the treated solids will be sterile as they exit the B.E.S.T. process. Therefore, for triethylamine biodegradation to occur, the treated solids would have to be inoculated with soil bacteria by mixing in untreated, clean sediment or soil.

The B.E.S.T. process operates near ambient pressure and temperature and at an alkaline pH. Temperatures of the liquid streams within the unit vary from about 40 to 170 degrees F, and elevated pressures are not required. This gives the B.E.S.T. process the advantage that it can use standard off-the-shelf processing equipment.

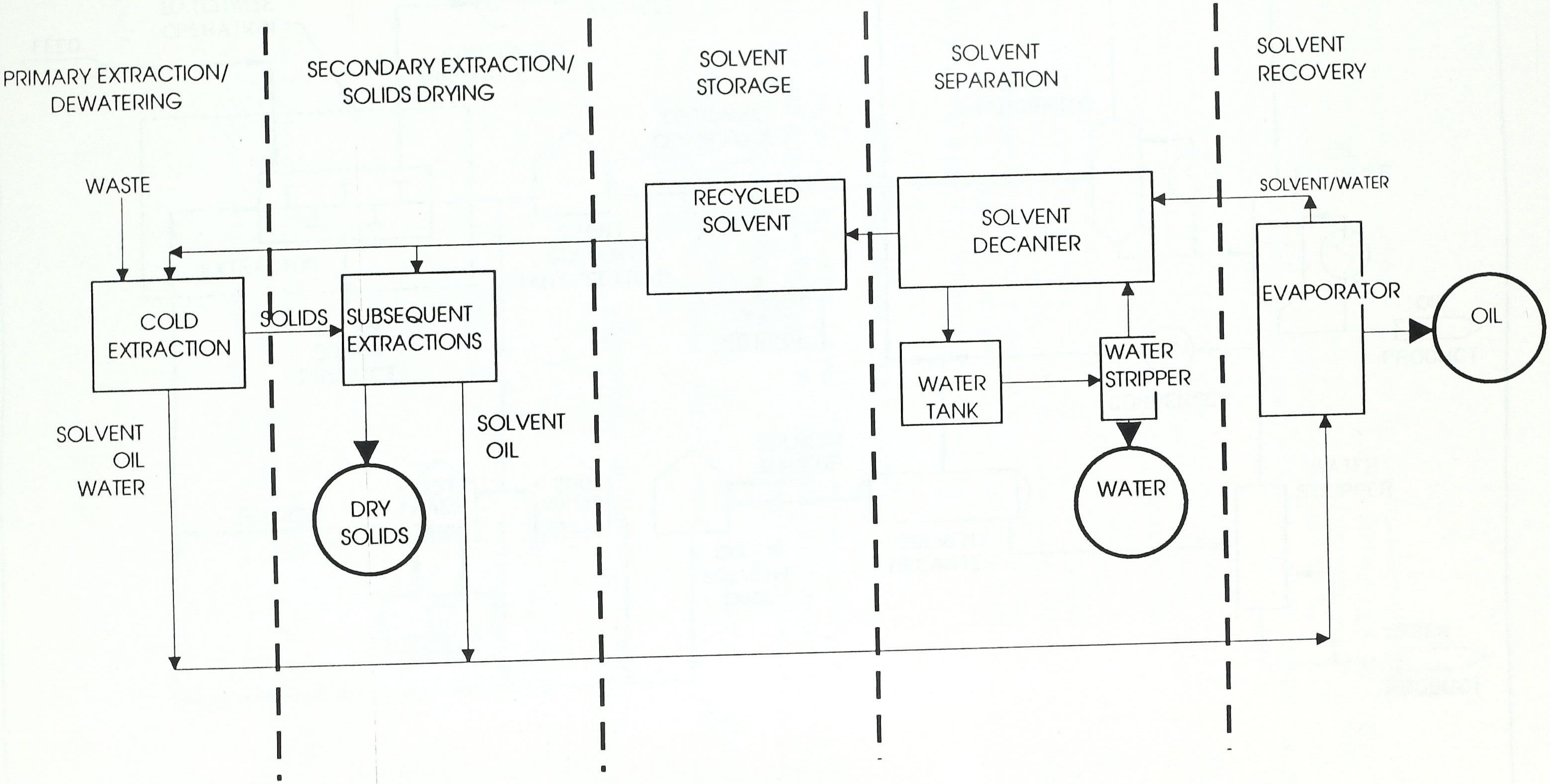
PILOT AND FULL-SCALE EQUIPMENT DESCRIPTION

RCC proposes using a B.E.S.T. Model 215 Solvent Extraction Unit to treat the contaminated, Thunder Bay sediment. A flow schematic representing how the Model 215 Unit operates is presented in Figure 2.

The B.E.S.T. Model 215 uses two extractor/dryer vessels to extract and dry the contaminated material. The extractor/dryers are horizontal, steam-jacketed vessels that allow for solvent contacting, mixing, solids/solvent separation, solids drying, and solids conditioning in one vessel. The extractor/dryer vessels are an off-the-shelf assembly that has a long history of reliable performance in a wide range of process industry applications.

Figure 1

B.E.S.T. SOLVENT EXTRACTION PROCESS



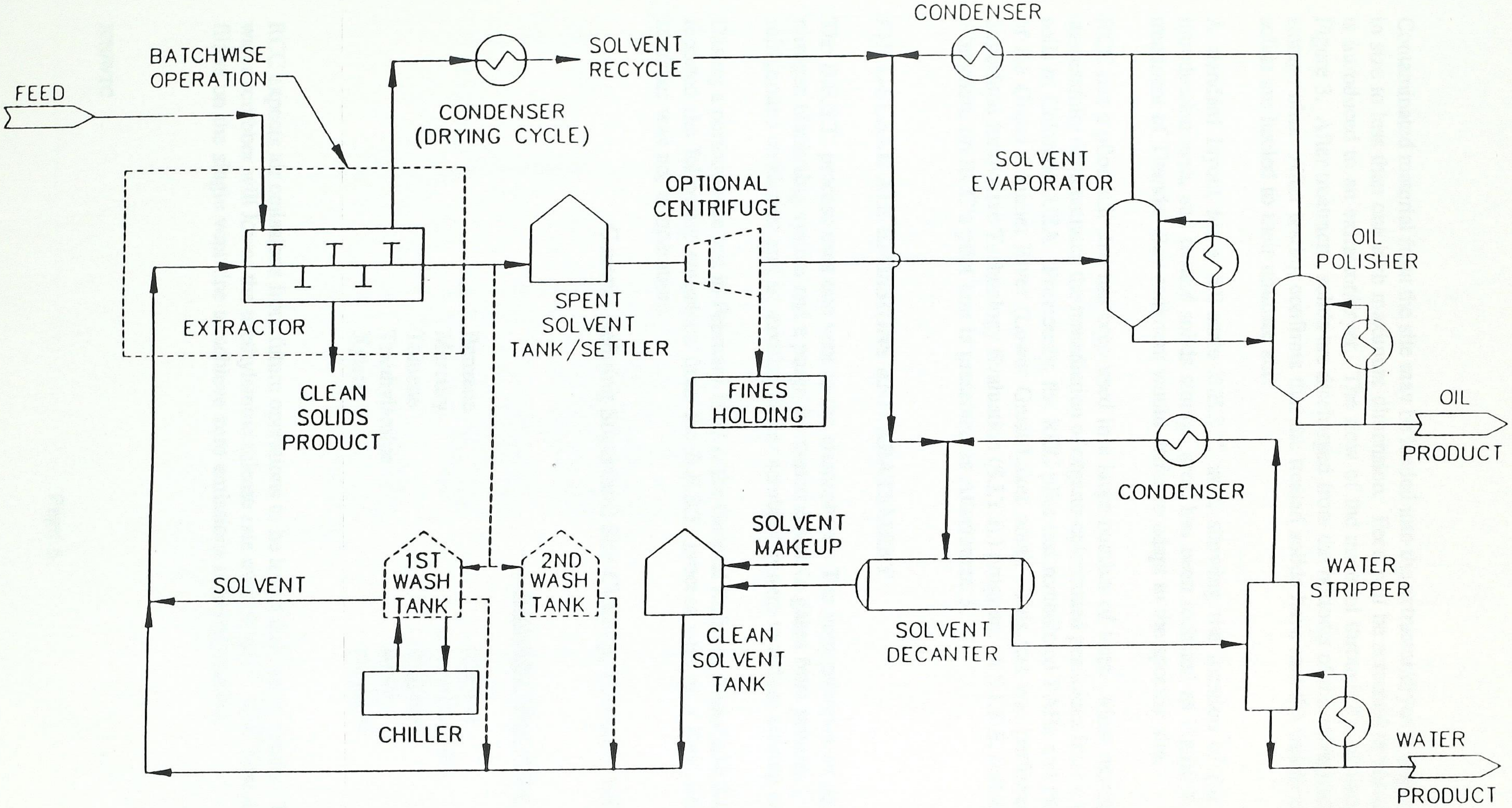


FIGURE 2

PROPRIETARY

This drawing is the property of Resources Conservation Co., and the information contained herein is proprietary information which is not to be disclosed to anyone without the prior written consent of said company. This drawing is to be used exclusively for the purposes expressly authorized by Resources Conservation Co through its officers and qualified representatives, and for no other purpose. Neither this drawing, nor any portion thereof, shall be reproduced without the prior written consent of said company, and any such authorized reproduction shall bear this notice.

RCC Resources Conservation Company

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CHECKED
PROJ ENGR
APPROVED

PROCESS FLOW SCHEMATIC

B.E.S.T.
FULL-SCALE UNIT

DWG NO. B-221
SHEET NO 1 OF 1
REV

Contaminated material from the site may be loaded into the extractor/dryer in hoppers. Material is limited in size to less than one inch maximum dimension. Feed will be screened to ensure no oversize material is introduced to an extractor/dryer. The flow of the material through the extractor/dryer is depicted in Figure 3. After treatment, solids are discharged from the bottoms of the extractor/dryers and collected in storage bins. After testing confirms that the treated solids have met the treatment standard, the treated solids are hauled to their ultimate site.

A standard layout for a full-scale B.E.S.T. unit, showing the location of the processing unit, feed introduction area, and treated solids storage area, has been included as Figure 4. The exact layout for treatment of Thunder Bay sediment would differ to adapt to the specific site.

RCC has a pilot unit that has been used in a large number of tests. Most recently, the RCC pilot unit successfully demonstrated the remediation of organo-chlorinated pesticides from a variety of contaminated soils in Colorado, USA. Previously, the RCC pilot test remediated PAHs and PCBs from sediment out of the Grand Calumet River (Lower Great Lakes area). This test was performed under the US EPA Superfund Innovative Technology Evaluation (S.I.T.E.) program. A S.I.T.E. bulletin on this pilot test and a brochure on RCC's pilot unit is presented as Attachment 3.

FULL-SCALE AIR EMISSIONS AND ABATEMENT

The B.E.S.T. process uses one vent to the atmosphere. The vent provides pressure equalization for the nitrogen blanketing system and a purge for noncondensible gases from process condensers. RCC uses a refrigerated condenser and an auxiliary water scrubber system to reduce solvent emissions from the vent.

During a performance test in February 1987 at the General Refining Superfund Site cleanup, a third party reported the following emissions from the B.E.S.T. process vent at a time when the auxiliary water scrubber was not in operation:

General Refining Superfund Site Cleanup, February 1987

	Emission Rate, lb/hr
Benzene	0.00114
Mercury	< 0.000000043
Toluene	0.000614
Triethylamine	0.0954
Xylene	0.000884

RCC expects air emissions from future operations to be lower than these results. The use of the auxiliary water scrubber will lower the triethylamine release rate even further. RCC now utilizes activated carbon filters on the single vent line to achieve zero emissions of triethylamine.

FIGURE 4

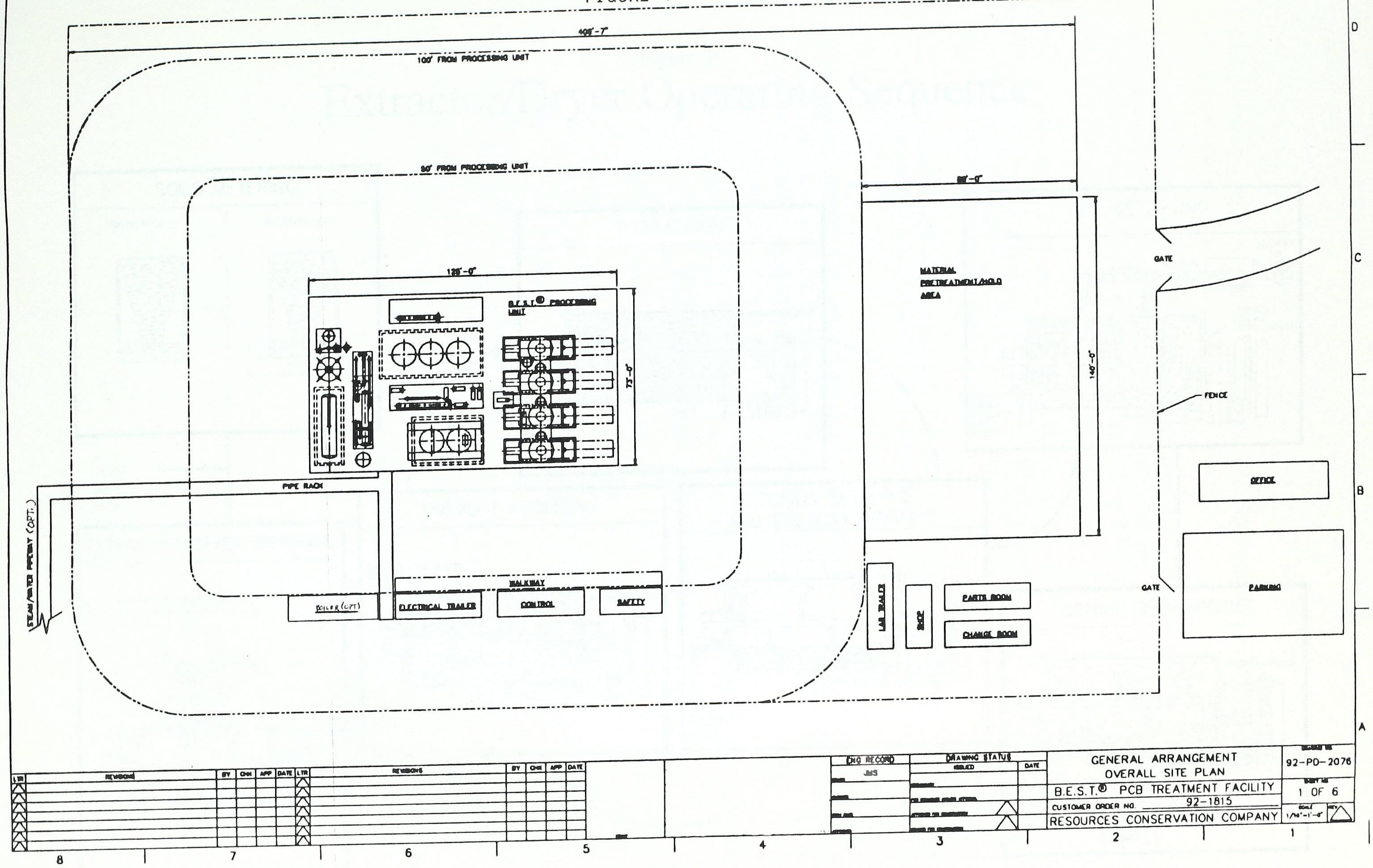
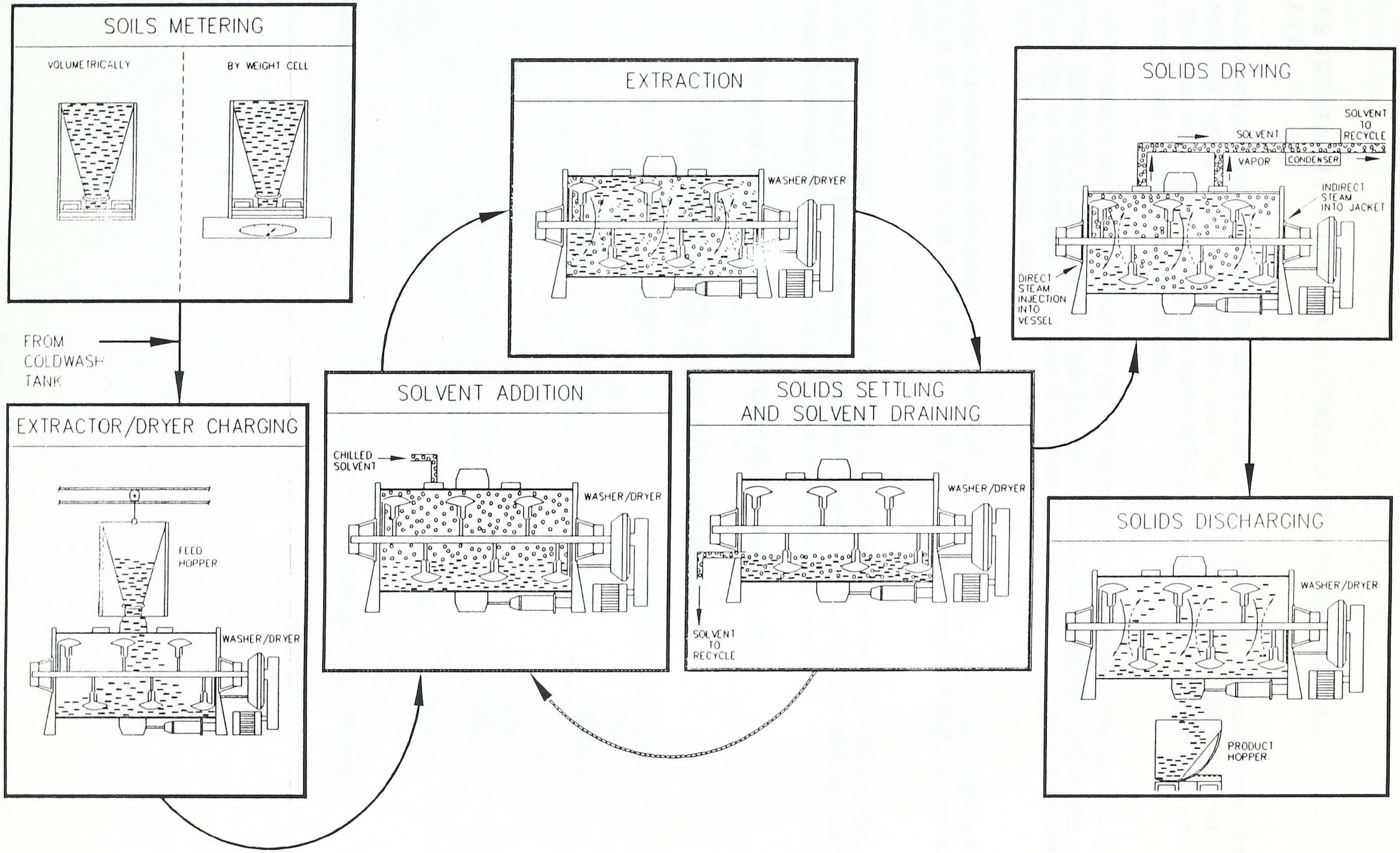

