Final Report

Bench Scale Studies of Thunder Bay Harbour Sediment

BioGenesis[SM] *Sediment Washing Process*

... Cleaning Today

for Tomorrow™

FINAL REPORT

BENCH SCALE STUDIES OF THUNDER BAY HARBOUR SEDIMENT

BIOGENESIS WASHING PROCESS

Submitted to:	Wastewater Technology Centre (WTC) 867 Lakeshore Road Burlington, Ontario L7R 4A6
Date:	August 31, 1993
WTC Contract:	No. 2-6020, December 7, 1992

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

File-N/Référénce
3896

January 24, 1994

Mr. Charles Wilde
BioGenesis Enterprises, Inc.
Washington, D.C. Office
10626 Beechnut Court
Fairfax Station, Virginia U.S.A.
22039-3559

Dear Mr. Wilde:

I have reviewed the final Biogenesis report on bench scale studies of Thunder Bay harbour sediment. Based on the findings, I recommended that WTC accept the report.

Please note that I have revised my comments on the report and include a copy of the comments with this letter. A copy of the comments will be incorporated into the final report prior to distributing it.

Sincerely,

John D. Goodin
Site Remediation Division

cc: C. Wardlaw

A REVIEW OF THE FINAL REPORT ON
BENCH SCALE STUDIES OF THUNDER BAY HARBOUR SEDIMENT
BIOGENESIS WASHING PROCESS

General Comments

The Biogenesis report is organized and easy to read. A random check of the tables and graphs presented indicates that data for PAH, Phenols, Hydrocarbons, Metals, PCB, sulphur and TOC are accurate.

Comparison of data from WTC and Galson Laboratories

The "cleaned" sediment at the end of the washing process was analyzed to determine the level of residual contamination. The analyses were performed by the WTC laboratories in Burlington, Ontario and by Galson Laboratories in Syracuse, New York. Table 1 shows the residual levels of PAH, TPH and PCB in the "after cyclone" sample (see Tables III and IV of the report).

TABLE 1

	Contaminant remaining (ppm)	
Contaminant	WTC	Galson
PAH	681	424
TPH	944	400
PCB	0.169	<0.3

The purpose of analyzing the sediment at WTC was to verify the results from Galson. Normally, one would expect the values from both labs to be fairly close, allowing for sampling and analytical error. It is apparent from the results in Table 1 that the labs found different levels of each contaminant in the sediment. This is particularly true for the WTC-TPH value which is more than double the Galson value.

Several factors could account for these discrepancies but perhaps the most important one is the sediment sample itself. Galson composited three sediment samples (MA7, MA8 and MA9) in order to have sufficient sample to analyze. This was done after WTC had obtained their sample for analysis. So in fact, the Galson and WTC samples were not true split samples. This could certainly account for a lot of the variability in the results from the two labs.

With respect to the TPH data, the different extraction procedures used by the labs may have further contributed to the difference in results. Our own experience with TPH analysis suggests that the data could be highly variable regardless of the methods used.

The higher PAH and TPH levels reported by WTC would reduce the % removals given in Tables III and IV of the report. PAH removal would be lowered to 83.14% from 89.5%. TPH removal would decline to 80% from 91.6%. However, given the differences in the sediment samples and analytical procedures, it may be appropriate to report that 80 to 90% of the PAH and TPH were removed.

Overall, it would appear that the Biogenesis washing process was successful in removing contaminants from Thunder Bay sediment. Based on these results the process could be considered a useful and effective technology for the remediation of other sediments.

TABLE 2

Contaminant	Concentration in Sediment (ppm)	
	WTC sample	Galson sample
TOTAL PAH	**13,172**	**4041.9**

Assuming that the WTC and Galson samples were identical, the large difference in total PAH (TPAH) concentrations suggests that WTC recovered more PAH than Galson from the untreated sediment. This trend is consistent with results for the washed sediment (Table 1) and indicates that WTC analytical methods were consistently biased towards higher contaminant concentrations.

Based on WTC data given in Tables 1 and 2, washing removed up to 94.82% of the PAH in the sediment. This result is higher than the 89.5% removal based on the Galson data (Table 3 of the Biogenesis Report). Approximately 80% of the TPH was removed, based on the initial Galson value (Table 4 of the BioGenesis Report) and the final WTC value (Table 1). This result is lower than the 91.6% removal based on the Galson data (Table 4 of the Biogenesis Report). TPH removal could be significantly higher if there is a similar bias in the WTC-TPH analytical method, however, this was not confirmed.

Given the differences in sediment samples and analytical procedures, it may be appropriate to report that 90 to 95% of the PAH and 80 to 92% of the TPH were removed by the Biogenesis washing process.