405'-7"
100' FROM PROCESSING UNIT
90' FROM PROCESSING UNIT
88'-0"
128'-0"
73'-0"
140'-0"
B.E.S.T.® PROCESSING UNIT
MATERIAL PRETREATMENT/HOLD AREA
GATE
FENCE
GATE
OFFICE
PARKING
PIPE RACK
STEAM/WATER PIPEWAY (OPT.)
WALKWAY
BOILER (OPT)
ELECTRICAL TRAILER
CONTROL
SAFETY
LAB TRAILER
SHOP
PARTS ROOM
CHANGE ROOM
A
B
C
D
1
2
3
4
5
6
7
8
LTR
REVISIONS
BY
CHK
APP
DATE
DWG RECORD
JMS
DRAWING STATUS
ISSUED
DATE
GENERAL ARRANGEMENT
OVERALL SITE PLAN
B.E.S.T.® PCB TREATMENT FACILITY
CUSTOMER ORDER NO. 92-1815
RESOURCES CONSERVATION COMPANY
92-PD-2076
1 OF 6
SCALE
1/16"=1'-0"
REV

Figure 3

Extractor/Dryer Operating Sequence



BENCH-SCALE TREATABILITY TEST DATA CORRELATION TO FULL-SCALE PERFORMANCE

In order to evaluate each potential application for the B.E.S.T. process, RCC has developed a low cost bench-scale treatability test protocol that provides data that closely simulates full-scale system performance. The bench-scale treatability test data allows RCC to evaluate the feasibility of the process on a particular sample and to estimate treatment costs.

The reliability of the bench-scale treatability tests to predict full-scale performance has been verified by the USEPA report <u>Evaluation of the B.E.S.T. Solvent Extraction Sludge Treatment Technology - Twenty-Four Hour Test</u>, by Enviresponse, Inc., under EPA Contract 68-03-3255. A quotation from this report evaluating the B.E.S.T. process states:

> "Resources Conservation Company has conducted many laboratory tests and developed correlations to which data from full-scale operations, such as the General Refining site, can be compared."

A comparison of bench-scale and full-scale operating performance data at the General Refining, Inc., Superfund site, as collected by an EPA contractor, is presented below. This data demonstrates the close correlation between bench-scale treatability test data and full-scale operating data.

General Refining, Inc., Superfund Site, February 1987

PERFORMANCE DATA COMPARISON

	FEED		TREATED SOLIDS	
	Bench Scale	Full Scale	Bench Scale	Full Scale
Oil, %	36.	27.	5.7	0.81
Water, %	56.	66.	< 1.0	< 0.5
Solids, %	8.	7.	> 94.	> 98.
PCBs, mg/kg (dry basis)	14.	13.5	0.02	< 0.13
PCB Extraction Efficiency	--	--	99.9 %	> 99.0 %

JCN/WTC

Bench-scale treatability testing provides valuable information about the use of the B.E.S.T. process at full-scale including:

- The PAH removal efficiency from the sample.
- Solids separation requirements for full-scale operation.
- The separation efficiency of water from the water/solvent/oil solution.
- General information on the partitioning of metals and organic compounds in the oil, water, and solids products.
- Full-scale operating parameters to develop treatment costs.

II. BENCH-SCALE TREATABILITY TESTING

OBJECTIVES

Resources Conservation Company (RCC) has conducted a bench-scale treatability test on a PAH contaminated sediment sample from the Thunder Bay Harbour site. The primary objective of this test was to determine the feasibility and cost effectiveness of the B.E.S.T. solvent extraction process for treating the contaminated sediment, specifically:

- Determine whether the B.E.S.T solvent extraction process can remediate the contaminated sediment from the Thunder Bay site.
- Determine capability of the process to separate the feed material into distinct phases (oil, water, solids).
- Conduct sufficient sampling and analyses to allow calculation of mass balances for oil, water, solids, and PAHs.
- Determine the PAH residual in the treated solids as a function of the number of extraction stages to allow determination of the number of extraction stages required. The main variable of the B.E.S.T. process is the number of extraction stages to achieve target goals for residual contamination in the treated solids.
- Record observations and data to predict performance of the B.E.S.T. process at full-scale.

BENCH-SCALE TREATABILITY TEST DOCUMENTATION AND WTC AUDIT

The documentation of the testing can be separated into three distinct categories. The following summarizes the procedures used for each step of the treatability process:

1. When the sample was received in the laboratory, the shipment was checked for correctness of accompanying paperwork, including Chain of Custody. The information was recorded both in a hardbound sample logbook and on a computer system that has been specifically designed by RCC for use in tracking samples. The sample was issued a discrete laboratory sample number and a test request form was completed. The sample was kept in a refrigerator under controlled and documented temperature prior to any lab analysis or the treatability study. Information received with the sample is kept as part of the project file.

2. The bench-scale treatability testing was conducted in accordance with a test plan, and all records and observations taken during the simulation of the process were recorded in laboratory notebooks. The laboratory notebooks are the property of RCC, and each analyst and engineer has been issued a notebook. The notebooks are retained by RCC as permanent record of raw data collection.

3. Samples that were collected during the bench-scale test, including samples internal to the process, were submitted to the RCC analytical chemistry laboratory for further analysis. Each sample collected was issued a discrete laboratory number. An analysis request form was completed. A file is maintained to store the accumulated test results from completion of the analytical testing.

WTC conducted an audit of RCC's laboratory during the bench-scale testing. The WTC audit report is presented in Attachment 7.

SAMPLE PREPARATION

A 5-gallon bucket of contaminated sediment sample from the Thunder Bay Harbour site, Lake Superior, Ontario arrived at RCC's laboratory in February 1994. The sample was a black-colored sediment with a pudding consistency. The sample was thoroughly blended to achieve homogeneity prior to withdrawal of any sample portions, in particular, to blend back into the sample water that which had separated during storage/shipment.

Bench-scale testing requires material (debris) greater than 1/4 inch be removed. Full-scale processing requires that the feeds be screened to remove only debris greater than 1 inch in diameter. There was no debris of any size observed in the sample.

FEED COMPOSITIONAL ANALYSIS

The sediment feed was analyzed per the following methods:

- The total petroleum hydrocarbons (TPH) and oil & grease content was determined by IR (US EPA SW-846 Methods 418.1 and 413.2, respectively). The oil & grease content was also determined by GC, flame ionization detector (FID) quantitated as Bunker C oil, US EPA modified Method 8015. In addition, the oil & grease content was determined gravimetrically per Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 503D, with two exceptions: the extraction time was extended from 4 to 16 hours and methylene chloride ($MeCl_2$) was substituted for Freon based on RCC experience that $MeCl_2$ is a better solvent for oils and greases. Freon was also used with a 16-hour extraction time.

- The water content was determined by weight loss at 105 degrees C.
- The particulate solids content was determined by difference.
- Loss-on-ignition was determined by muffling a sample at 550 degrees C that had been pre-dried at 105 degrees C.
- The PAH concentrations were determined by two methods The first method was per US EPA Publication SW846 Test Methods for Evaluating Solid Waste, Method 8270. (This analysis was performed by an RCC subcontract laboratory, Sound Analytical Laboratories, Inc.) The second method was performed by RCC per the WTC method, see Attachment 4.

The results of feed characterization analyses are presented in the following table.

Feed Compositional Analysis
(as-received basis unless noted)

Analyte	Results
TPH, Freon IR, mg/kg	1,100
Oil & Grease, Freon IR, mg/kg	1,300
Oil & Grease, $MeCl_2$, mg/kg	3,500
Oil & Grease, GC/FID, mg/kg	1,800
TOC, % by weight	4.6
Loss-on-ignition, % by weight, dry basis	8
Solids, % by weight	44
Water, % by weight	56
PAHs, total, mg/kg, dry basis	
US EPA Analytical Method	790
WTC Analytical Method	810

US EPA analytical method yielded virtually identical PAH results as the WTC method. The predominant PAHs present were naphthalene and phenanthrene. The total PAH concentrations are the sum of 16 PAH compounds. The individual PAH concentrations are given in Section SAMPLE EXTRACTION TREATED SOLIDS below. The RCC subcontractor lab report for PAHs, (US EPA Analytical Method) is given in Attachment 5. As can also be seen from the above, the oil & grease concentration in the feed is very low.

TRIETHYLAMINE COMPATIBILITY TEST

Triethylamine, $(C_2H_5)_3$ N, is a compound with a unique chemical structure. The geometry of the structure is tetrahedral with the nitrogen atom at the center. The four points of the tetrahedron are occupied by three ethyl functional groups and one electron cloud. This structure gives triethylamine dual polarity characteristics. The ethyl groups are essentially nonpolar; the electron cloud is polar. Although triethylamine is a very stable solvent, there is a very remote possibility that the electron pair can react with certain types of materials. In order to determine if this will occur with a sample, a compatibility test is performed. This involves mixing the sample with triethylamine and making observations as to the heat of solution and any other visual signs of reaction.

When the feed sample was mixed with cold triethylamine, visible sign of adverse reaction was not observed, and the heat of solution, as determined by measuring the temperature rise, was in a normal range. The triethylamine was observed to darken upon mixing, indicating that extraction of the organic compounds was occurring.

SAMPLE EXTRACTION/TREATED SOLIDS

First Bench Test

For the first extraction stage, a portion of sediment along with prechilled triethylamine was added to a resin kettle immersed in a temperature controlled water bath at 1 degree C. Mixing was performed by an air-driven propeller mixer. As expected, the triethylamine solvent became colored indicating extraction of organic compounds was occurring. The mixing was stopped and settling characteristics, such as the settling rate, were observed and recorded. The liquid extract in the mixture was decanted off. This triethylamine/water/oil extract was free of suspended solids and therefore centrifuging was not required. The triethylamine/water/oil mixture was temporarily set aside for later processing.

A total of nine extraction stages was performed on the sample. Improved (faster) settling characteristics were observed during these extractions as expected since the water native in the sediment was no longer present. (The density of triethylamine, approximately 0.7 g/cc is low and, therefore, particulate solids usually settle well in it in the absence of water that has a density of 1 g/cc.) A sample of the particulate solids after the third and sixth extraction stage was taken for later analysis. The quantity of triethylamine used was proportionately scaled-down for the next extraction stage after solids were removed for analysis to account for the solids removed, i.e., the triethylamine to solids ratio was kept constant.

The bulk of the triethylamine collected with the interstage solids samples was then removed by evaporation. In order to efficiently recover the triethylamine from the solids phase fraction product, the pH of the final, treated solids should be approximately 10-11. (Triethylamine can be ionized at low pH to triethylammonium salts that cannot be removed from the treated solids.) The as-is pH of the dried, treated solids was 7.0.

Therefore, these solids were treated with deionized water along with 0.07 mls 6N caustic soda (NaOH) per gram of treated solids and dried. The alkaline water when evaporated removes virtually all of the remaining triethylamine as an azeotrope. (RCC holds patents for this procedure.) The final pH of the treated solids was in the range desired, i.e., 10.9.

Second Bench Test

The procedure of the second bench test was virtually identical since low PAH residuals were achieved and no difficulties were encountered. The only difference during the second test was that a sample of the third extraction solids was not collected since it was determined from the first bench test the total PAH residual in this sample was not close to the Ontario guidelines for sediment quality. (It is not currently known if these guidelines will apply to the Thunder Bay site, however, they are the only guidelines available.) An audit by WTC was conducted during the second bench test. Treated solids samples were analyzed by RCC per the following methods:

- For the first bench-test, the polynuclear aromatic hydrocarbon concentration was determined per US EPA SW846 Test Methods for Evaluating Solid Waste, Method 8270, by an RCC subcontract lab. For the second bench-test, the residual polynuclear aromatic hydrocarbon concentrations were determined per the WTC method, see Attachment 4.

- The total petroleum hydrocarbons (TPH) and oil & grease content was determined by IR (US EPA SW-846 Methods 418.1 and 413.2, respectively). The oil & grease content was also determined by GC, flame ionization detector (FID) quantitated as Bunker C oil, US EPA modified Method 8015. In addition, the oil & grease content was determined gravimetrically per Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 503D, with two exceptions: the extraction time was extended from 4 to 16 hours and methylene chloride ($MeCl_2$) was substituted for Freon based on RCC experience that $MeCl_2$ is a better solvent for oils and greases. Freon was also used with a 16-hour extraction time.

- Loss-on-ignition was determined by muffling a sample at 550 degrees C that had been pre-dried at 105 degrees C.

- The triethylamine residual was determined by packed column gas chromatography with a flame ionization detector.

- Bulk density was determined by filling a 100-cc graduate, recording the net weight, recording the volume after lightly tamping the cylinder for two minutes, and then compacting the contents as tightly as possible.

Analytical results from the feed and treated solids are presented in the following tables:

Solids Analysis
(dry basis)

Extraction Stage	Total PAHs, mg/kg First Bench Test (EPA Analytical Method)	Second Bench Test (WTC Analytical Method)
Feed	790	810
Third	20	--
Sixth	3.0	4.9**
Ninth	1.5*	3.7

* 3.3 mg/kg WTC analytical method, only for PAHs above detection limit
** total for PAHs above detection limit only

Second Bench Test
Ninth Extraction Stage
(dry basis)

Analyte	Results
TPH, Freon IR, mg/kg	20
Oil & Grease, Freon IR, mg/kg	19
Oil & Grease, GC/FID, mg/kg	43
Oil & Grease, $MeCl_2$, %	< 0.1
Oil & Grease, Freon, %	< 0.1
Triethylamine, mg/kg	100
Loss-on-ignition, %	8.3
Bulk Density, g/cc	
not tamped	0.78
lightly tamped	0.93
heavily tamped	1.17
PAHs, mg/kg, total, WTC Analytical Method	3.7

As can be seen from the above, the US EPA PAH analytical method yields the same result on the feed sediment, but only approximately 50% of the value on the treated solids. The first bench test treated solids were analyzed with both methods confirming this disparity in the methods. Attachment 6 gives the side-by-side WTC versus US EPA method results for the first bench test treated solids.

The PAH concentration in the treated solids could likely be lowered by further extractions if required. However, the more required number of extraction stages, the more costly full-scale processing will be. The subcontractor lab report for PAHs (US EPA Analytical Method) for the first bench test is presented in Attachment 5. The individual PAH compound analysis results for the first and second bench tests are summarized on the next two pages. The detection limits of the ninth extraction solids are lower than those of the sixth solids for the second treatability study. This is because RCC reran the heavy PAHs in ninth extraction solids for the sole purpose of lowering their detection limits. This was to allow a definitive assessment if the Ontario guidelines for sediment quality were all achieved.

THUNDER BAY
First Treatability Study PAH Results
(US EPA SW846; GC/MS, Method 8270)

All results in mg/kg, dry basis

	Contaminated Sediment	3rd Extraction Solids	6th Extraction Solids	9th Extraction Solids	Sediment Quality Guidelines [6]
Naphthalene	180	4.8	1.7	1.1	--
Acenaphthylene	ND [1]	ND [2]	ND [3]	0.008 [5]	--
Acenaphthene	48	0.86	0.13	0.017 [5]	--
Fluorene	41	0.86	0.13	0.004 [5]	0.19
Phenanthrene	180	4.5	0.54	0.19	0.56
Anthracene	20	0.68	0.13	0.038	0.22
Fluoranthene	109	2.8	0.15	0.041	0.75
Pyrene	98	1.9	0.79	0.025 [5]	0.49
Benzo(a)anthracene	32	0.68	ND [3]	0.008 [5]	0.32
Chrysene	ND [1]	0.51	0.32 [5]	0.009 [5]	0.34
Benzo(b)fluoranthene	50	0.91	0.060	0.018 [5]	--
Benzo(k)fluoranthene	ND [1]	0.27	0.018 [5]	0.006 [5]	0.24
Benzo(a)pyrene	23	0.53	0.034 [5]	0.008 [5]	0.37
Indeno(1,2,3-cd)pyrene	ND [1]	0.30	0.025 [5]	0.008 [5]	0.20
Dibenzo(a,h)anthracene	ND [1]	0.043	ND [3]	ND [4]	0.06
Benzo(g,h,i)perylene	10	0.23	0.017	0.005 [5]	0.17
TOTALS	790	19.9	3.0	1.5	4.0

---

[1] Practical Quantitation Limit (PQL) is 4.3. PQL is the lowest standard in the calibration range that corresponds to > 2x the MDL.