Overall, it would appear that the Biogenesis washing process was successful in removing contaminants from Thunder Bay sediment. Based on these results the process could be considered a useful and effective technology for the remediation of other sediments.

Abstract

Sediment contaminated from former wood-treating operations at Thunder Bay Harbour, Ontario, was washed in BioGenesis[SM] sediment washing equipment. Pre-washing contamination levels tested at 9% oil and grease; 2% semi-volatile hydrocarbons; 5,000 ppm total petroleum hydrocarbons; and 4,000 ppm poly-aromatic hydrocarbons. Over 80% of the sediment was medium silt and finer. Results using a prototype pilot washing machine showed extraction efficiencies of 96% oil and grease, 92% TPH, 90% SVHCs, and 90% PAHs. BioGenesis Enterprises, Inc. projects extraction efficiencies at full scale of 97 to 99% for PAHs. Future tests are planned for extracting PCBs, dioxins, pesticides, and metals from sediment.

Table of Contents

List of Figures

List of Tables

I. Introduction

In mid-1992 Wastewater Technology Centre (WTC) requested proposals for bench scale studies of Thunder Bay Harbour, Ontario, sediment. The testing is part of WTC's Contaminated Sediment Treatment Technology Program sponsored by Environment Canada' Great Lakes Cleanup Fund. The purpose of the program was to assess contaminated sediment treatment technologies which may be used in future years as part of the overall effort to clean up 43 "Areas of Concern" identified by the International Joint Commission, a joint Canada-U.S. body tasked to administer the Great Lakes Water Quality Agreement.

BioGenesis Enterprises, Inc. had responded in 1991 to a similar request for proposal, and offered the BioGenesis℠ Soil Washing process as a candidate for evaluation. BioGenesis℠ soil washing technology was subsequently tested during 1992 in the U.S. EPA Superfund Innovative Technology Evaluation program. Document EPA/540/MR-93/510, BioGenesis Soil Washing Technology Demonstration Bulletin, summarizes the results of that demonstration. At the request of WTC, BioGenesis updated and adapted its 1991 proposal to apply to Thunder Bay sediments. Following refinement of the proposal in conjunction with project authorities, WTC shipped 150 pounds of Thunder Bay sediment to BioGenesis during December 1992. Contracting was finalized in January 1993.

The major contaminants at Thunder Bay Harbour are PAHs, with low levels of PCBs, phenols, and several metals. The PAHs were determined to be the primary target of the washing test. Over 80% of the sediment had grain sizes less than 38 microns, i.e. over 80% was medium silt and finer.

The scope of the contract was to perform a bench scale treatability study by washing sediments from Thunder Bay Harbour. The overall objective was to obtain sufficient information to be able to move from bench to pilot scale testing in succeeding phases of the program.

Dr. Mohsen C. Amiran was the Principal Investigator and responsible for all technical aspects of the work. Dr. Amiran's specialty is physical organic chemistry. He is the developer of all BioGenesis cleaners and the inventor of the BioGenesis washing equipment. Mr. Charles Wilde was the Project Manager and responsible for all administrative, financial, and coordinating aspects of the work. The testing was performed at BioGenesis Enterprises, Inc. facilities at 610 W. Rawson Ave., Milwaukee, Wisconsin 53154, 414/571-2468.

External laboratory services were provided by Galson Laboratories, 6601 Kirkville Road, East Syracuse, New York 13057, 800/950-0506.

Mr. John Goodin, Wastewater Technology Centre project officer, observed the testing which took place on June 1, 1993. Split samples were take by the project officer to maintain the integrity of the testing.

II. Technology Background

A. Description of the Technology

OVERVIEW

Ex-situ Surfactant Extraction of Contaminants from Soil and Sediment. BioGenesis washing is an ex-situ extraction technology which uses a family of complex, bioremediating surfactants and water. The process is capable of extracting volatile and non-volatile oils, chlorinated hydrocarbons, pesticides, most other organics, and metals from most types of soil including clays. Throughput ranges up to 35 cubic meters per hour depending on contaminant, contamination level, and soil type. Costs range from $40 to $180 per MT for oils. Hazardous chemical cleaning costs are higher. Cleaning solutions containing dissolved metals are made available for subsequent processing using conventional techniques.

STATUS OF DEVELOPMENT

Commercial. Initial U.S. commercial operations began in October 1992. BioGenesis completed demonstration of the washing technology for particles larger than 0.5 mm in the U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program. The first treatability testing took place in May 1992 at Santa Maria, California. The main demonstration occurred in November 1992 at a midwest refinery. Full commercial operations ongoing in the upper midwest United States. Equipment is readily deployable to other locations.