[2] PQL is 0.062.

[3] PQL is 0.035.

[4] PQL is 0.033.

[5] Estimated.

[6] Ontario sediment quality guidelines, lowest effect level.

THUNDER BAY
Second Treatability Study PAH Results
WTC Analytical Method
All results in mg/kg, dry basis

	Contaminated Sediment	6th Extraction Solids	9th Extraction Solids	Sediment Quality Guidelines [1]
Naphthalene	85	2.0	2.0	--
Acenaphthylene	2	0.029 J [2]	0.024	--
Acenaphthene	53	0.16	0.12	--
Fluorene	48	0.052 J [2]	0.050	0.19
Phenanthrene	185	0.8	0.54	0.56
Anthracene	24	0.33	0.18	0.22
Fluoranthene	118	0.40	0.18	0.75
Pyrene	91	0.24	0.12	0.49
Benzo(a)anthracene	23	0.087 J [2]	0.041	0.32
Chrysene	37	0.096 J [2]	0.15	0.34
Benzo(b+k)fluoranthene [3]	68	< 1.0	0.20	0.24
Benzo(a)pyrene	33	< 0.5	0.60	0.37
Indeno(1,2,3-cd)pyrene	25	< 0.5	< 0.050	0.20
Dibenzo(a,h)anthracene	4	< 0.5	< 0.050	0.060
Benzo(g,h,i)perylene	16	< 0.5	< 0.050	0.17
TOTALS	810	4.2 - 7.2 [4]	3.7 - 3.8 [4]	4.0
Surrogate Recoveries (%)				
1,4 Dichlorobenzene (D4)	68	60	61	
Naphthalene (D8)	104	63	62	
Acenaphthene (D10)	104	70	74	
Phenanthrene (D10)	83	98	101	
Chrysene (D12)	91	81	89	
Perylene (D12)	123	104	61	

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[1] Ontario sediment quality guidelines, lowest effect level.

[2] J flag (standard US EPA nomenclature): Concentration given is estimated since below PQL (PQL is 100). See page 16 for definition of PQL.

[3] The sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene is reported.

[4] Range reflects concentration of PAHs reported below quantitation limits are at 0% to 100% of the quantitation limit concentration.

Contaminant removal efficiency is determined by comparing the amount of contaminant in the feed to the amount remaining in the product solids. The fraction remaining in the product solids is calculated by dividing the contaminant content of the product solids by the contaminant content of the feed, on a dry basis. The PAH calculation for the Thunder Bay sample from the second bench test which was assayed using the WTC analytical method is as follows:

PAH Removal Efficiency Calculation
(Ninth extraction stage)

……

$$\text{Fraction of PAHs remaining in product solids} = \frac{\text{Product solids PAH content (dry basis)}}{\text{Feed PAH content (dry basis)}}$$

$$= \frac{3.7\ \text{mg/kg}}{810\ \text{mg/kg}} = 0.0046$$

……

$$\text{\% Removal} = 100 \cdot (1 - \text{fraction of PCBs remaining in product solids})$$

$$= 100 \cdot (1 - 0.0046)$$

$$= 99.5\ \%$$

DECANTATION OF SOLVENT FROM WATER

The solvent recovered from each extraction stage was separated into its aqueous (water), oil and solvent components. Only the extract from the first and second extraction stages had a significant amount of water in solution, so only the water in these extracts is recovered.

As discussed under the Section THE B.E.S.T. SOLVENT EXTRACTION PROCESS, there are two ways to recover the water that was native to the feed sediment. Decantation of the triethylamine/water/oil phase by heating it to separate the water from the triethylamine/oil phase was not effective due to formation of an emulsion. Therefore, the water was separated from the triethylamine/water/oil extract solution by evaporation. When the triethylamine/oil/water extract was evaporated, the distilled and condensed solvent carried with it water in the form of an azeotrope, leaving the oil behind. The water was then separated from the triethylamine of the condensed triethylamine/water azeotrope by decantation. The triethylamine/water recovered was heated to 140 degrees F then poured into a 4-liter separatory funnel. Separation of the triethylamine and water occurred immediately. This separation was highly effective as expected because there is virtually no oil or solids in the condensed triethylamine/water that could hinder the separation of triethylamine from water by decantation. Another advantage of this procedure is that it generates a high (distilled) quality water product. Residual triethylamine was then steam stripped from the water. The evaporation of the triethylamine/oil/water extract is performed in a rotovap that has no reflux or rectification provision, unlike RCC's pilot or full-scale units. Thus, the quality of the recovered triethylamine and water product from the pilot or full-scale units will be better than that from bench tests for volatile compounds, such as naphthalene.

WATER PRODUCT

Analysis results of the water recovered by evaporation (distillation) for the second bench test from the step described in the prior section for PAHs per the WTC method is given on the following page. As can be seen from this page, the PAH residuals in the water product are very low as expected. The total organic carbon (TOC) concentration of the water was 150 mg/l. The triethylamine residual in the product water was 8 mg/l. The limited quantity of water generated from the bench test precluded additional analysis.

OIL CONCENTRATE

The oil, along with the PAH compounds in the feed, extracted from the feed, remained in the boiling flask of the rotary evaporator during recovery of the water by evaporation as described in the prior section DECANTATION OF SOLVENT FROM WATER. Only a small amount of oil was present because of the low oil content in the feed sample. Therefore, the oil in the evaporator flask was dissolved in a known quantity of hexane that allowed the oil to be completely transferred from the evaporator flask and made the oil homogeneous. This is very important for the integrity of the oil mass balance.

The PAH analysis of oil concentrate was determined by further dilution of the hexane/oil in hexane, followed by the WTC method, see Attachment 4. The oil concentrate analysis results of the oil on a neat basis alongside the recovered solvent, follows. The oil was expressed on a neat basis to reflect full-scale operation. (To express the oil PAH results on a neat basis, the hexane diluent in the oil was factored out by multiplying the weight of the hexane/oil (131 g) by the total solids residue at 70 degrees C, as a fraction, of the hexane/oil. The total solids residue was 3.1% and, thus, the weight of the oil on a neat basis was 4.1 g.)

As expected, the naphthalene concentration was low in the oil and high in the recovered solvent. This is because naphthalene volatilized during evaporation of the triethylamine/oil extract as discussed in Section DECANTATION OF SOLVENT FROM WATER. During bench testing, the evaporation of the triethylamine/oil/water extract is performed in a rotovap that has no reflux or rectification provision unlike RCC's pilot unit. Thus, the recovered triethylamine from bench tests will contain volatile compounds, such as naphthalene.

THUNDER BAY

Second Treatability Study PAH Results

All results in µg/l (ppb)

	Product Water
Naphthalene	< 2
Acenaphthylene	< 2
Acenaphthene	< 2
Fluorene	< 2
Phenanthrene	< 2
Anthracene	< 2
Fluoranthene	< 2
Pyrene	< 2
Benzo(a)anthracene	< 2
Chrysene	< 2
Benzo(b+k)fluoranthene [1]	< 20
Benzo(a)pyrene	< 10
Indeno(1,2,3-cd)pyrene	< 10
Dibenzo(a,h)anthracene	< 10
Benzo(g,h,i)perylene	≤ 10
Total	< 80
Surrogate Recoveries (%)	
1,4 Dichlorobenzene (D4)	31
Naphthalene (D8)	27
Acenaphthene (D10)	38
Phenanthrene (D10)	87
Chrysene (D12)	74
Perylene (D12)	47

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[1] The sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene.

THUNDER BAY

Second Treatability Study PAH Results

All results in mg/kg

	Product Oil Neat Basis	Recovered Solvent
Naphthalene	< 30	3.0
Acenaphthylene	180	< 0.1
Acenaphthene	84	0.35
Fluorene	320	0.18
Phenanthrene	7,700	0.36
Anthracene	1,200	0.27
Fluoranthene	15,000	< 0.10
Pyrene	12,000	0.050 J [1]
Benzo(a)anthracene	2,500	< 0.10
Chrysene	4,500	< 0.10
Benzo(b+k)fluoranthene [3]	7,400	< 0.50
Benzo(a)pyrene	2,400	< 0.50
Indeno(1,2,3-cd)pyrene	3,400	< 0.50
Dibenzo(a,h)anthracene	520	< 0.50
Benzo(g,h,i)perylene	2,100	< 0.50
Total	59,000	4 - 7 [4]
Surrogate Recoveries (%)		
1,4 Dichlorobenzene (D4)	DO [2]	
Naphthalene (D8)	DO [2]	
Acenaphthene (D10)	DO [2]	
Phenanthrene (D10)	DO [2]	
Chrysene (D12)	DO [2]	
Perylene (D12)	DO [2]	

---

[1] J flag; Estimated concentration is given since the concentration is below the PQL (PQL 0.1 mg/kg).

[2] Surrogate was diluted-out (DO).

[3] The sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene is reported.

[4] Range reflects concentration of PAHs reported below quantitation limits are at 0% to 100% of the quantitation limit concentration.

III. MASS BALANCES

The data gathered during the bench-scale treatability test provides the data required to calculate mass balances. Mass balances for the second bench test have been calculated into four fractions: solids, oil, water, and PAHs.

SOLIDS MASS BALANCE

The mass balance for the second bench test for solids is a comparison of the solids input during the test to the solids recovered after the test. The mass of solids input during the test includes the solids portion of the feed extracted and the solids portion of caustic soda added. The solids portion of the feed extracted was calculated by multiplying the weight of feed extracted by the solids content as determined by analysis. The solids portion of the caustic soda added was calculated by multiplying the weight of the 50 percent NaOH solution added by 0.50.

The mass of the solids recovered from the test is equivalent to the sum of the product solids and samples taken for stage-by-stage assays. A summary of this data follows:

<u>Solids Mass Balance</u>

Total Feed Extracted, Wet Basis		1,170	g
Solids Portion of Feed		515	g
Solids Portion of Caustic	+	8	g
Total Calculated Solids Input	=	523	g

……

Weight of Final Treated Solids Recovered		440	g
Weight of Solids Samples Recovered	+	76	g
Total Solids Recovered	=	516	g
Recovery, %		99	

OIL MASS BALANCE

The oil mass balance was computed via the same method used in calculating the solids mass balance. The oil & grease content of the feed was determined by extracting a sample of the feed with methylene chloride. This oil & grease content (by $MeCl_2$) was multiplied by the weight of the feed input to determine the amount of oil input. The mass of oil recovered from the test was equivalent to the oil concentrate recovered.

The oil mass balance (based on methylene chloride) follows:

Oil Mass Balance

Calculated Oil Input	Oil Recovered	% Recovery
4.1 g	4.1 g	100

Virtually all of the PAHs and other organic compounds from the sediment sample now reside in the oil concentrate that had a mass of 4.1 grams on a hexane-free basis. Based on the bench-scale tests, the mass of contaminated material can be reduced by 290-fold, the ratio of feed mass to oil concentrate mass.

WATER MASS BALANCE

The water mass balance for the second bench test was computed similarly to the method used for solids. The mass of water input came from the water in the feed. The mass of water recovered was equivalent to the mass of decant water produced. However, the portion of the water in the feed that remained with the solids after extraction #2 was not recovered since only the extract from extractions #1 and #2 was decanted during the bench tests. The extracts from extraction #3 to #9 (the last extract) contain too little water to effectively separate and recover the water. The amount of water in these subsequent extracts was determined analytically by Karl Fisher method and added to the balance of water recovered. In RCC's Pilot Unit, and Full-Scale Unit, all water is recovered since the triethylamine is recycled and a constant purge of product water prevents water accumulation in the system. A summary of this data follows:

Water Mass Balance

Total Feed Extracted, Wet Basis		1,170	g
Water Portion of Feed		655	g
Total Calculated Water Input	=	655	g
Weight of Decant Water Recovered		281	g
Weight of water not recovered in extracts		330	g
Total Water Recovered	=	610	g
Recovery, %		93	

PAH MASS BALANCE

The mass of PAHs input was calculated by multiplying the weight of the feed by the PAH concentration as determined by analysis. The vast majority of the PAHs were recovered from the test reside in the product oil. The PAHs in the treated solids and product water are negligible when calculating a PAH mass balance. The portion of PAHs in the recovered triethylamine, treated solids, as well as the oil, are taken into account in the mass balance. The mass of PAHs recovered in the oil, solids, recovered triethylamine and product water was calculated by multiplying the weight of the respective fractions recovered, by the PAH concentration, respectively. The PAH mass balance was as follows:

PAH Balance

Calculated PAHs Input	Calculated PAHs Recovered	Total PAH % Recovery
430 mg	310 mg	72

SUMMARY OF MASS BALANCE CALCULATIONS

The following table summarizes the mass balance calculations for each constituent considered. The mass balances were based on the amount of the fraction recovered from the simulation divided by the calculated input amount to the simulation.

Mass Balance Summary, %

Solids	Oil	Water	PAHs
99	100	93	72

IV. CONCLUSIONS AND RECOMMENDATIONS

The contaminated sediment sample from the Thunder Bay Harbour site is suitable for treatment with the B.E.S.T. solvent extraction process. No problems were observed during testing of the sample and low PAH residuals in the treated solids were achieved. Therefore, pilot-scale testing is recommended as the next step in testing. Specific findings are as follows:

1. The B.E.S.T. process was very effective at separating the sediment into distinct oil, water, and solids phases. One of the key advantages of triethylamine as a solvent is that it is readily miscible in the large amount of water in the sediment, as well as oil in the sediment, when the mixture is cold. Therefore, the PAHs in the sediment were effectively removed, as expected.

2. The total PAH concentration in the sediment sample was 810 mg/kg, dry basis. After nine extractions with triethylamine, the total PAH residual concentration was 3.7 mg/kg, and thus the PAH removal efficiency was 99.5%.

3. The current, total PAH Ontario sediment quality guideline of 4 mg/kg, as well as that for individual PAHs, was achieved after nine extraction stages.

4. Decantation of the triethylamine/water/oil phase by heating to separate the water from the oil that was extracted from the sediment sample was not effective. Therefore, this solution was simply evaporated which always is effective in separating the oil from the triethylamine/water phase. The water can then readily be decanted from the triethylamine upon warming of the triethylamine/water phase as expected. The advantage of this procedure is that it generated a high quality water product.

5. Centrifugation is not required to separate the triethylamine extract from the particulate solids. This will simplify operation and minimize the capital cost of a full-scale B.E.S.T. unit.

6. Virtually all of the contaminants from the sample are concentrated into the oil product. The mass of contaminated material can be reduced almost 300-fold via the B.E.S.T. process.

7. The US EPA PAH analytical method yields the same result as the WTC method on the feed sediment, but yields only approximately 50% of the concentration results of the WTC PAH method on the treated solids.

8. A rectification unit in the pilot or full-scale solvent evaporator will be required to prevent contamination of the recovered triethylamine with naphthalene.

* * * * *

ATTACHMENT 1

Background
Contaminated Sediment Treatment Technology Program (COSTTEP)

B.E.S.T. BENCH-SCALE TREATABILITY TEST
FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

GREAT LAKES ACTION PLAN

Great Lakes Environment Office
Environment Canada
Ontario Region

CLEANUP FUND
FACT SHEET

CONTAMINATED SEDIMENT TREATMENT TECHNOLOGY DEMONSTRATION SERIES

NUMBER 1

Contaminated Sediment Treatment Technology Program Overview

Summary

Environment Canada's Great Lakes Cleanup Fund, one component of the federal Great Lakes Action Plan was initiated in 1991. The program focuses on Canada's 17 Areas of Concern identified by the International Joint Commission. The Cleanup Fund is designed to help meet federal commitments in the development and implementation of cleanup options. One priority of the program is to develop and demonstrate new and innovative technology on the safe removal and treatment of contaminated sediments. To evaluate sediment treatment technologies the Contaminated Sediment Treatment Technology Program (COSTTEP) was initiated.

The mandate of COSTTEP is to foster the development and demonstration of technologies to remediate contaminated sediment and to communicate the results of the program to persons involved with Great Lakes remediation projects. Funds are provided to COSTTEP by the Cleanup Fund and are used to sponsor technology demonstration projects. Any technology is eligible for funding provided it has excellent technical merit, is innovative and has the potential to treat Great Lakes sediment in a cost-effective manner.

The program has three levels of projects which it will fund: bench scale, pilot scale and full scale. In general the program is to progress from bench through to pilot and then full scale projects. The program has been advertised nationally and internationally resulting in a very large response from technology developers and vendors. A database of technologies has been created based on the initial data submitted by these firms.

Background

The 1972 Great Lakes Water Quality Agreement signed by the United States and Canada commits both countries to cleaning up the Great Lakes by controlling point and non-point sources of pollution and by remediating those areas with in-place pollutants. The two countries have identified 42 Areas of Concern (AOCs) which are either badly polluted or are major sources of pollution. Seventeen of these AOCs are on the Canadian side of the Great Lakes. For each of these seventeen areas the Canadian Government and the government of the Province of Ontario under the Canada-Ontario Agreement have initiated a Remedial Action Plan (RAP) process to deal with the site-specific problems. Each RAP is being prepared in consultation with local government officials, industry representatives and citizens. Most of the RAP Teams have now completed Stage One of the process which is to *assess* their AOC. With a completed assessment document the RAP Team will know where the pollution problems are and what level of cleanup is necessary to provide the desired environmental recovery.

The RAP Teams are now moving into Stage Two of the process which is to *investigate remedial options*. Stage Three will be to actually implement the action plan. To assist RAP Teams with the Stage Two evaluation process the Great Lakes Environment Office of Environment Canada has channelled the current funds from the Cleanup Fund into a number of technology and cleanup strategy assessment programs. The programs are being carried out in partnership with the Province of Ontario, industry and municipal governments.

Approximately one-third of the Cleanup Fund budget is being directed towards contaminated sediment remediation. There are two reasons why the cleaning of sediments has been given such a high priority. The first is that pollutants in the sediment are absorbed into or ingested by organisms and plants which live in or on sediment. These benthic organisms are either directly impaired (killed by toxic effects, deformed at birth, caused to develop cancer) or pass the toxins up through the food chain (bioaccumulation, biomagnification) where toxic effects can show up at the higher trophic levels including humans. The second reason sediment remediation is a priority is that sediments have now been identified as a major *source* of pollution to the water column above. During past years of heavy industrial and municipal pollution, sediments absorbed a great deal of pollution from the water column. Now, however, industrial and municipal discharges have been greatly reduced so that the water is generally cleaner than the sediment in a relative sense. Thus the pollutants stored in the sediments are now diffusing back into the water. This is a major obstacle to improving Great Lakes water quality since it could take hundreds of years for all of the pollutants to diffuse out of the sediment.

Canada

Great Lakes Cleanup Fund Sediment Programs

In 1990, when the Cleanup Fund was initiated, three distinct sediment programs were created. The three programs created are the Contaminated Sediment *Removal* Technology Program, the Contaminated Sediment *Treatment* Technology Program and the Contaminated Sediment *Assessment* Program. Projects initiated deal with innovative dredging technologies, specialized bioassays of treated and untreated sediment, enhanced natural sediment remediation processes, chemical treatment of in place sediments, physical barriers to pollutant diffusion from sediment and a variety of others. This Fact Sheet describes the Contaminated Sediment Treatment Technology Program (COSTTEP). For more information on the other programs and projects contact Environment Canada, Great Lakes Environment Office, Toronto, Ontario.

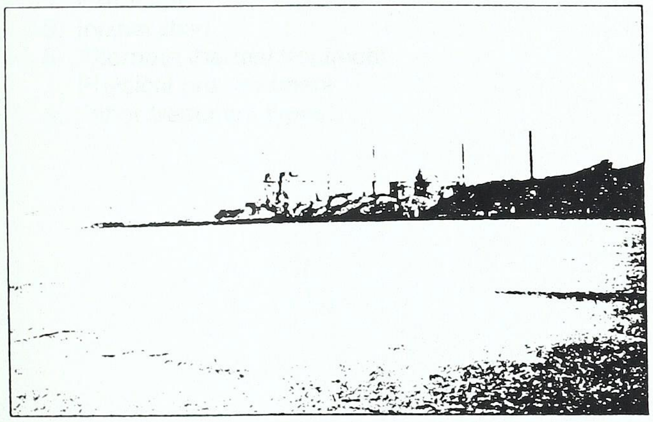

FIGURE 1: View of Hamilton Harbour. This harbour has one of the most serious sediment contamination problems of all Canadian AOCs.

Mandate and Coordination of the Contaminated Sediment Treatment Technology Program

The Great Lakes Environment Office has contracted with the Wastewater Technology Centre to administer COSTTEP. The Wastewater Technology Centre (WTC) is a federal government owned, privately operated institution dedicated to developing and commercializing promising technologies for wastewater treatment and environmental protection.

The principle mandate of COSTTEP is to encourage the development of new technologies to remediate contaminated sediment by funding the demonstration of selected technologies at bench, pilot and full scale. The program will move from bench scale demonstrations in the first two years to pilot scale demonstrations to full scale demonstrations. A full scale demonstration would not necessarily clean up an entire sediment "hotspot" but would process enough sediment to prove that the technology is technically and economically viable. To fund these demonstrations the program has been allocated a total budget of almost six million dollars. The projected year by year budget for the first four years of the program is shown in *Table 1*.

TABLE 1
Program Budget

FISCAL YEAR	PROGRAM STORAGE	BUDGET (000s)
1990/91	Bench scale	$ 450
1991/92	Bench/Pilot	$1300
1992/93	Bench/Pilot/Full	$2100
1993/94	Full scale	$2100
TOTAL		**$5950**

The second part of the program's mandate is to communicate the nature of the program and the results of demonstrations to as wide an audience as possible with particular attention to the RAP groups and the environmental authorities of the U.S.A. To address this part of the mandate a number of actions have been initiated.

The program was widely advertised in the fall of 1990 in Canadian and international publications. A very large number of technology "vendors" responded and the technologies were evaluated. Some of these technologies have now been funded under the program. All of the technologies meeting the minimum criteria have now been entered into a computerized database. This is currently one of the only such databases in North America. The database is available to anyone for a moderate fee.

The program is also communicating through a number of other channels. This Fact Sheet is one channel. A Fact Sheet will be produced for each funded demonstration. Copies of the final reports of funded projects will also be available. Program staff also actively participate in a number of key committees including the U.S. Assessment and Remediation of Contaminated Sediment Committee, several site specific cleanup committees and the Remedial Action Plan Program Sediment Subcommittee. A slide presentation has been prepared and has been given at a number of conferences and RAP workshops. The program will also host a series of workshops on sediment treatment technologies.

Selection for Funding Under COSTTEP

To be considered for funding under COSTTEP, technologies must meet certain criteria: The technology must either remove, segregate or destroy contaminants in sediment or the pore water associated with wet sediment; must have at least one innovative feature; must be at least at the bench scale stage (ie. the program will not fund research leading to technology creation); and, must appear to be economically feasible.

To be *selected* for funding a technology must be rated superior to other technologies in the same category. The criteria used to evaluate technologies are:

- Technical merit
- Innovative nature
- Cost/value
- Company reputation
- Laboratory capabilities
- Environmental benefit
- Applicability to AOCs
- Scale-up potential.

As well, preference will be given to mobile technologies which can treat sediment near the site and to companies which are either Canadian owned or have demonstrated a high level of commitment to establishing themselves in Canada.

Treatment categories are defined as follows:

1. Chemical treatment
2. Biological treatment
3. Solidification/Stabilization
4. Extraction
5. Incineration
6. Alternate thermal treatment
7. Physical pre-treatment
8. Other treatment types.

A number of bench and pilot scale projects covering all categories have been funded at this time. Future Fact Sheets in this series will provide more information.

Additional Information

For more information on COSTTEP contact:

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Wastewater Technology Centre
P.O. Box 5068
Burlington, Ontario
L7R 4L7 FAX: 416-336-4765

For more information on the Great Lakes Cleanup Fund or for other Fact Sheets contact:

Griff Sherbin

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ATTACHMENT 2

US EPA/Research Triangle Institute Study on B.E.S.T.

B.E.S.T. BENCH-SCALE TREATABILITY TEST FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

PUBLISHED SINCE 1893

Seattle Daily
Journal of Commerce
and Northwest Construction Record

Daily Journal of Commerce, Seattle, Washington, Wednesday, December 30, 1987

EPA rates local PCB method No.1

Bellevue--(BW)--A recent independent research report funded by the U.S. Environmental Protection Agency rates the B.E.S.T. process number one in desirability for treating PCB-contaminated sediments.

The B.E.S.T. process was developed by Resources Conservation Co., of Bellevue. The study was conducted by the Research Triangle Institute in North Carolina to form the basis for further EPA funding and development.

Eight processes, varying widely in their basic technology, were evaluated. Technologies included solvent extraction, ultrasonics, ultraviolet light, microbes, several chemical treatments and in situvitrification. The report finds some merit in all processes evaluated, but recommends the top three, of which B.E.S.T. was the highest rated, for further testing.

"This could be the breakthrough we've been seeking to get going on actual site cleanups," said Paul McGough, vice president of product development for RCC. "We have a field-tested, transportable, 100-ton-per-day unit available for processing hazardous wastes and we are eager to begin."

RCC's 100-ton-per-day B.E.S.T. unit has been successfully demonstrated in a Superfund clean up of a PCB-contaminated, used oil refining site near Savannah, Ga.

The contaminated sediments specified in the EPA-sponsored report are those that occur in pond, lake, river and harbor bottoms. The B.E.S.T. process is particularly attractive because it separates these sediments into three components, water, oil and solids, for ease of handling and potential recycling.

In this way a permanent cleanup solution is created, rather than the traditional relocation and burial, which merely postpones the disposal problem.

RCC's B.E.S.T. process uses a unique solvent, triethylamine, to separate sludges into water, oil and solid residue. Triethylamine is unique because at near-freezing temperatures, around 40 degrees Fahrenheit, it will dissolve both oil and water; at room temperature, 65 degrees Fahrenheit, it dissolves only oil. This change in solvent characteristic forms the basis for the B.E.S.T. process.

Resources Conservation Co., a wholly owned subsidiary of Reading & Bates Corp., has been in business since 1970 and has a worldwide reputation in waste-water processing.

ATTACHMENT 3

EPA S.I.T.E. Demonstration Bulletin & RCC Pilot Unit Information

B.E.S.T. BENCH-SCALE TREATABILITY TEST FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

United States
Environmental Protection
Agency

EPA/xxx/xx-xx/017
DRAFT FINAL (April 1993)

SITE

*Superfund Innovative
Technology Evaluation*

Technology Demonstration Summary

Resources Conservation Company Basic Extractive Sludge Treatment (B.E.S.T.®); Grand Calumet River - Gary, Indiana

An evaluation of Resources Conservation Company's (RCC) Basic Extractive Sludge Treatment (B.E.S.T.®) pilot plant was conducted between July 1 and July 22, 1992, during a demonstration by the U.S. Environmental Protection Agency (EPA), under the Superfund Innovative Technology Evaluation Program (SITE). The Demonstration evaluation was conducted in Gary, Indiana; the material treated was contaminated river bottom sediments collected from the Grand Calumet River (GCR). Figure 1 shows the general locations of the Demonstration Test area, test sediment collection points in the GCR, and major regional features.

This demonstration was part of an intraagency cooperative effort. In addition to the EPA SITE Program, other agencies involved included EPA's Great Lakes National Program Office (GLNPO); the U.S. Army Corps of Engineers (COE), Chicago District; and EPA Region V. The GLNPO Assessment and Remediation of Contaminated Sediments Program through the COE in cooperation with EPA Region V arranged for the developer's services and the location where the demonstration was conducted.

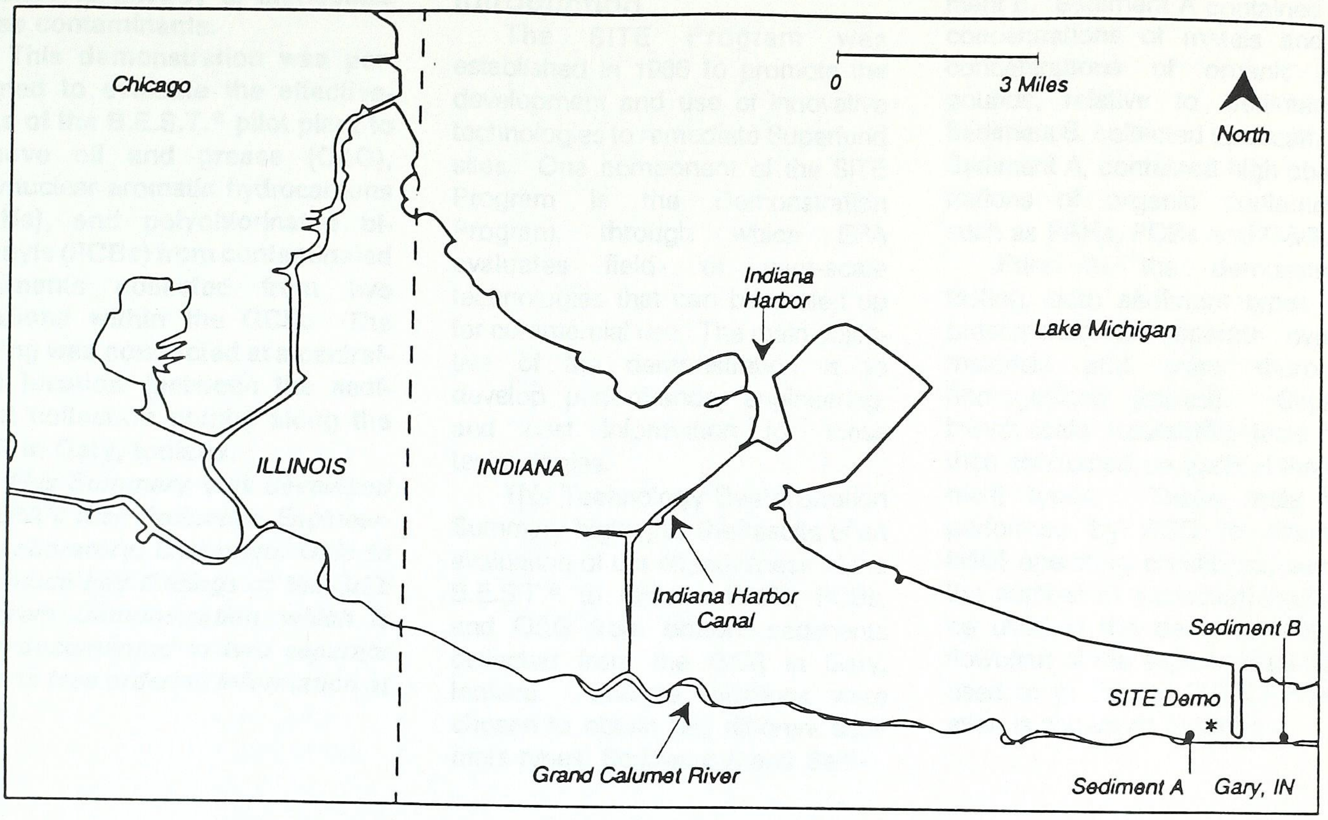


Figure 1. Regional location map.

GLNPO leads efforts to carry out the provisions of Section 118 of the Clean Water Act (CWA). Under Section 118(c)(3) of the CWA, GLNPO is responsible for undertaking a 5-year study and demonstration program of methods for the assessment and remediation of contaminated sediments. Areas of Concern (AOC) are specified for priority consideration, one of which is the GCR. The COE (Chicago District) has authorization (Rivers and Harbors Act of 1910) to maintain harbor channels by periodic dredging. This includes the federal channel at Indiana Harbor downstream of the GCR. However, EPA has designated the bottom sediments as moderately polluted, heavily polluted, and toxic. As a result, materials to be dredged from the Indiana Harbor and Canal are not suitable for open-water disposal in Lake Michigan. At the present time, an environmentally accepatable disposal facility for dredged materials from Indiana Harbor does not exist. Consequently, dredging to maintain adequate navigation depths has not been conducted at this harbor since 1972.

The B.E.S.T.® Process is a patented solvent extraction system that uses triethylamine at different temperatures to separate organic contaminants from sludges, soils, and sediments. The organics are concentrated in an oil phase, thereby reducing the volume of wastes that require further treatment. Multiple extractions are conducted at predetermined process conditions and are followed by solvent recovery, oil polishing, solids drying, and water stripping.

The use of triethylamine as the extracting agent distinguishes B.E.S.T.® from other solvent extraction and soil washing technologies. Triethylamine has a property known as inverse miscibility. At temperatures below 60°F, triethylamine is miscible with water; above 60°F triethylamine is only slightly miscible with water. Therefore, at temperatures below 60°F solids can be dewatered and organic contaminants can be extracted simultaneously. This process is referred to as a cold extraction. Following cold extractions, the extraction temperature is raised above 60°F, and any remaining organic contaminants are removed. These warm and hot extractions are usually conducted at temperatures ranging between 100°F and 170°F. The organic contaminants initially present in the sludge or soil are concentrated in the oil fraction; additional treatment (i.e., incineration) is

required to destroy or immobilize these contaminants.

This demonstration was performed to evaluate the effectiveness of the B.E.S.T.® pilot plant to remove oil and grease (O&G), polynuclear aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) from contaminated sediments collected from two locations within the GCR. The testing was conducted at a centralized location (between the sediment collection points) along the GCR in Gary, Indiana.

This Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, Ohio to announce key findings of the SITE Program Demonstration which is fully documented in two separate reports (see ordering information at back).

Introduction

The SITE Program was established in 1986 to promote the development and use of innovative technologies to remediate Superfund sites. One component of the SITE Program is the Demonstration Program, through which EPA evaluates field- or pilot-scale technologies that can be scaled up for commercial use. The main objective of the demonstration is to develop performance, engineering, and cost information for these technologies.

This Technology Demonstration Summary highlights the results of an evaluation of the effectiveness of the B.E.S.T.® to remove PAHs, PCBs, and O&G from bottom sediments collected from the GCR in Gary, Indiana. Sample locations were chosen to obtain two different sediment types, Sediment A and Sediment B. Sediment A contained high concentrations of metals and low concentrations of organic compounds, relative to Sediment B. Sediment B, collected upstream from Sediment A, contained high concentrations of organic contaminants such as PAHs, PCBs and O&G.

Prior to the demonstration testing, both sediment types were prescreened to separate oversize materials and were thoroughly homogenized (mixed). Separate bench-scale treatability tests were then conducted on each of the sediment types. These tests were performed by RCC to determine initial operating conditions, such as the number of extraction cycles, to be used in the demonstration. A flowchart of the experimental design used to guide the B.E.S.T.® evaluation is shown as Figure 2.