EQUIPMENT & MANPOWER

- Manpower. The mobile washing system requires five personnel: a system supervisor, a test director, two operators, and a material loading operator.

- Soil Washing Equipment.
  - Soil handling equipment.
  - Truck mounted washer unit holding up to 35 cubic meters.
  - Hydrocyclones, centrifuges, and flotation units for the separation of fines.
  - Gravity separators and coalescing filters for oil water separation.
  - Bioreactors for residual water treatment.

- Sediment Washing Equipment.
  - Sediment handling equipment.
  - Continuous flow sediment washing units, skid mounted.

- Hydrocyclones and centrifuges for fines dewatering.
- Water treatment equipment.

B. Benefits and Limitations of the Technology

SPECIAL ADVANTAGES

- Wastes are reduced to reusable oil, treatable water, and active soil/sediment suitable for on-site backfill.
- Treats both volatile and non-volatile oils, organics, and metals.
- Treats soils with high clay content and those which have been contaminated for long periods.
- Complex, bioremediating surfactants used are safe, 100% rapidly biodegradable, and have very low toxicity.
- Processing rate up to 35 cubic meters per hour for one unit with one wash. Sediment washing is continuous flow.
- Organics do not combine with the surfactants.
- The surfactant enhances the biodegradation of residual contamination not extracted.
- Potentially effective on broad range of chlorinated hydrocarbons and pesticides.
- No air pollution except for excavation.

LIMITATIONS

- Working space of approximately 150' x 150'.
- Feasibility of soil/sediment excavation.

C. Pre- and Post- Treatment Needs of the Process

Pretreatment needs for BioGenesis are handled with standard particle sizing equpment. Gross oversize material such as timbers and boulders need to be removed prior to washing. Particles larger than 0.5 mm are treated in the soil washer. Particles smaller than 0.5 mm are cleaned in the sediment washer.

Post-treatment needs are also minimal. For organics, sediments are normally clean enough to be returned to the excavation site immediately. If BG-Clean 411, an acidic solution, is used to wash metals, the wash solution must be neutralized and precipitated to remove the metals prior to wash water disposal. This can be accomplished with standard industrial techniques. The solids resulting from treatment with BioGenesis using BG-Clean 411 are also acidic. In this case the soil needs to be neutralized and reconditioned, again using standard techniques. No unusual wastewater treatment problems are associated with the process.

D. Relative Technical/Economic Merit of the Technology

The technical merits of BioGenesis are:

- Range of Use. Ability to wash the broadest range of organic materials together with metals.
- Organic content. Ability to treat sediment high in organics.
- Soil/sediment type. Ability to treat sediment with clay fines between 30 and 100%.
- Throughput. Up to 35 cubic meters per hour for soil in the current batch process. Sediment washing capacity with continuous flow is projected to be 50-75 cubic meters per hour at full scale.
- Capital cost. Relatively low. $400,000 to $800,000 per washing unit set depending on configuration.
- Mobility. Setup time is less than 24 hours.
- Testability and verifiability. i.e. The sediment is either clean or it's not. This can be tested immediately with portable equipment and confirmed in the laboratory.
- Environmental acceptability. Air emissions are minimal or nonexistent. Chemicals used are benign. Quality control monitoring is simple and straightforward. Washing is an understandable process for the public.
- Pre, Post Treatment Needs. Negligible, using conventional technology.
- Tailorability to a Treatment Train. High.

E. Cost Efficiency at Full Scale

- Soil washing is a batch process. The cost at full scale is estimated at US $40 to 180 per MT based on the type of sediment, the contaminants, the degree of contamination, and the target cleanup level. With a job size of 10,000 tons or greater, BioGenesis would be converted to a continuous process with correspondingly lower costs.

- Sediment washing is a continuous process. Costs are estimated at $30 to $100 per MT.

F. Innovative Nature of the Technology

- Current soil washing techniques have been well developed in Holland using technology borrowed from the mineral mining industry. This washing technology takes a particle classification approach which results in volume reduction, but not true cleaning of the contaminant. It also is incapable of treating high organic and high fine content soils and is limited to water soluble contaminants with lower surface tension between the soil and contaminant.

- BioGenesis soil and sediment washing is fundamentally different in three respects:

  - First, we have adopted an approach of optimizing the surfactant to efficiently separate both organic and non-organic pollutants from sediment/soil.

  - Second, we use **bioremediating** surfactant solutions which, in themselves are environmentally acceptable and benign, and also accelerate the biodegradation of residual contaminants not removed in washing.

  - Third, we use equipment for washing which both reduces particle sizing considerations and also, and most importantly, washes the contaminant efficiently and quickly. We obtain up to 35 cubic meters per hour with, essentially, one washer unit and one trailer load of auxiliary equipment. Sediment washing uses similar scale equipment.

G. Transition from Bench Scale to Pilot Scale

Few if any problems are foreseen in transitioning from the current prototype pilot unit to full pilot scale of 5 to 7 cubic yards per hour. The basic functional mechanism of the collision chamber and collision scrubber remains the same except in dimensions. No additional chemical development is needed. Sediment handling and feed equipment is available off-the-shelf.

H. Integration into an Overall Treatment Train

BioGenesis is easily integrated into an overall treatment train if that is desirable because the equipment is relatively compact and mobile, the bioremediating surfactant solution can be tailored to the pollutant, the by-products of cleaning are known and well understood, and the break points between technologies are discreet. For example, BioGenesis can wash metals from sediment very efficiently. The effluent containing the metals is easily passed to a different segment of the treatment train if that is needed.

I. Environmental Impact and Benefits of the Process

The environmental impact and benefits of BioGenesis are as follows:

- BioGenesis is highly efficient in removing pollutants.
- The cleaners used in BioGenesis are non-polluting themselves. They contain no heavy metals, petroleum derivatives, phosphates, nitrates, dangerous, or hazardous materials. They contain no known or suspect carcinogens, mutagens, or teratogens. The cleaners only require normal good handling practices consistent with the pH of the products.
- Remediation of organics continues after cleaning to provide final polishing cleanup through bioremediation. No other known cleaning technique provides this benefit.
- The impact on the environment of BioGenesis cleaning operations is minimal--the equipment is mobile, relatively small, and non-polluting.
- BioGenesis wastes are negligible, minimal, or treatable.
- BioGenesis performance is easily monitored and quality controlled in the field with portable equipment.
- From a public relations point of view, the process is understandable, explainable, and believable.

III. Technical Approach to Thunder Bay Harbour Testing

A. Initial Technical Approach

The initial demonstration approach was to model existing BioGenesis^{SM} washing equipment to bench scale to simulate the cleaning action of a full scale sediment washing. The equipment was to demonstrate each of the essential steps in the BioGenesis^{SM} process: washing, sedimentation, separation, and filtration. Figure 1 illustrates the process.

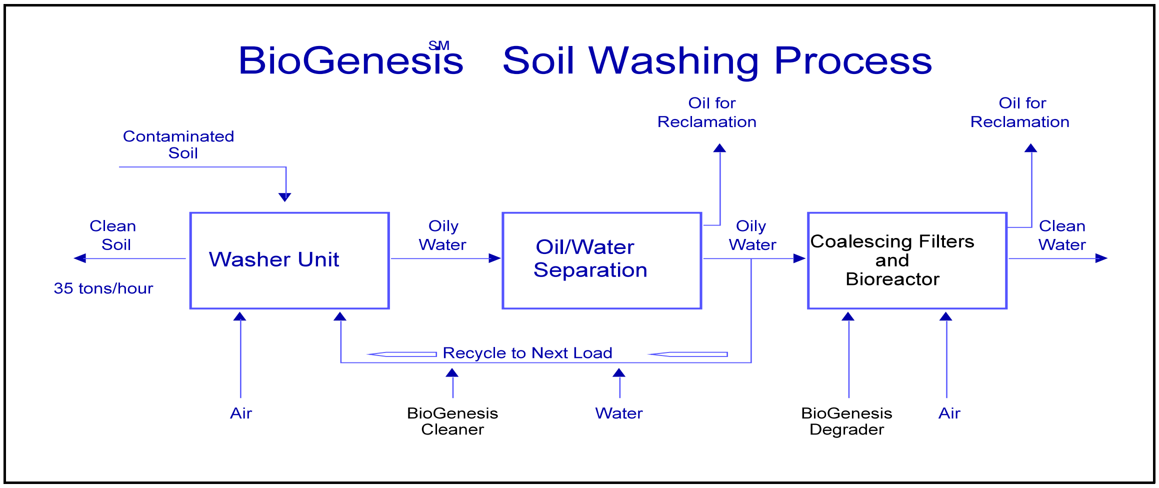

Figure 1. BioGenesis Soil Washing Process Flow

The BioGenesis℠ washing process uses a family of proprietary, bioremediating, complex surfactants whose component proportions and pH are balanced depending on the contaminant(s) to be extracted. In planning the Thunder Bay cleaning, the initial plan was to extract metals with a low pH cleaner and the heavier oils with a high pH cleaner.