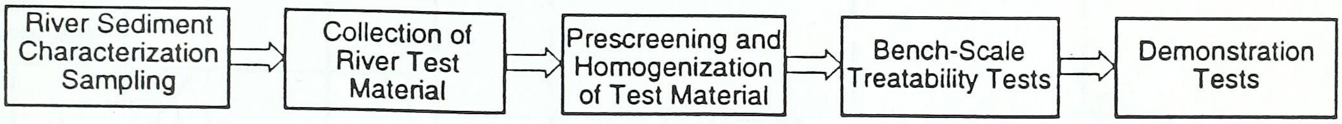


Figure 2. Experimental design flowchart.

The demonstration consisted of two separate tests, one for each sediment type. Each test consisted of two phases. Phase I involved determination of the optimum process variables from the results of three runs, and Phase II consisted of two additional runs at the determined optimum conditions. Samples of the untreated sediments, product solids, product water, and product oil were collected during each of the five runs (Phases I and II). These samples were analyzed for total PAHs, PCBs, and O&G. Residual triethylamine solvent was also analyzed in the product solids, product water, and product oil.

Results of the demonstration showed that the process met (or exceeded) the vendor's claims for organic contaminant removal efficiency for treating both of the test sediments. The analytical results for Sediment A indicated that the process removed greater than 98 percent of the O&G, greater than 99 percent of the PCBs, and 96 percent of the PAHs. The residual solvent in the product solids and product water generated from Sediment A was 45 mg/kg and less than 2 mg/L, respectively. A final oil product was not generated for Sediment A because of a lack of oil (less than 1 percent) in Sediment A feed. The analytical results for Sediment B indicated that the process removed greater than 98 percent of the O&G and greater than 99 percent of the PCBs and PAHs. The residual solvent in the product solids, product water, and product oil generated from Sediment B was 103 mg/kg, less than 1 mg/L, and 730 mg/kg, respectively.

Process Description

The B.E.S.T.® pilot-scale system is designed to separate organic contaminants from soils, sludges, and sediments, thereby reducing the volume of the hazardous waste that must be treated. Triethylamine is used as the extracting agent because it exhibits several beneficial characteristics. These characteristics include:

- A high vapor pressure (therefore the solvent can be easily recovered from the extract of oil,water, and solvent) through simple steam stripping
- Formation of a low-boiling azeotrope with water (therefore the solvent can be recovered from the extract to very low residual levels, typically less than 100 ppm)
- A heat of vaporization one-seventh of water (therefore, solvent can be recovered from the treated solids by simple heat with a very low energy input)
- Triethylamine is alkaline (pH=10) (therefore some heavy metals are converted to metal hydroxides, which can precipitate and exit the process with the treated solids).

The generalized B.E.S.T.® solvent extraction process is shown in Figure 3. Contaminated materials are initially screened to less than ½-inch diameter (⅛ inch for this demonstration). The screened material is added to a refrigerated Premix Tank with a predetermined volume of 50 percent sodium hydroxide. The Premix Tank is sealed, purged with nitrogen, and then filled with chilled triethylamine solvent. The chilled mixture is agitated and allowed to settle. The resulting solution from this cold extraction consists of a mixture of solvated oil, water, and solvent. The mixture is decanted from the solids and centrifuged, and the solvent and water are separated out of the mixture by distillation.

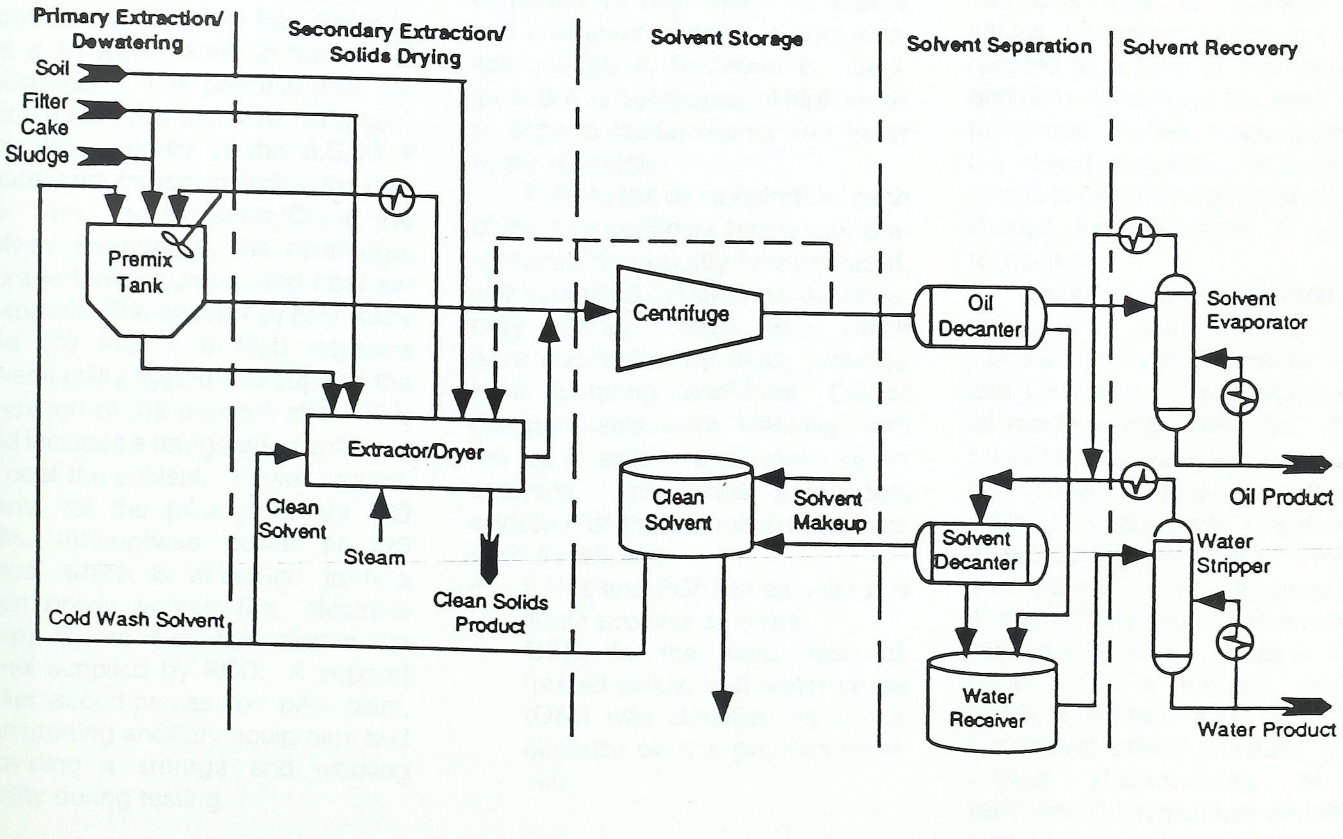


Figure 3. *Generalized diagram of the RCC B.E.S.T.® solvent extraction process.*

The cold extractions are repeated as additional feed is added to the Premix Tank to accumulate enough solids to perform subsequent extraction cycles. Solids with high moisture contents may require more than one cold extraction. During this demonstration Sediment A (containing 41 percent moisture) required two cold extractions.

Once a sufficient volume of moisture-free solids is accumulated, it is transferred to a steam-jacketed Extractor/Dryer. Warm triethylamine is then added to the solids. This mixture is heated, agitated, settled and decanted. The warm and hot extractions result in separation of the organics not removed during the initial cold extractions. Three products are derived from the total process: product solids, product water, and concentrated oil containing the organic contaminants.

The pilot plant used for this demonstration is a self-contained mobile unit which allows onsite testing to be performed at a pilot scale. It consists of two portable skids that are mounted on a low boy trailer (8 feet x 45 feet) on which the unit is transported. The process skid (20 feet x 8 feet) has two levels and contains the majority of the B.E.S.T.® process equipment including the Premix Tank, the Extractor/Dryer, the Solvent Evaporator, the centrifuge, storage tanks, pumps, and heat exchangers. The second smaller utility skid (10 feet x 8 feet) contains several utility systems to support the operation of the process skid. This skid includes a refrigeration unit used to cool the solvent. Power requirements for the pilot plant are 480 volts, three-phase power at 225 amps, which is accessed from a main power source (i.e., electrical drop) by an electrical distribution panel supplied by RCC. A support trailer accompanies the pilot plant, transporting ancillary equipment and providing a storage and working facility during testing.

Test Program

The primary objective of this SITE demonstration was to evaluate the effectiveness of the B.E.S.T.® solvent extraction technology on two test sediments having different contaminants or contrasting concentration levels of the same contaminants. Therefore, the sediments treated were collected at two different transect locations along the east branch of the GCR (see Figure 1). Sediments collected and homogenized from Transect 28 were designated Sediment A, and sediments collected and homogenized from Transect 6 were designated Sediment B. The transect locations were located approximately 2 miles apart. The Sediment A (Transect 28) location was located slightly downstream of an oil-skimmed settling lagoon, which receives wastewater from primary bar plate mills and Basic Oxygen Process (BOP) shops. Sediment B (Transect 6) was located slightly downstream from the discharge of a coke plant. Sediment A consisted of high levels of metals and low levels of organic contaminants relative to Sediment B. Sediment B was composed of high levels of organic contaminants and lower levels of metals.

Prior to the demonstration, each of the two sediment types was prescreened, thoroughly homogenized, and subjected to bench-scale treatability testing. These tests, which were conducted by RCC, provided initial operating conditions. Critical measurements were identified with the aid of sediment characterization analyses. The critical parameters selected for the demonstration tests were as follows:

- PAHs and PCBs in all solid and liquid process streams
- O&G in the feed material, treated solids, and water phase (O&G was identified as critical because oil is a process residual)
- Triethylamine in the treated solids, water phase, and oil phase
- Moisture in the feed material and treated solids
- Toxic Characteristic Leachate Procedure (TCLP) metals in the feed material and treated solids
- Masses of feeds (including steam and caustic)
- Masses of treated residuals (solids, oil, water, and recovered solvent)

After the initial conditions and critical measurements were determined, the actual demonstration testing was initiated. Two demonstration tests were conducted, one for each sediment type. Each demonstration test consisted of two phases. Phase I involved the determination of optimum process variables for each test sediment. These variables included number of extraction cycles, mixing times, and extraction temperature. Three sets of conditions, determined by RCC, were tested. Phase II consisted of two additional runs at optimum conditions determined in Phase I. This resulted in a total of three runs at optimum conditions for each sediment type. Tables 1 and 2 present the actual sequence of extraction cycles conducted during the demonstration for Sediments A and B, respectively.

Samples were collected and analyzed for each process stream specified in Table 3. PAHs, PCBs, and O&G were critical analyses for all media except vent gas. These contaminants were known to be in both sediment types and were the primary constituents targeted for removal using the B.E.S.T.® Process. Triethylamine was targeted for analysis in the product streams and vent gas emission because of its potential as a process residual. Moisture content and TCLP were considered critical because of the original characteristics of the sediments (high moisture and metals contents).

TABLE 1. EXTRACTION SEQUENCE USED FOR SEDIMENT A

	EXTRACTION TEMPERATURE (°F)				
	PHASE I			PHASE II	
Extraction Cycle	Run 1	Run 2	Run 3	Run 4	Run 5
1	cold (62)	cold (50)	cold (53)	cold (48)	cold (52)
2	warm (106)	cold (40)	cold (45)	cold (42)	cold (46)
3	warm (95)	cold (38)	warm (100)	warm (110)	warm (97)
4	warm (95)	warm (98)	hot (155)	hot (155)	hot (152)
5	warm (103)	warm (125)	hot (166)	hot (163)	hot (167)
6	hot (170)	hot (160)	hot (166)	hot (164)	hot (160)
7	—	hot (160)	warm (120)	warm (118)	warm (121)

Note: Shaded columns indicate the three optimum runs.

TABLE 2. EXTRACTION SEQUENCE USED FOR SEDIMENT B

	EXTRACTION TEMPERATURE (°F)				
	PHASE I			PHASE II	
Extraction Cycle	Run 1	Run 2	Run 3	Run 4	Run 5
1A 1	cold (49)	cold (28)	cold (32)	cold (28)	cold (51)
1A 2	cold (47)	cold (42)	cold (40)	cold (48)	cold (41)
1A 3	(NC)	cold (38)	cold (40)	cold (39)	cold (39)
1B 1	cold (41)	cold (39)	cold (29)	cold (51)	cold (39)
1B 2	cold (53)	cold (47)	cold (38)	cold (53)	cold (45)
1B 3	cold (52)	cold (36)	cold (46)	cold (46)	cold (44)
2	hot (145)	hot (152)	hot (151)	hot (147)	hot (146)
3	hot (152)	hot (157)	hot (150)	hot (156)	hot (160)
4	hot (161)	hot (150)	hot (152)	hot (170)	hot (153)
5	hot (148)	hot (152)	hot (151)	hot (155)	hot (154)
6	hot (157)	hot (151)	hot (146)	hot (158)	hot (152)
7	hot (143)		hot (150)		

Notes:

- Shaded columns indicate the three optimum runs.
- Because of the high moisture content of Sediment B, both sediment and solvent were fed to the Premix Tank in portions to limit the temperature rise of the solvent/water phase due to the heat of the solution to an acceptable level.
- NC = Not conducted

TABLE 3. SUMMARY OF ANALYSES CONDUCTED FOR THE RCC B.E.S.T.® SITE DEMONSTRATION

Parameter	Untreated Sediment (Raw Feed)	Treated Sediment (Product Solids)	Water Phase (Product Water)	Decant Water (from Raw Feed)	Oil Phase (Product Oil)	Intermediate Solvent/Oil Mixture	Solvent Feed and Recycled Solvent	Vent Gas
Critical								
PAHs[1]	●	●	●	●	●	●	●	▨
PCBs	●	●	●	●	●	●	●	▨
Oil and Grease	●	●	●	●	▨	▨	▨	▨
Moisture[2]	●	●	●	▨	●	▨	▨	▨
Triethylamine	▨	●	●	▨	●	▨	▨	●
TCLP Metals[3]	●	●	▨	▨	▨	▨	▨	▨
Non-Critical								
TSS	▨	▨	●	●	▨	▨	●	▨
Proximate/Ultimate	●	●	▨	▨	●	▨	▨	▨
Total Metals[4]	●	●	●	●	▨	▨	▨	▨
TRPH	●	●	●	●	▨	▨	▨	▨
Volatile Solids	●	●	●	▨	▨	▨	▨	▨
Total Cyanide	●	●	●	▨	▨	▨	▨	▨
Reactive Cyanide	●	●	▨	▨	▨	▨	▨	▨
Reactive Sulfide	●	●	▨	▨	▨	▨	▨	▨
Particle Size	●	●	▨	▨	▨	▨	▨	▨
Total Phosphorus	●	●	●	▨	▨	▨	▨	▨
pH	●	●	●	▨	▨	▨	▨	▨
TDS	▨	▨	●	●	▨	▨	▨	▨
TOC/TIC	▨	▨	●	▨	▨	▨	▨	▨
BOD	▨	▨	●	▨	▨	▨	▨	▨
Conductivity	▨	▨	●	▨	▨	▨	▨	▨
Special Studies								
Biodegradation	▨	●	▨	▨	▨	▨	▨	▨

[1] Specific PAH compounds analyzed for are presented in Table 4.
[2] Moisture was critical for all samples except for the oil phase.
[3] TCLP metals include As, Ba, Cd, Cr, Pb, Hg, Se, and Ag.
[4] Total metals include Sb, As, Ba, Be, Cd, Cr, Cu, Mn, Hg, Ni, Se, Tl, Va, and Zn.

Six main process streams were sampled and analyzed for each of the two tests. These process streams included untreated sediments (raw feed), product solids, product water, product oil or oil/solvent mix, recycled solvent, and vent emissions. Decant water collected from buckets holding the feed material from one of the Sediment B batches was also sampled. Each lot of product triethylamine was sampled prior to use.

Results

The following data summary is derived from this SITE Demonstration and other test results:

- Contaminant reductions of greater than 96 percent for total PAHs and greater than 99 percent for total PCBs were achieved from treatment of bottom sediments collected from Transect 28 (Sediment A) of the GCR. Contaminant reductions of greater than 99 percent for total PAHs and greater than 99 percent for total PCBs were achieved from treatment of bottom sediments collected from Transect 6 (Sediment B) of the GCR. Table 4 provides a summary of the PAH removal efficiencies from test sediments. Table 5 summarizes the PCB removal efficiencies from test sediments.
- O&G removal efficiencies in excess of 98 percent were achieved in the treated solids generated from both sediment types, as shown in Table 6.
- Overall mass balances of 108 percent and 114 percent were achieved during testing of Sediment A and Sediment B, respectively. These values were obtained by comparing the mass of the feed material entering RCC's treatment system to the total mass of the products exiting the system (solids, water, and oil).
- The products generated using the B.E.S.T.® Process were consistent with RCC's claims with regard to residual triethylamine concentrations. Average triethylamine concentrations of 103 mg/kg, less than 1 mg/L, and 730 mg/kg for solid, water, and oil products, respectively, were generated during the treatment of Sediment B (Transect 6). Solid and water products generated from the treatment of Sediment A achieved average residual triethylamine concentrations of 45 mg/kg and less than 2 mg/L, respectively. Product oil was not generated from treatment of Sediment A because Sediment A originally contained very little oil (less than 1%). A summary of RCC's claims, and actual triethylamine concentrations in the treated solids, product water, and product oil are presented in Table 7.
- This technology has been demonstrated to be effective on organic contaminants from varied sources, including primary steel manufacturing, aluminum manufacturing, petroleum refining, machining operations, and wood treating. Details are available in the Applications Analysis Report.