To measure the effect of accelerated biodegradation associated with the surfactant blends, initial test planning called for measuring the effect of biodegradation on the residual contaminants.

B. Preliminary Sample Evaluation

In late January, Dr. Amiran examined the Thunder Bay samples using our standard technique for evaluating samples. The purpose was to confirm that the BioGenesis℠ washing process and equipment design could satisfactorily clean Thunder Bay sediments.

The evaluation included the following:

- Prior Testing Review. On most jobs a substantial amount of testing has already been completed. This is documented in engineering reports which are reviewed to determine the type of soil, amount of contaminant, and type of contaminant.

  In the case of Thunder Bay sediment, we reviewed the testing results on sediments collected in May 1992 and tested June to September 1992. These results showed concentrations of about 6,000 mg/l oil & grease and high concentrations of PAHs, with a total PAH content in the range of 57,000 to 84,000 mg/l. Heavy metals concentrations were relatively low. So as recommended by the project authority during contract discussions, metals were determined not to be included in the evaluation.

Sieve analysis results provided by WTC were also reviewed. These showed that 81% of the sediment was less than 38 microns in size. Characterization of grain size distribution is exceedingly important in the case of washing technologies because it affects bonding forces of contaminant to sediment grains and also because of the impact on surface area to be cleaned.

- Extraction & Pollutant Examination. Using solvent extraction methods, the pollutant is removed from the sediment. The extract is then examined to determine its physical characteristics. Based on the results, we select and then optimize the components of the cleaning chemical. These decisions affect costing with respect to the amount and type of chemicals needed, and whether or not wash water heating will be needed. A portion of the extract is reserved for subsequent use in thin layer chromatography (TLC) testing.

  In the case of Thunder Bay sediment, proposal plans had been to evaluate testing using both a neutral cleaning chemical blend and a high pH cleaning blend. Dr. Amiran performed an extended series of extractions on the sediment comparing both solvents and a range of BioGenesis[SM] cleaning solutions, both neutral and high pH. The results of these evaluations showed that neither neutral nor high pH was optimum, but rather that an aqueous surfactant blend between 9 and 10 pH gave best performance.

- Soil Matrix Examination. Then we test the settling characteristics of the soil matrix. Our objective is to determine how much of the soil will settle in 5 to 7 minutes following agitation. The breakpoint is roughly 5 microns. This tells us the type of processing equipment which will be needed for effluent treatment.

  In the case of Thunder Bay sediment, testing the sediment matrix showed settling times far in excess of 5-7 minutes. As a result, Dr. Amiran concluded that the existing full scale BioGenesis[SM] washing equipment design would be inadequate to provide reasonably good extraction efficiency (80-90%) at a reasonable production rate (25-30 tons per hour).

  Given that the cleaning chemical blend was capable of removing the oil & grease and PAHs, the task then was to adapt the fundamental characteristics of the BioGenesis[SM] process to in an equipment design suitable for washing Thunder Bay sediments.

C. Cleaning Chemical Design Modifications

Based on Dr. Amiran's testing and examination of the pollutant extract and the sediment matrix, the testing plan was further revised to use one chemical blend with a pH of 10. Such a blend was clearly superior in the preliminary sample evaluation and it was BioGenesis' judgment that running variations would provide little additional information of use. The Project Authority approved this modification.

D. Equipment Design Modifications

The key parameters of BioGenesis℠ cleaning are the surfactant blend, wash temperature, and mixing efficiency. Given these fundamentals, and the determination during Dr. Amiran's preliminary testing that Thunder Bay sediment could not be most efficiently cleaned in the current washing gondola, we redesigned the approach to the bench test setup. The redesigned approach maintained the key parameters of the process, but implemented these in such a way as to handle the fine grain size at Thunder Bay. The revised equipment functional flow is depicted in figure 2, and described in succeeding paragraphs.