Costs

Operating and equipment capital cost estimates were developed for the proposed full-scale B.E.S.T.® system. The cost estimates were based on information provided by the vendor and on several assumptions. These assumptions were based on the experiences of this demonstration and a previous full-scale test conducted at a site in Georgia. Certain cost factors which were not included in the treatment cost estimate were assumed to be the responsibility of the site owner/operator. Costs associated with system mobilization, site preparation, startup, and demobilization were also excluded from the treatment cost estimate. The reasoning used in making these estimates, or omitting a particular cost category, is discussed in the Applications Analysis Report.

The pilot-scale unit utilized during the SITE demonstration operated at an average feed rate of 90 pounds of contaminated sediment per day. The full-scale commercial unit is projected to be capable of treating 186 tons of contaminated soil or sludge per day (TPD). The cost estimates are based on the remediation of contaminated soil, sludge or sediment using the proposed full-scale unit. The treatment cost is estimated to be $112 per ton if the system is on-line 60 percent of the time or $94 per ton if the system is on-line 80 percent of the time.

TABLE 4. PAH REMOVAL EFFICIENCIES

PAH Analyte	SEDIMENT A Feed[a]	SEDIMENT A Treated Solids[a]	SEDIMENT A % Removal[b]	SEDIMENT B Feed[a]	SEDIMENT B Treated Solids[a]	SEDIMENT B % Removal[b]
Acenaphthene	68	1.3	98.1	12800	42	99.7
Acenaphthylene	<16	<0.8	—	210	6.6	96.9
Anthracene	22	1.3	94.1	2370	16	99.3
Benzo(a)anthracene	25	0.52	97.9	1050	4.7	99.6
Benzo(a)pyrene	24	0.34	98.6	810	4.6	99.4
Benzo(b)fluoranthene	23	0.36	98.4	857	4.1	99.5
Benzo(k)fluoranthene	17	0.22	98.7	533	3.6	99.3
Benzo(ghi)perylene	15	0.20	98.6	457	2.3	99.5
Chrysene	25	0.52	97.9	937	4.7	99.5
Dibenz(a,h)anthracene	<18	<0.76	—	140	<2.9	>97.9
Fluoranthene	76	1.4	98.2	4280	16	99.6
Fluorene	51	1.9	96.3	7290	35	99.5
Indeno(1,2,3-cd)pyrene	15	0.18	98.8	547	2.2	99.6
2-Methylnaphthalene	25	3.7	85.2	6410	83	98.7
Naphthalene	<18	5.1	—	18700	230	98.8
Phenanthrene	92	3.6	96.1	10800	41	99.6
Pyrene	67	1.0	98.5	2810	12	99.6
Total PAHs	**548**	**22**	**96.0**	**70920**	**510**	**99.3**

[a] Concentrations reported in mg/kg (dry weight basis) and are the average of the three optimum runs for each sediment. (Sediment A = Runs 3, 4,and 5; Sediment B = Runs 2, 4, and 5.)

[b] Percent Removals = $$\frac{\text{Feed Concentration - Treated Solids Concentration}}{\text{Feed Concentration}} \text{ X } 100$$

TABLE 5. PCB CONCENTRATIONS AND REMOVAL EFFICIENCIES - SEDIMENTS A AND B FEEDS AND TREATED SOLIDS

	Test Runs						
Parameter	R1	R2	R3	R4[a]	R5	Avg[b]	Standard Deviation[b]
Sediment A							
Total PCBs - Feed (mg/kg - dry weight)	7.33	6.41	8.01	11.8	16.4	10.0/12.1	4.1/4.2
Total PCBs - Treated Solids (mg/kg - dry weight)	<0.07	0.20	0.05	0.04	0.04	0.08/0.04	0.07/0.006
Percent Removal (%)	**>99**	**96.9**	**99.4**	**99.7**	**99.8**	**99.2/99.7**	—
Sediment B							
Total PCBs - Feed (mg/kg - dry weight)	364	316	495	462	497	427/425	82/96
Total PCBs - Treated Solids (mg/kg - dry weight)	1.5	2.1	1.2	1.8	1.4	1.6/1.8	0.35/0.35
Percent Removal (%)	**99.6**	**99.3**	**99.8**	**99.6**	**99.7**	**99.6/99.6**	—

a Concentrations reported for Run 4 are the average of three replicate measurements.

b Two values are given; the first pertains to all five runs and the second pertains to the three optimum runs (Sediment A = Runs 3, 4, and 5 and Sediment B = Runs 2, 4, and 5).

TABLE 6. OIL AND GREASE CONCENTRATIONS AND REMOVAL EFFICIENCIES - SEDIMENTS A AND B FEEDS AND TREATED SOLIDS

	Test Runs						
Parameter	R1	R2	R3	R4[a]	R5[c]	Avg[b]	Standard Deviation[b]
Sediment A							
Total Oil & Grease - Feed (mg/kg - dry weight)	9400	7800	7400	6600	6700	7580/ 6900	1030/436
Total Oil & Grease - Treated Solids (mg/kg - dry weight)	195	169	203	66	65	140/111	69/79
Percent Removal (%)	**97.9**	**97.8**	**97.3**	**99.0**	**99.0**	**98.2/98.4**	—
Sediment B							
Total Oil & Grease - Feed (mg/kg - dry weight)	66,400	116,000	67,300	167,000	99,100	103,000/ 127,000	41,600/ 35,300
Total Oil & Grease - Treated Solids (mg/kg - dry weight)	1800	1330	1490	1230	1810	1530/ 1460	266/310
Percent Removal (%)	**97.3**	**98.9**	**97.8**	**99.3**	**98.2**	**98.5/98.9**	—

a Concentrations reported for Run 4 are the average of three field replicate measurements.

b Two values are given; the first pertains to all five runs and the second pertains to the average of the three optimum runs. (Sediment A = Runs 3, 4, and 5 and Sediment B = Runs 2, 4, and 5.)

c Concentrations reported for Run 5 are the average of samples analyzed in triplicate.

TABLE 7. TRIETHYLAMINE CONCENTRATIONS - SEDIMENTS A- AND B-TREATED SOLIDS, PRODUCT WATER, AND OIL PHASES

		Test Runs[a]						
Parameter	Claim	R1	R2	R3	R4[b]	R5	Avg[c]	Standard Deviation[c]
Sediment A								
Triethylamine in Treated Solids (mg/kg)	<150	61.7	93.1	27.8	28.0	79.6	58/45	29.6/29.8
Triethylamine in Product Water (mg/L)	<80	<1	<1	<1	<1	2.2	<2/<2	—
Triethylamine in Oil Phase (%)	NA	—	—	—	—	—	65.8[d]	—
Sediment B								
Triethylamine in Treated Solids (mg/kg)	<150	106	88.7	55	130	89.3	94/103	27.4/23.7
Triethylamine in Product Water (mg/L)	<80	<1	1.0	<1	<1	<1	<1/<1	NA
Triethylamine in Product Oil (mg/kg)	<1000	—	—	—	—	—	733[d]	—

[a] Concentrations reported for each of the five test runs for each sediment are the average of laboratory triplicate analysis conducted on the sample.

[b] Concentrations reported for Run 4 are the average of three field replicate measurements, each of which are the average of laboratory triplicate analysis.

[c] Two values are given for treated solids and product water; the first pertains to all five runs and the second pertains to the three optimum runs (Sediment A = Runs 3, 4, and 5; Sediment B = Runs 2, 4, and 5).

[d] The % values reported for the Sediment A oil/solvent mixture and the Sediment B product oil are the averages of five aliquot (field replicate) measurements.

Conclusions

The B.E.S.T.® solvent extraction process is designed to treat sludges, soils, and sediments contaminated with organic compounds. The system is capable of physically separating organic contaminants, such as PAHs, PCBs, and oil and grease from contaminated media and concentrating the organics for contaminant volume reduction. The prototype full-scale system is only applicable to sludges, but the proposed full-scale system will be applicable to soils and sediments as well.

This technology has been demonstrated to be effective on organic contaminants from varied sources, including primary steel manufacturing, aluminum manufacturing, petroleum refining, machining operations, and wood treating.

The effectiveness of treatment can be illustrated from this Demonstration and from the previous case studies. This demonstration removed at a minimum 96 percent of the PAHs, greater than 99 percent of the PCBs, and greater than 98 percent of the O&G from the contaminated sediments. Other demonstrations have resulted in PCB removals ranging from 98.8 percent to 99.9 percent, PAH removals ranging from 99 percent to 99.2 percent and an O&G removal of 99.6 percent.

The EPA Project Officer, **Mr. Mark Meckes,** is with the Risk Reduction Engineering Laboratory, Cincinnati, OH 45268 (see below)

The complete report, entitled "Technical Evaluation Report: SITE Program Demonstration; Resources Conservation Company Basis Extractive Sludge Treatment (B.E.S.T.®); Grand Calumet River; Gary, Indiana" (Order No. xxxx-xxx xxx/xx; Cost: $xx.xx, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

A related report, entitled "Application Analysis Report: Resources Conservation Company, Inc. Basic Extractive Sludge Treatment (B.E.S.T.®)(EPA/xxxx/xx-xxx/xxx) is available.

The EPA Project Officer can be contacted at:

Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

"Technical Evaluation Report: SITE Program Demonstration; Resources Conservation Company Basis Extractive Sludge Treatment (B.E.S.T.); Grand Calumet River; Gary, Indiana" (Order No. EPA/540/R-92/079a)

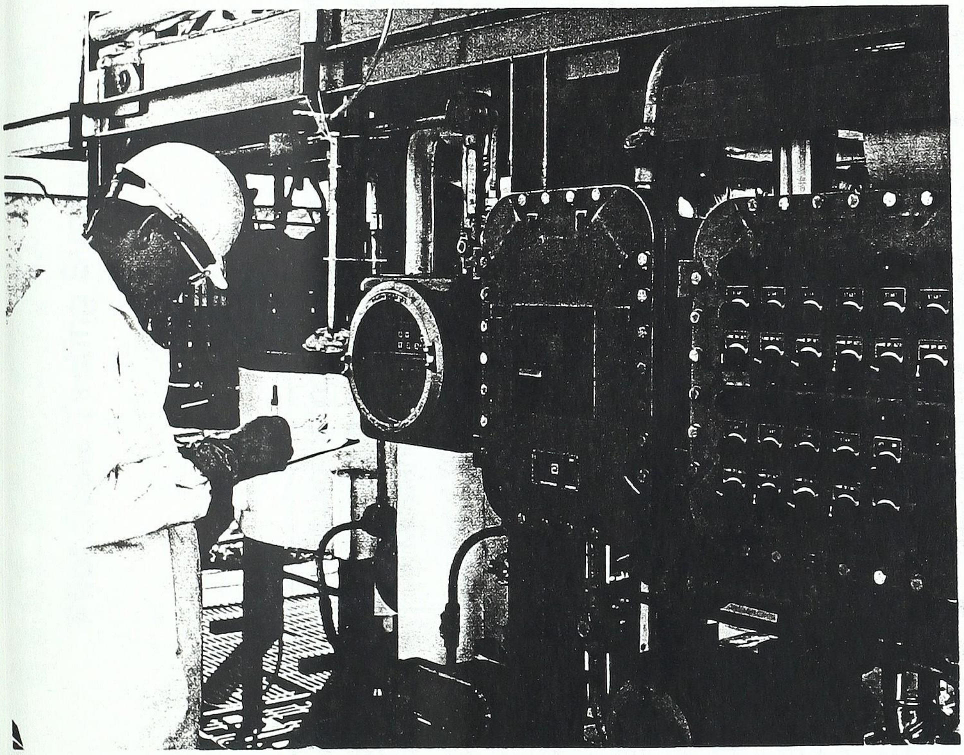
Application Analysis Report: Resources Conservation Company, Inc. Basic Extractive Sludge Treatment (B.E.S.T.) (EPA/540/R-92/079)

Superfund site

Ohio

Ohio site with B.E.S.T. pilot plant in left background.

The B.E.S.T.® pilot plant treated 1000 pounds of soil contaminated with PCBs, exceeding EPA treatment standards.



Taking readings on pilot plant.

Equipment:
B.E.S.T. pilot plant

Features:
- Skid-mounted unit is easily transported by truck
- Separate utility skid provides cooling water and refrigeration
- RCC lab supports field efforts

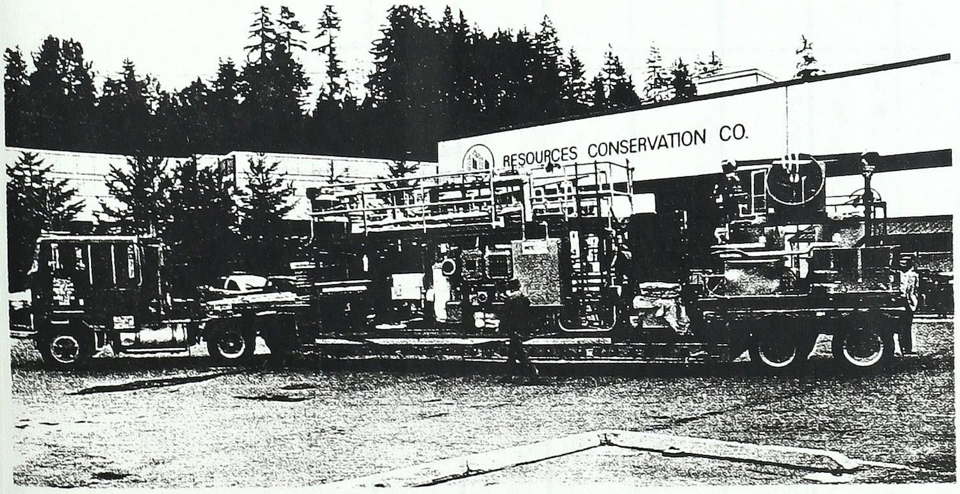
Capacity:
100 pounds/day

Input:
Dry soil with average PCB concentrations of 130 ppm

Output:
Decontaminated soil, with PCB concentrations below EPA standards

PCBs concentrated for final disposal

Operational:
Oct. 23 - Nov. 10, 1989



Skid-mounted pilot plant returning from Ohio.

RCC Resources Conservation Company

3006 Northup Way
Bellevue, Washington
98004-1407

Phone: 206 828-2400
Telex: 350166 RCC SEA
Fax: 206 828-0526

B.E.S.T. Solvent Extraction Process
Pilot Scale Testing Summary

Site Tested	Grand Calumet River	Soluble Oil Lagoon	Waste Lubricating Oil Landfill	60 Acre Lagoon	Sanitary Lagoon	Oily Waste Landfill	Dennison Crossroads
Test Location	Gary, Indiana	Massena, New York	Massena, New York	Massena, New York	Massena, New York	Massena, New York	Massena, New York
Test Sponsor	USEPA S.I.T.E. Program	ALCOA, Massena	ALCOA, Massena	ALCOA, Massena	ALCOA, Massena	ALCOA, Massena	ALCOA, Massena
Time of Test	July 1992	Sep - Oct 1991	Sep - Oct 1991	Sep - Oct 1991	Sep - Oct 1991	Sep - Oct 1991	Sep - Oct 1991
Matrix Tested	Sediment	Sludge	Soil	Sludge	Sludge	Soil	Soil
Target Contaminant(s)	PCBs, PAHs	PCBs	PCBs	PCBs	PCBs	PCBs	PCBs
Source of Contamination	Primary Steel, Coke, Petroleum	Aluminum Mfg.	Aluminum Mfg.	Aluminum Mfg.	Aluminum Mfg.	Aluminum Mfg.	Aluminum Mfg.
Initial Concentration	PCBs-650 mg/kg PAHs-85560 mg/kg	530 mg/kg	800 mg/kg	480 mg/kg	137 mg/kg	13 mg/kg	5 mg/kg
Treated solids Concentration	PCBs-1.0 mg/kg PAHs-670 mg/kg	0.7 mg/kg	1.0 mg/kg	1.0 mg/kg	0.6 mg/kg	0.3 mg/kg	0.2 mg/kg
Test Objective	PAH Removal > 96%	PCBs < 2.0 mg/kg	PCBs < 2.0 mg/kg	PCBs < 2.0 mg/kg	PCBs < 2.0 mg/kg	PCBs < 2.0 mg/kg	PCBs < 2.0 mg/kg
Objectives Met ?	YES	YES	YES	YES	YES	YES	YES

B.E.S.T. Solvent Extraction Process
Pilot Scale Testing Summary

Site Tested	Jennison Wright	Bayou Bonfouca	Textron Inc.	Exxon
Test Location	Vicksburg, Mississippi	Vicksburg, Mississippi	Greenville, Ohio	Baton Rouge Louisiana
Test Sponsor	USEPA CS & D BDAT	USEPA CS & D BDAT	Textron Inc.	Exxon
Time of Test	June, 1991	June, 1991	December, 1989	February 1989
Matrix Tested	Soil	Soil	Soil	Sludge
Target Contaminant(s)	PAHs	PAHs	PCBs	O&G, PAHs
Source of Contamination	Wood Treatment Wastes	Wood Treatment Wastes	Machining Ops. Lubricant Disposal	Petroleum Refining
Initial Concentration	10,900 mg/kg	14,000 mg/kg	130 mg/kg	O&G 26%
Treated solids Concentration	109 mg/kg	8.2 mg/kg	2.5 mg/kg	O&G: 0.09 % PAHs: 11.6 mg/kg
Test Objective	Determine BDAT Std.	Determine BDAT Std.	PCBs < 10 mg/kg	K048-K052 BDAT Std.
Objectives Met ?	YES	YES	YES	YES

ATTACHMENT 4

WTC Analytical Method for PAHs
Second Bench Test

B.E.S.T. BENCH-SCALE TREATABILITY TEST FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

METHOD FOR DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS BY GC/MS

1. SCOPE AND APPLICATION

This method is for the determination of polyaromatic aromatic hydrocarbons (PAHs) in solid samples. A complete list of the compounds to be determined by this method can be found in Table 1.