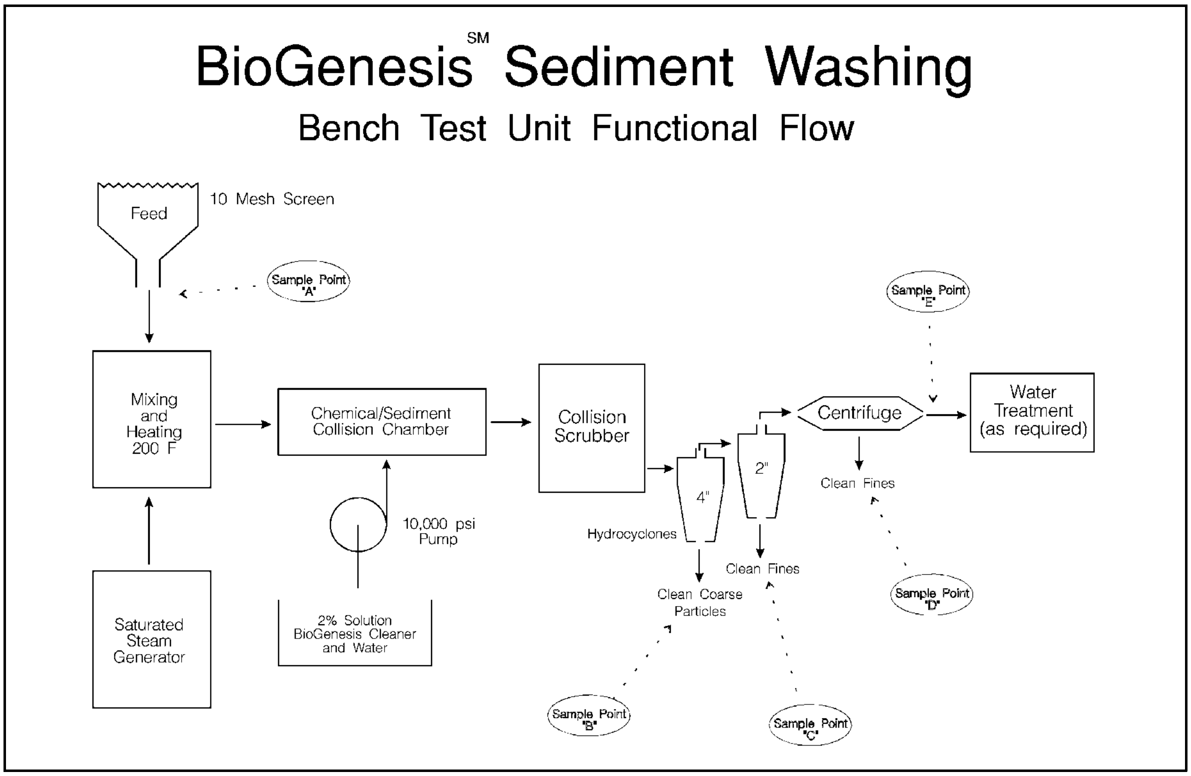

Figure 2. BioGenesis Sediment Washing, Functional Flow

First a sizing step manually removed large particles. These were not further tested based on the rationale that contamination is concentrated on the particles which pass the screen. If the smaller particles and sediment can be cleaned, then large particles are easy.

Then, using saturated steam, the sediment is heated to 140 to 200°F. Note: for the June test, sediment was washed at 80 to 90°F.

Next the heated sediment is mixed with BioGenesis™ cleaner and water under up to 10,000 psi pressure. The combination of chemical and physical force of impact begins loosening the bonding forces between the small sediment particles and the contaminant.

The loosening process is completed in a collision scrubber wherein the charges on the contamination particles are aligned to facilitate separation.

Finally, using standard hydrocyclones and, if required, a centrifuge, the oil and water are separated from the sediment.

Depending on the type of centrifuge used (two-phase or three-phase), water treatment using standard chemicals, filtration, or biodegradation may be used. Water treatment was not modeled for this testing.

E. Testing Protocol

The initial testing plan provided for extensive, multiple testing of both solid and liquids resulting from the testing. These included baseline, intermediate process, and after process sampling for 16 metals and inorganics, pH, sulfur, TOC, C_{10-22} hydrocarbons, oil and grease, TPH, chlorophenols, 16 PAHs, and total PCBs. Two factors led to amendments in the testing: reduced need for metals, PCB, and phenols testing because of low contaminant levels and restrictions on test extent because of limited sample quantities and the need for split samples.

The resulting testing plan is illustrated in Table I. It was designed to provide a thorough baseline result and end result, with intermediate results assigned less importance. Final adjustments were made to the test matrix following the test in coordination with the project authority and laboratory director to maximize information derived.

SEDIMENT WASHING TEST MATRIX						
Test	**Baseline**	**After Cycle 1**	**After Cycle 2**	**After Cycle 3**	**At Buffer Tank**	**After Cyclone**
Metals	X					X
pH	X					X
Sulfur	X					X
TOC	X					X
C_{10-23}HC	X	X				X
Oil & Grease	X					X
TPH	X	X	X	X	X	X
16 PAHs	X	X	X		X	X
PCBs	X	X		X	X	X

Table I. Sediment washing test matrix

IV. Sediment Washing Test

A. Test Conduct

Dr. Amiran tested the Thunder Bay Harbour sediment on June 1, 1993, at the BioGenesis facility in Milwaukee, Wisconsin. Mr. John Goodin represented Wastewater Technology Centre during the testing.

For this test, the sediment washing unit was configured so that sediment could make multiple passes through the machine. Considering the relatively small amount of sediment available for cleaning, and the relatively large capacity of the machine compared to the sediment amount, Dr. Amiran decided to recirculate the sediment through the machine three times. In a full scale machine, sediment will not be recirculated through the same unit, but will be passed successively through from 3 to 5 machines depending on the situation. This will achieve continuous flow through the machine set.

With the exception of a leaking seal which was replaced, the test apparatus operated as designed. Wash water/chemical temperatures were 80 to 90°F.

B. Test Data

Sediment samples were identified as follows to correlate with the test matrix:

Sample Identification	
Original sediment (unwashed)	MA 14
Solids after scrubber cycle 1	MA 1 and MA2 (combined into one)
Solids after scrubber cycle 2	MA 3 and MA4 (combined into one)
Solids after scrubber cycle 3	MA5 and MA 6 (combined into one)
Solids at the buffer tank	MA11
Solids after the cyclone (clean output)	MA7, MA8, and MA9 (combined into one)
Liquid after the cyclone	MA10
Wastewater	MA12 and MA13 (combined into one)

Table II. Sample identification reference

Samples were shipped via Federal Express to Galson Laboratory on June 2, 1993 and received by the laboratory on June 3, 1993. Galson reported results on June 29, 1993 and July 2, 1993. Table III, Phenols and Poly-aromatic Hydrocarbons, and Table IV, Hydrocarbons, Metals, PCBs, and Miscellaneous, tabulate the data from individual test sheets contained in Appendix A, Galson Laboratory Test Report Data Sheets. Appendix B, Galson Laboratory Test Report Data Sheets with Mass Spectra for Semi-volatiles, bound separately, contains detailed mass spectra data.

BioGenesis Sediment Washing, Thunder Bay Harbour Sediment
Testing for Wastewater Technology Centre, 6/1/93

Phenols and Polyaromatic Hydrocarbons (PAHs)

CAS No.	Compound	Before Cleaning (ppb) MA14 SOLID	After Cycle 1 (ppb) MA1/2 SOLID	After Cycle 2 (ppb) MA3/4 SOLID	After Cyclone (ppb) MA7/8/9 SOLID	At Buffer Tank (ppb) MA11 SOLID	After Cyclone (ppb) MA10 LIQUID	After Cyclone (ppb) MA12/13 LIQUID
POLYAROMATIC HYDROCARBONS								
91-20-3	Naphthalene	1,400,000	1,000,000	170,000	73,000	300,000	5,600	1,400
208-96-8	Acenaphthylene	16,000	13,000	2,400	1,500	4,500	99	65
83-32-9	Acenaphthene	305,000	270,000	55,000	34,000	100,000	1,500	1,100
86-73-7	Fluorene	240,000	215,000	45,000	30,000	86,000	1,250	780
85-01-8	Phenanthrene	770,000	700,000	130,000	88,000	240,000	3,550	2,000
120-12-7	Anthracene	110,000	98,000	21,000	16,000	40,000	560	290
206-44-0	Fluoranthene	400,000	385,000	83,000	59,000	160,000	2,150	990
129-00-0	Pyrene	300,000	280,000	59,000	44,000	110,000	1,700	740
56-55-3	Benzo(a)anthracene****	115,000	105,000	23,000	19,000	46,000	680	260
218-01-9	Chrysene****	75,000	67,000	15,000	12,000	28,000	430	150
205-99-2	Benzo(b)fluoranthene****	120,000	110,000	24,000	19,000	47,000	720	270
207-08-9	Benzo(k)fluoranthene****	42,000	32,000	6,500	6,100	12,000	240	71
50-32-8	Benzo(a)pyrene****	82,000	74,000	15,000	12,000	29,000	490	180
193-39-5	Indeno(1,2,3-cd)pyrene****	30,000	28,000	5,900	5,000	12,000	200	67
53-70-3	Dibenzo(a,h)anthracene****	8,900	8,600	BDL	1,400	BDL	54	100
191-24-2	Benzo(g,h,i)perylene	28,000	27,000	5,000	3,900	9,200	200	68
	TOTAL PAHs	4,041,900	3,412,600	659,800	423,900	1,223,700	19,423	8,531

**** = Carcinogenic PAHs

	After Cycle 1	After Cycle 2	After Cyclone
Total % Difference of PAHs from MA14	**-15.6%**	**-83.7%**	**-89.5%**