2. SUMMARY OF METHOD

A ten gram sample is spiked with a known amount of surrogate mixture of deuterated PAHs and then extracted in a Soxhlet apparatus with an acetone-hexane (59:41) solvent mixture. The organic extract is base partitioned with 2% (20 g in 1 L) potassium bicarbonate solution to separate the acidic compounds from the PAHs and other neutral compounds. The aqueous medium is back-extracted with 50 mL of hexane and the organic fractions combined. The combined organic extract is dried through sodium sulphate and concentrated to ca. 3-5 mL.

3. STOCK SOLUTIONS AND STANDARDS

3.1 Hexane is used in making up working standards for the calibration of the target PAHs. Certified standards of the PAHs are obtained and diluted to an appropriate final concentration (200ppm) for storage. All stock solutions and standards are stored at all times in amber vials in the freezer. Diluted standards are not kept longer than two months.

3.2 An internal standard solution is prepared from individual stock solutions prepared and stored at 1000ppm. An internal standard solution of fluoronaphthalene and fluoranthene-d_{10} is prepared in hexane at 50ppm. Each calibration standard and sample extract is combined with 100 microlitres of internal standard mixture just prior to analysis by GC/MS.

3.3 Surrogate solutions are mixed in hexane from individual stock solutions prepared in the laboratory at 1000ppm in toluene. Each sample is spiked with a known level of surrogate mixture and the recoveries are recorded and tracked after analysis. The surrogate is made up of naphthalene-d_8, acenaphthene-d_{10}, fluorene-d_{10}, phenanthrene-d_{10}, pyrene-d_{10}, and chrysene-d_{12} at 50ppm each.

3.4 Calibration standards for the analysis of the samples are prepared just prior to analysis, at the same time that the sample extracts are mixed with internal standard. These standards contain a mixture of the PAH target compounds, the deuterated PAH surrogate mixture, as well as the internal standard. Calibration standards are prepared at 0.5ppm, 1.0ppm, 5.0ppm, 10.0ppm, 25.0ppm and 50.0ppm.

4. EQUIPMENT OPERATION

GC/MS: HP 5890 GC equipped with a DB-5, 30m narrowbore column (0.25mm ID), 0.25um film thickness interfaced to an HP 5988 mass spectrometer.

GC/MS Operating conditions are as follows:

GC temperature program:	initial temperature 30 °C, hold for 1.0 minute ramp at 6 degrees/minute to 285 °C, hold 16.5 minutes
Electron multiplier voltage:	autotune value
GC/MS Interface Temperature:	280 °C
MS Source Temperature:	250 °C

5. SAMPLE COLLECTION AND HANDLING

5.1 All samples must be stored in amber glass jars with teflon lined caps.

5.2 All samples must be kept refrigerated at 4 °C from the time of collection until extraction.

5.3 No sample preservation is necessary.

5.4 Extraction should occur within 7 days of sample collection.

6. SAMPLE EXTRACTION

6.1 The sample is allowed to come to room temperature.

6.2 Approximately 10 grams of the sample is removed from the sample container and weighed accurately into a tared cellulose Soxhlet thimble. If the sample is inhomogeneous, then the subsample should be taken by coning and quartering the entire sample in successive steps as required to achieve the approximate sample weight. Simultaneously, a representative sample is weighed into a tared container and placed in an oven at 110°C overnight for a moisture content determination.

6.3 The thimble is placed in a Soxhlet extractor fitted with a 500 mL round bottom flask containing 350 mL acetone:hexane (59:41) and a few boiling chips. The sample is spiked with 1.0 mL of the deuterated PAH surrogate mixture. The temperature of the Soxhlet heating mantle is adjusted to obtain a reflux of approximately 5 cycles/hour. After extracting for 20 hours, the Soxhlet apparatus is dismantled and the sediment is discarded.

6.4 When the solvent in the 500 mL round bottom flask has cooled, it is transferred to a 1 litre separatory funnel and 400 mL of 2% potassium bicarbonate is added. The funnel is shaken vigorously for 1 minute with frequent venting. The layers are allowed to separate. The aqueous (bottom) layer is drained into a 500mL separatory funnel. Fifty (50) mL of hexane is added to the aqueous phase in the 500 mL separatory funnel and the funnel is shaken vigorously for 1 minute with frequent venting.

6.5 The two organic layers in the separatory funnels are passed through a 65 mm diameter glass funnel plugged with silanized glass wool and filled with anhydrous sodium sulphate and collected in a 500 mL round bottom flask. The separatory funnels are washed with 2 x 10 mL hexane which is passed through the sodium sulphate. The combined organic extract is rotary evaporated with a 30°C water bath, to ca. 3 mL. The extract is submitted for GC/MS analysis.

7. SAMPLE ANALYSIS

7.1 Just prior to analysis by GC/MS calibration standards and check standards are mixed in the following manner:

MIX

0.5	PAH "Supelpreme" Mix at 200ppm
0.6	Deuterated PAH surrogate at 100ppm
0.5	DCM

1.6 mL

STD 50	STD 25	STD 10
0.4mL MIX	0.2mL MIX	0.08mL MIX
0.1mL ISTD	0.2mL Hexane	0.32mL Hexane
	0.1mL ISTD	0.1mL ISTD

STD 5	STD 1	STD 0.5
0.4mL 1:10* MIX	0.08mL 1:10* MIX	0.04mL 1:10* MIX
0.1mL ISTD	0.32mL Hexane	0.36mL Hexane
	0.1mL ISTD	0.1mL ISTD

* 1:10 Dilution of MIX in hexane

7.2 Four hundred (400) microlitres of the sample extract is combined with 100 microlitres of the internal standard.

7.3 Five point (minimum) calibration curves are constructed for each of the target and surrogate compounds. If any parameter in a sample is found at a concentration higher than the highest calibration standard, the sample is diluted and rerun for that parameter.

7.4 For parameters that are below the lowest calibrated level, a single-point calibration with the lowest standard is used for quantitation.

7.5 All target concentrations are reported on a dry weight basis. Surrogates are reported based on a percent recovery of the amount spiked into the original sample.

8. QUALITY CONTROL

8.1 Check standards are analyzed after every five samples in the GC/MS run. Check standards are extra standards which are mixed just prior to analysis which are used to monitor instrument performance and to verify the calibration curves for that particular set of samples.

8.2 Internal standards are used to monitor instrument performance and to correct for any fluctuations.

8.3 Surrogate recoveries are checked to monitor the efficiency of the sample extraction. The recoveries are checked to make sure they fall within acceptable limits of recovery which have been set based on historical data.

8.4 Sample blanks are extracted and run with each sample set to determine if there are any interferences which may have arisen from the extraction method itself.

8.5 Sample duplicates are extracted and run to demonstrate the reproducibility of the method as well as the homogeneity of the sub-sampling procedure.

8.6 Duplicates, surrogate recoveries and blanks are all charted by a laboratory information management system (LIMS).

TABLE 1 - POLYNUCLEAR AROMATIC HYDROCARBONS

PAHs
NAPHTHALENE
ACENAPHTHYLENE
ACENAPHTHENE
FLUORENE
PHENANTHRENE
ANTHRACENE
FLUORANTHENE
PYRENE
BENZO(A)ANTHRACENE
CHRYSENE
BENZO(B)FLUORANTHENE
BENZO(K)FLUORANTHENE
BENZO(A)PYRENE
INDENO(1,2,3-C,D)PYRENE
DIBENZO(A,H)ANTHRACENE
BENZO(G,H,I)PERYLENE

August 6/1993

SOXHLET METHOD FOR THE GC/MS ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS IN SOLID MATRICES

SCOPE AND APPLICATION

This method is applicable to the qualitative and quantitative gas chromatographic/mass spectrometric determination of polynuclear aromatic hydrocarbons (PAHs) in solid samples. It has been used for oily sludges and sewage treatment plant sludges.

PRINCIPLE AND THEORY

The sample is spiked with a known amount of surrogate mixture of deuterated PAHs and then extracted in a Soxhlet apparatus with an acetone-hexane (59:41) solvent mixture.
The organic extract is base partitioned with 2% (20 g in 1 L) potassium bicarbonate solution to separate the acidic compounds from the PAHs and other neutral compounds.
The aqueous medium is back-extracted with 50 mL of hexane and the organic fractions combined. The combined organic extract is dried through sodium sulphate and concentrated to ca. 3-5 mL.

SAMPLING PROCEDURE AND STORAGE

Sludge samples should be collected and frozen immediately in an all-glass system or metal container. Teflon-lined caps are recommended for the sample jars to prevent contamination of the sediment from contact from the cap. If Teflon lining is unavailable, the use of solvent washed aluminum foil beneath the cap is acceptable. Samples should be kept frozen, in the dark, and should be extracted as soon as possible.

SAMPLE PREPARATION

No special preparation is required.

PROCEDURE

Weigh a 10.0 g (this amount may vary - discuss with analyst first) sample of a homogeneous sludge sample into a cellulose thimble. Simultaneously, weigh a representative sample aliquot into a tared container and place in a drying oven at approximately 110°C overnight. Remove from oven and let cool and weigh for moisture content determination.

Spike the sample with the deuterated surrogates of the target PAHs. Place the thimble in a Soxhlet extraction tube fitted with a 500 mL round bottom flask containing 350 mL acetone/hexane (59:41) and a few boiling chips. Adjust the temperature of the Soxhlet heating mantle to obtain a reflux of approximately 5 cycles/hour. After extracting for 20 hours, dismantle the Soxhlet apparatus and discard the sediment.

When the solvent in the 500 mL round bottom flask has cooled, transfer to a 1 L separatory funnel and add 400 mL of 2% potassium bicarbonate. Shake vigorously for 1 min. with frequent venting. Allow the layers to separate and drain the aqueous (bottom) layer into a 500mL separatory funnel. Add 50 mL hexane to the aqueous phase in the 500 mL separatory funnel and shake vigorously for 1 minute with frequent venting.

Pass the two organic layers in the separatory funnels through a 65 mm diameter glass funnel plugged with silanized glass wool and filled with sodium sulphate. Collect in a 500 mL round bottom flask. Wash the separatory funnels with 2 x 10 mL hexane and pass through the sodium sulphate. Rotary evaporate the combined organic extract with a 30°C water bath, to an appropriate final volume. The extract is submitted for GC/MS analysis.

REMARKS

For extremely dirty sludge samples, it is recommended that a dilution be made prior to analysis (up to 100 times dilution).

REFERENCES

(1) Lee,H.B., Dookhran, G., and Chau, A.S.Y., Analyst, 1987, 112, 31.

FACSIMILE COVER SHEET
RESOURCES CONSERVATION COMPANY
LABORATORY FACILITY
11113 N.E. 33rd Place
Bellevue, WA 98004

Date: 3/25/94

To: Wayne Randle

Firm or Company: WTC

From: Jay Swift

Number of pages including cover sheet: 1

Receiving Operator's Phone Number: 905-336-8914	FAX Machine Phone Number: 905-336-8913

We are transmitting from a Panasonic Panafax Model 145, 206/828-4143, whose speed adjusts automatically. If you are having difficulty with this transmission, please call 206/828-2400, ext. 477.

Wayne,

Here is a copy of RCC's deviations (small) to the PAH method. I faxed this earlier to Brian MacGilivray and Pat Falletta. Pat and I agreed that it was OK over the phone.

As agreed to in phone conversations with Brian and Pat:

The following are RCC's deviations for the "Method for Determination of Polynuclear Aromatic Hydrocarbons by GC/MS" supplied by WTC:

- A Finnigan ITD-MS Mass Spectrometer will be employed instead of the prescribed HP5988.
- A J&W DB5.625 column will be used instead of the DB5 described. The column and film dimensions are identical; the stationary phase is virtually identical -- the DB5.625 gives you more inertness and less column bleed.
- RCC will substitute 1,4 Dichlorobenzene and Perylene-(d12) for Fluorene-(d10) and Pyrene-(d10) as surrogates. The other four surrogates will be identical.

Please call if you have comments or questions.

ATTACHMENT 5

Subcontractor Lab Report for PAHs
First Bench Test
(US EPA Analytical Method)

B.E.S.T. BENCH-SCALE TREATABILITY TEST FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

SOUND ANALYTICAL SERVICES, INC.

SPECIALIZING IN INDUSTRIAL & TOXIC WASTE ANALYSIS

4813 PACIFIC HIGHWAY EAST, TACOMA, WASHINGTON 98424 - TELEPHONE (206)922-2310 - FAX (206)922-5047

TRANSMITTAL MEMORANDUM

DATE: March 11, 1994

TO: Shirley Schartung
Resources Conservation Co.

PROJECT NAME: WTC/Thunder Bay
LABORATORY NUMBER: 38240

Enclosed are the original and one copy of the Tier I data deliverables package for Laboratory Work Order Number 38240. Four samples were received for analysis at Sound Analytical Services, Inc., on February 22, 1994.

Semivolatile Organic results are presented in spreadsheet format; all other results are in the standard format.

If there are any questions regarding this data package, please do not hesitate to call me at (206) 922-2310.

Sincerely,

Lela A Transue

for Thomas Boyden
Project Manager

TB:tm

port is issued solely for the use of the person or company to whom it is addressed. This laboratory accepts responsibility only for the due performance of analysis in accordance with
y acceptable practice. In no event shall Sound Analytical Services, Inc. or its employees be responsible for consequential or special damages in any kind or in any amount

SOUND ANALYTICAL SERVICES, INC.

SPECIALIZING IN INDUSTRIAL & TOXIC WASTE ANALYSIS

4813 PACIFIC HIGHWAY EAST, TACOMA, WASHINGTON 98424 - TELEPHONE (206)922-2310 - FAX (206)922-5047

Report To: Resources Conservation Co. Date: March 4, 1994

Report On: Analysis of Solid Lab No.: 38240

IDENTIFICATION:

Samples received on 02-22-94

Project: WTC/Thunder Bay

ANALYSIS:

Lab Sample No. 38240-1

Client ID: 940208-01
Contaminated
Sediment

TPH Per EPA Method 418.1
Date Extracted: 3-3-94
Date Analyzed: 3-3-94
Units: mg/kg

Parameter	Result	PQL	Flag
Total Petroleum Hydrocarbons	1,100	23	

Lab Sample No. 38240-2

Client ID: 940208-2
3rd Extraction
Solids

TPH Per EPA Method 418.1
Date Extracted: 3-3-94
Date Analyzed: 3-3-94
Units: mg/kg

Parameter	Result	PQL	Flag
Total Petroleum Hydrocarbons	120	10	

ND - Not Detected
PQL - Practical Quantitation Limit

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Resources Conservation Co.
Project: WTC/Thunder Bay
Lab No. 38240
March 4, 1994

Lab Sample No. 38240-3

Client ID: 940208-03
6th Extraction
Solids

TPH Per EPA Method 418.1
Date Extracted: 3-3-94
Date Analyzed: 3-3-94
Units: mg/kg

Parameter	Result	PQL	Flag
Total Petroleum Hydrocarbons	2,100	10	

Lab Sample No. 38240-4

Client ID: 940208-04
9th Extraction
Solids

TPH Per EPA Method 418.1
Date Extracted: 3-3-94
Date Analyzed: 3-3-94
Units: mg/kg

Parameter	Result	PQL	Flag
Total Petroleum Hydrocarbons	83	10	

ND - Not Detected
PQL - Practical Quantitation Limit

port is issued solely for the use of the person or company to whom it is addressed. This laboratory accepts responsibility only for the due performance of analysis in accordance with
acceptable practice. In no event shall Sound Analytical Services, Inc. or its employees be responsible for consequential or special damages in any kind or in any amount

QUALITY CONTROL REPORT

TPH Per EPA Method 418.1

Client:	Resources Conservation Co.
Lab No:	38240qc
Units:	mg/kg

METHOD BLANK

Date Extracted: 3-3-94
Date Analyzed: 3-3-94

Parameter	Result	PQL
Total Petroleum Hydrocarbons	ND	10

ND - Not Detected
PQL - Practical Quantitation Limit

ort is issued solely for the use of the person or company to whom it is addressed. This laboratory accepts responsibility only for the due performance of analysis in accordance with acceptable practice. In no event shall Sound Analytical Services, Inc. or its employees be responsible for consequential or special damages in any kind or in any amount.

SOUND ANALYTICAL SERVICES, INC.

Client Name	Resource Conservation Co.
Client ID:	940208-01 Contaminated Sediment
Lab ID:	38240-1
Date Received:	2/22/94
Date Extracted:	2/24/94
Date Analyzed:	2/26/94

Semivolatile Organics by USEPA Method 8270

Surrogate	**% Recovery**	**Flags**	**Recovery Limits**	
			Low	**High**
Nitrobenzene - d5	75		23	120
2 - Fluorobiphenyl	76		30	115
p - Terphenyl - d14	115		18	137

Sample results are on an as received basis.

Analyte	**Result (ug/kg)**	**PQL**	**Flags**
Naphthalene	78000	1900	
Acenaphthylene	ND	1900	
Acenaphthene	21000	1900	
Fluorene	18000	1900	
Phenanthrene	79000	1900	
Anthracene	9000	1900	
Fluoranthene	48000	1900	
Pyrene	43000	1900	
Benzo(a)anthracene	14000	1900	
Chrysene	ND	1900	
Benzo(b)fluoranthene	22000	1900	
Benzo(k)fluoranthene	ND	1900	
Benzo(a)pyrene	10000	1900	
Indeno(1,2,3-cd)pyrene	ND	1900	
Dibenz(a,h)anthracene	ND	1900	
Benzo(g,h,i)perylene	4400	1900	

SOUND ANALYTICAL SERVICES, INC.

Client Name	Resource Conservation Co.
Client ID:	940208-2 3rd Extraction Solids
Lab ID:	38240-2
Date Received:	2/22/94
Date Extracted:	3/8/94
Date Analyzed:	3/9/94

Semivolatile Organics by USEPA Method 8270

Surrogate	% Recovery	Flags	Recovery Limits Low	Recovery Limits High
Nitrobenzene - d5	43		23	120
2 - Fluorobiphenyl	44		30	115
p - Terphenyl - d14	59		18	137

Sample results are on an as received basis.

Analyte	Result (ug/kg)	PQL	Flags
Naphthalene	4800	310	D
Acenaphthylene	ND	62	
Acenaphthene	860	62	
Fluorene	860	62	
Phenanthrene	4500	310	D
Anthracene	680	62	
Fluoranthene	2800	310	D
Pyrene	1900	310	D
Benzo(a)anthracene	680	62	
Chrysene	510	62	
Benzo(b)fluoranthene	910	62	
Benzo(k)fluoranthene	270	62	
Benzo(a)pyrene	530	62	
Indeno(1,2,3-cd)pyrene	300	62	
Dibenz(a,h)anthracene	43	62	J
Benzo(g,h,i)perylene	230	62	

SOUND ANALYTICAL SERVICES, INC.

Client Name	Resource Conservation Co.
Client ID:	940208-03 6th Extraction Solids
Lab ID:	38240-3
Date Received:	2/22/94
Date Extracted:	3/8/94
Date Analyzed:	3/9/94

Semivolatile Organics by USEPA Method 8270

Surrogate	% Recovery	Flags	Recovery Limits Low	Recovery Limits High
Nitrobenzene - d5	15	X9	23	120
2 - Fluorobiphenyl	23	X9	30	115
p - Terphenyl - d14	28		18	137

Sample results are on an as received basis.

Analyte	Result (ug/kg)	PQL	Flags
Naphthalene	1700	180	D
Acenaphthylene	ND	35	
Acenaphthene	130	35	
Fluorene	130	35	
Phenanthrene	540	180	D
Anthracene	130	35	
Fluoranthene	140	35	
Pyrene	79	35	
Benzo(a)anthracene	ND	35	
Chrysene	32	35	J
Benzo(b)fluoranthene	60	35	
Benzo(k)fluoranthene	18	35	J
Benzo(a)pyrene	34	35	J
Indeno(1,2,3-cd)pyrene	25	35	J
Dibenz(a,h)anthracene	ND	35	
Benzo(g,h,i)perylene	17	35	J

SOUND ANALYTICAL SERVICES, INC.

Client Name	Resource Conservation Co.
Client ID:	940208-04 9th Extraction Solids
Lab ID:	38240-4
Date Received:	2/22/94
Date Extracted:	3/8/94
Date Analyzed:	3/9/94

Semivolatile Organics by USEPA Method 8270

Surrogate	% Recovery	Flags	Recovery Limits Low	Recovery Limits High
Nitrobenzene - d5	17	X9	23	120
2 - Fluorobiphenyl	28	X9	30	115
p - Terphenyl - d14	35		18	137

Sample results are on an as received basis.

Analyte	Result (ug/kg)	PQL	Flags
Naphthalene	1100	160	D
Acenaphthylene	7.7	33	J
Acenaphthene	17	33	J
Fluorene	3.8	33	J
Phenanthrene	190	160	D
Anthracene	38	33	
Fluoranthene	41	33	
Pyrene	25	33	J
Benzo(a)anthracene	7.8	33	J
Chrysene	9	33	J
Benzo(b)fluoranthene	18	33	J
Benzo(k)fluoranthene	6.3	33	J
Benzo(a)pyrene	7.7	33	J
Indeno(1,2,3-cd)pyrene	7.8	33	J
Dibenz(a,h)anthracene	ND	33	
Benzo(g,h,i)perylene	4.9	33	J

Client Name	Resource Conservation Co.
Client ID:	-
Lab ID:	Method Blank - s11216
Date Received:	-
Date Extracted:	2/24/94
Date Analyzed:	2/25/94

Semivolatile Organics by USEPA Method 8270

Surrogate	% Recovery	Flags	Recovery Limits Low	Recovery Limits High
Nitrobenzene - d5	75		23	120
2 - Fluorobiphenyl	75		30	115
p - Terphenyl - d14	121		18	137

Sample results are on an as received basis.

Analyte	Result (ug/kg)	PQL	Flags
Naphthalene	ND	670	
Acenaphthylene	ND	670	
Acenaphthene	ND	670	
Fluorene	ND	670	
Phenanthrene	ND	670	
Anthracene	ND	670	
Fluoranthene	ND	670	
Pyrene	ND	670	
Benzo(a)anthracene	ND	670	
Chrysene	ND	670	
Benzo(b)fluoranthene	ND	670	
Benzo(k)fluoranthene	ND	670	
Benzo(a)pyrene	ND	670	
Indeno(1,2,3-cd)pyrene	ND	670	
Dibenz(a,h)anthracene	ND	670	
Benzo(g,h,i)perylene	ND	670	

Client Name	Resource Conservation Co.
Client ID:	-
Lab ID:	Method Blank - s11245
Date Received:	-
Date Extracted:	3/8/94
Date Analyzed:	3/8/94

Semivolatile Organics by USEPA Method 8270

Surrogate	% Recovery	Flags	Recovery Limits Low	Recovery Limits High
Nitrobenzene - d5	65		23	120
2 - Fluorobiphenyl	61		30	115
p - Terphenyl - d14	99		18	137
Phenol - d5	16		24	113
2 - Fluorophenol	32		25	121
2,4,6 - Tribromophenol	63		19	122

Sample results are on an as received basis.

Analyte	Result (ug/kg)	PQL	Flags
Naphthalene	ND	33	
Acenaphthylene	ND	33	
Acenaphthene	ND	33	
Fluorene	ND	33	
Phenanthrene	ND	33	
Anthracene	ND	33	
Fluoranthene	ND	33	
Pyrene	ND	33	
Benzo(a)anthracene	ND	33	
Chrysene	ND	33	
Benzo(b)fluoranthene	ND	33	
Benzo(k)fluoranthene	ND	33	
Benzo(a)pyrene	ND	33	
Indeno(1,2,3-cd)pyrene	ND	33	
Dibenz(a,h)anthracene	ND	33	
Benzo(g,h,i)perylene	ND	33	

SOUND ANALYTICAL SERVICES, INC.

4813 PACIFIC HIGHWAY EAST, TACOMA, WASHINGTON 98424 • TELEPHONE 206-922-2310 • FAX 206-922-5047

DATA QUALIFIER FLAGS

: The analyte was analyzed for and positively identified, but the associated numerical value is an estimated quantity.

B1: This analyte was also detected in the associated method blank. The reported sample results have been adjusted for moisture, final exract volume, and/or dilutions performed during extract preparation. The analyte concentration was evaluated prior to sample preparation adjustments, and was determined not to be significantly higher than the associated method blank (less than ten times the concentration reported in the blank).

B2: This analyte was also detected in the associated method blank. However, the analyte concentration in the sample was determined to be significantly higher than the method blank (greater than ten times the concentration reported in the blank).

E: The concentration of this analyte exceeded the instrument calibration range.

D: The reported result for this analyte is calculated based on a secondary dilution factor.

X1: Contaminant does not appear to be "typical" product. Elution pattern suggests it may be

______________________________.

X2: Contaminant does not appear to be "typical" product. Further testing is suggested for identification.

X3: Identification and quantification of peaks was complicated by matrix interference; GC/MS confirmation is recommended.

X4: RPD for duplicates outside QC limits. Sample was re-analyzed with similar results.

X4a: RPD for duplicates outside QC limits due to analyte concentration near the method practical quantitation limit/detection limit.

X5: Matrix spike was diluted out during analysis.

X6: Recovery of matrix spike outside QC limits. Sample was re-analyzed with similar results.

X7: Recovery of matrix spike outside QC limits. Matrix interference is indicated by blank spike recovery data.

X7a: Recovery and/or RPD values for MS/MSD outside QC limits due to high contaminant levels.

X8: Surrogate was diluted out during analysis.

X9: Surrogate recovery outside QC limits due to matrix composition.

RCC Resources Conservation Company

11113 NE 33rd Place
Bellevue, WA 98004-1407
Phone (206) 828-2400 Fax (206) 828-4143

Chain of Custody Record

Custody ID	000024	**Return Original**	Yes
Client / Project	WTC / Thunder Bay	**Shipped From**	RCC Lab
Prepared By	SCS	**Shipped To**	Sound Analytical
Date Shipped	2/22/94	**Shipped VIA**	Sound Analytical

Comments PAHs are by Method 8270 and we need these on a 5 day turnaround. The CAL ST TPH (GC/FID) we just need a 10 day turnaround.

Sample Number and Description	Comp/ Grab	Number of Jars	Analysis To Be Performed	Preservation
940208-01 Contaminated Sediment	Grab	1	PAHs Cal St TPH (GC/FID)	None
940208-02 3rd Extraction Solids	Grab	1	PAHs Cal St TPH (GC/FID)	None
940208-03 6th Extraction Solids	Grab	1	PAHs Cal St TPH (GC/FID)	None
940208-04 9th Extraction Solids	Grab	1	PAHs Cal St TPH (GC/FID)	None

Relinquished By: (Name/Signature/Organization)	Date/Time	Accepted By: (Name/Signature/Organization)	Date/Time
S. Schatun (SCHARTUNG)	2/22	2-22	-94 10:30
Relinquished By: (Name/Signature/Organization) SAS	Date/Time 2-22 12:25P	Accepted By: (Name/Signature/Organization) Mary Cuter	Date/Time 2/22/94 12:25
Relinquished By: (Name/Signature/Organization)	Date/Time	Accepted By: (Name/Signature/Organization)	Date/Time

ATTACHMENT 6

Comparative Analytical Results WTC versus US EPA PAH Analytical Methods

B.E.S.T. BENCH-SCALE TREATABILITY TEST FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

THUNDER BAY
First Treatability Study
Ninth Solids
PAH Analytical Method Comparison
All results in ppb

	WTC Method (RCC #940208-04)	US EPA Method (RCC #940208-04)
Naphthalene2,400	1,100	
Acenaphthylene	< 100	8 [1]
Acenaphthene	115	17 [1]
Fluorene	< 100	4 [1]
Phenanthrene	640	190
Anthracene	140	38
Fluoranthene	< 100	41
Pyrene	< 100	25 [1]
Benzo(a)anthracene	< 100	8 [1]
Chrysene	< 500	9 [1]
Benzo(b+k)fluoranthene [3]	< 1,000	24 [1]
Benzo(a)pyrene	< 500	8 [1]
Indeno(1,2,3-cd)pyrene	< 500	8 [1]
Dibenzo(a, h)anthracene	< 500	ND [2]
Benzo(g, h, i)perylene	< 500	5 [1]
TOTALS	3,300	1,500

---

[1] Estimated.

[2] PQL 33.

[3] The sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene is reported.

ATTACHMENT 7

WTC Audit Report
of
RCC Laboratory

B.E.S.T. BENCH-SCALE TREATABILITY TEST
FINAL REPORT

Thunder Bay Site

for

Wastewater Technology Centre

Wastewater Technology Centre
operated by RockCliffe Research Management Inc.

Centre Technique des Eaux Usées
dirigé par Gestion de Recherche RockCliffe Inc.

867 Lakeshore Road
P.O. Box 5068, Burlington
Ontario, Canada, L7R 4L7
✆ (416) 336-4855
Fax (416) 336-4765

wtc

File-N/Reference
Project 4895

30 May 1994

Mr. James C. Nowak
Laboratory Manager
Resources Conservation Company
3006 Northup Way
Bellevue, WA
98004-1407

Dear Mr. Nowak:

RE: B.E.S.T. Solvent Extraction Process- COSTTeP Treatability Study Draft Report

We have completed our review of your revised draft report for the Thunder Bay Harbour sediment treatability investigations, dated May 1994. Specific comments and suggestions for revision to be included in the final report have been marked within the text of the enclosed original copy of the draft report. In general, the report was well written and the format presented was consistent with requirements for reporting for the COSTTeP program. One requirement we do have, however, is the inclusion of cost estimates for conducting pilot scale and full scale studies on Thunder Bay Harbour sediments. If possible, can you provide cost estimates based upon treatment of 40,000-150,000 m^3 of contaminated sediment.

The attachment of this letter concerns the WTC audit conducted at the RCC laboratory on March 22. This audit report should be included as an Appendix in your final report.
If you have any questions or concerns about our review, please feel free to contact me at (905) 336-8914.

Yours Sincerely,

Wayne Randle

Wayne Randle
Contaminated Sediment Treatment Technology Program
Site Remediation Division

enclosures

cc. Craig Wardlaw

B.E.S.T. Solvent Extraction Process
Bench-scale Demonstration and WTC Laboratory Audit

Wastewater Technology Centre (WTC) personnel visited the RCC laboratory on March 22 to observe the B.E.S.T treatability study conducted with Thunder Bay Harbour Sediment. The bench study was conducted by RCC under contract to the WTC as part of the Contaminated Sediment Treatment Technology Program (Environment Canada's Great Lakes Cleanup Fund).

During the WTC visit arrangements were made with the Project Leader, Mr. Jim Nowak, to have samples of untreated sediment, extracted solids, and oil concentrate sent to the WTC for analysis in WTC laboratories. This exercise was conducted as a standard check on the quality of the analytical data generated in all CoSTTeP studies conducted under contract to WTC.

This letter and its enclosures summarize the WTC analytical data and my observations based on a comparison with the RCC data in the draft report. Both the letter and enclosures should be included in an appendix in the final report.

Raw sediment and solids samples from the sixth, and ninth extractions in addition to product oil recovered from rotary evaporation were analysed for polycyclic aromatic hydrocarbons (PAHs). Table 1 compares WTC's laboratory analytical results for the split samples to the results reported by RCC for the second bench test (see pages 17, & 21). To ensure the validity of the comparison, both the WTC and RCC laboratories performed analytical testing for PAH's as per the method described in Attachment 4 of the draft report.

There is generally very good agreement between the WTC and RCC data (Table 1.) for the untreated sediment, the extracted solids, and the recovered product oil concentrate. Both laboratories detected relatively low (< 10 µg/g) concentrations of the individual PAH's in the extracted solids, while the contaminant rich oil phase, was measured at approximately 62,000 and 59,300 µg/g total PAH (the sum of the 16 priority PAH compounds) by the WTC and RCC laboratories, respectively. From these results, it was clear that the B.E.S.T process was relatively effective at separating the contamination from the Thunder Bay Harbour sediment. A total of nine extractions were required to reduce (reduction efficiency of 99%) the PAH contamination of the raw sediment to just slightly below (RCC data) the Ontario Lowest Effects Level of 4 µg/g. With the establishment of the technical merit of this technology, a detailed cost assessment would be necessary to determine its pilot and full-scale potential for treating large volumes of highly contaminated sediment, as in the case of Thunder Bay Harbour sediments.

POLYCYCLIC AROMATIC HYDROCARBONS	Raw Sediment		6th Extraction Solids		9th Extraction Solids		Product Oil		Province of Ontario Sediment Quality Guidelines for Polycyclic Aromatic Hydrocarbons	
	WTC	RCC	WTC	RCC	WTC	RCC	WTC	RCC	Lowest Effect Level	Severe Effect Level[1]
Naphthalene	151	85	2.0	2.0	2.8	2.0	14	< 30	NA	NA
Acenaphthylene	3.0	2.0	< 0.3	0.03	< 0.3	0.02	160	180	NA	NA
Acenaphthene	74	53	< 0.4	0.16	< 0.4	0.12	100	84	NA	NA
Fluorene	64	48	< 0.3	0.05	< 0.3	0.05	340	320	0.190	7.36
Phenanthrene	252	185	1.3	0.80	0.80	0.54	7700	7,700	0.560	43.7
Anthracene	32	24	< 0.3	0.33	< 0.3	0.18	1300	1,200	0.220	17.0
Fluoranthene	168	118	0.3	0.40	0.22	0.18	14,700	15,000	0.750	46.9
Pyrene	100	91	< 0.4	0.23	< 0.4	0.12	11,500	12,000	0.490	39.1
Benzo(a)anthracene	36	23	< 0.4	0.09	< 0.4	0.04	4700	2500	0.320	68.0
Chrysene	26	37	< 0.2	0.10	< 0.2	0.15	3600	4500	0.340	21.2
Benzo(b+k)fluoranthene	54	68	< 0.4	< 1.0	< 0.4	0.20	8600	7400	0.240	61.6
Benzo(a)pyrene	27	33	< 0.2	< 0.5	< 0.2	0.06	4200	2400	0.370	66.2
Indeno(1,2,3-c,d)pyrene	14	25	< 0.3	< 0.5	< 0.3	< 0.05	2100	3400	0.200	14.7
Dibenzo(a,h)anthracene	2	4	w	< 0.5	w	< 0.05	730	520	0.060	5.98
Benzo(g,h,i)perylene	13	16	< 0.3	< 0.5	< 0.3	< 0.05	2200	2100	0.170	14.7
Total:	1016	812	4.6-7.1*	4.2-7.2*	4.7-7.3*	3.7-3.8*	62,000	59,300	4	460

Notes:
w No detectable response
* Range reflects concentration of PAH's reported below detection limits are at 0% to 100% of the detection limit concentration.
1. Represenets bulk sediment value, calculated from actual TOC (4.6%) content of sediment
All units are μg/g (dry weight) basis unless otherwise stated

TABLE 1. WTC and RCC data. The concentrations of polycyclic aromatic hydrocarbons determined from split samples of the untreated and treated sediment solids from the B.E.S.T. process treatability test performed by RCC using Thunder Bay Harbour sediment.

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