CAS No.	Compound	Before Cleaning (ppb) MA14 SOLID	After Cycle 1 (ppb) MA1/2 SOLID	After Cycle 2 (ppb) MA3/4 SOLID	After Cyclone (ppb) MA7/8/9 SOLID	At Buffer Tank (ppb) MA11 SOLID	After Cyclone (ppb) MA10 LIQUID	After Cyclone (ppb) MA12/13 LIQUID
PHENOLS								
108-95-2	Phenol	BDL	BDL	BDL	BDL	BDL	BDL	110
95-57-8	2-Chlorophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
88-75-5	2-Nitrophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
105-67-9	2,4-dimethylphenol	7,800	BDL	BDL	BDL	BDL	59	420
120-83-2	2,4-Dichlorophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
59-50-7	4-Chloro-3-methylphenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
88-06-2	2,4,6-Trichlorophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
51-28-5	2,4-Dinitrophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
100-02-7	4-Nitrophenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
534-52-1	4,6-Dinitro-2-methylphenol	BDL	BDL	BDL	BDL	BDL	BDL	BDL
87-86-5	Pentachlorophenol	BDL	BDL	BDL	BDL	BDL	26	BDL
	TOTAL PHENOLS	7,800	0	0	0	0	85	530

BDL = Below Detection Limits (analyzed for but not detected)

Table III. Test data, phenols and polyaromatic hydrocarbons (PAHs), BioGenesis washing, Thunder Bay Harbour sediment

BioGenesis Sediment Washing, Thunder Bay Harbour Sediment
Testing for Wastewater Technology Centre, 6/1/93

Hydrocarbons, Metals, PCBs, Miscellaneous

	Before Cleaning (ppm) MA14 SOLID	After Cycle 1 (ppm) MA1/2 SOLID	After Cycle 2 (ppm) MA3/4 SOLID	After Cycle 3 (ppm) MA5/6 SOLID	After Cyclone (ppm) MA7/8/9 SOLID	At Buffer Tank (ppm) MA11 SOLID	After Cyclone (ppm) MA12/13 LIQUID
HYDROCARBON MEASURES							
Semivolatile Petroleum Hydrocarbons (SVHC)	21,000				2,200		
Oil & Grease (O&G)	91,600				3,940	16,300	
Total Petroleum Hydrocarbons (TPH)	4,770	4,840	1,670	1,290	400	770	

Total % reduction of SVHC from MA14				**-89.5%**
Total % reduction of O&G from MA14				**-95.7%**
Total % reduction of TPH from MA14	**1.5%**	**-65.0%**	**-73.0%**	**-91.6%**

	MA14	MA1/2	MA3/4	MA5/6	MA7/8/9	MA11	MA12/13	**% Removal**
METALS								
Aluminum	15,000				8,300			44.7%
Antimony	1				0.8			20.0%
Arsenic	15				9.1			39.3%
Beryllium	1				0.3			63.5%
Cadmium	1				1.4			-40.0%
Chromium	71				32			54.9%
Copper	73				46			37.0%
Iron	34,000				21,000			38.2%
Lead	41				20			51.2%
Magnesium	11,000				8,200			25.5%
Manganese	420				270			35.7%
Nickel	34				18			47.1%
Selenium	1				0.8			20.0%
Silver	8				5			37.5%
Thallium	1				0.8			20.0%
Zinc	160				140			12.5%
TOTAL METALS	60,827				38,044			31.7%

Total % reduction of tested metals from MA14	-37.5%
Mean % reduction of each metal from MA14	-31.7%

	MA14	MA1/2	MA3/4	MA5/6	MA7/8/9	MA11	MA12/13
MISCELLANEOUS							
Total Organic Carbon (TOC)	11.5%				2.9%		
Sulfur	0.30%				0.30%		

Total % reduction of TOC from MA14	74.8%

	MA14	MA1/2	MA3/4	MA5/6	MA7/8/9	MA11	MA12/13
PCBs (Araclor)							
1016	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05
1221	< 0.2	< 0.3		< 0.2	< 0.2	< 0.2	< 0.1
1232	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05
1242	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05
1248	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05
1254	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05
1260	< 0.1	< 0.2		< 0.1	< 0.1	< 0.1	< 0.05

Table IV. Test data, hydrocarbons, metals, PCBs, and miscellaneous, BioGenesis washing, Thunder Bay Harbour sediment

V. Evaluation of Results

The particle size distribution for Thunder Bay Harbour sediment is shown at the right in figure 3. This distribution was reported by WTC based on testing of samples during 1992. Using Wentworth classification scales, 81% of the sediment is medium silt and finer, about 8% is a coarser silt, and 6% is very fine sand. This distribution of small grain sizes has heretofore been considered untreatable using soil washing techniques.

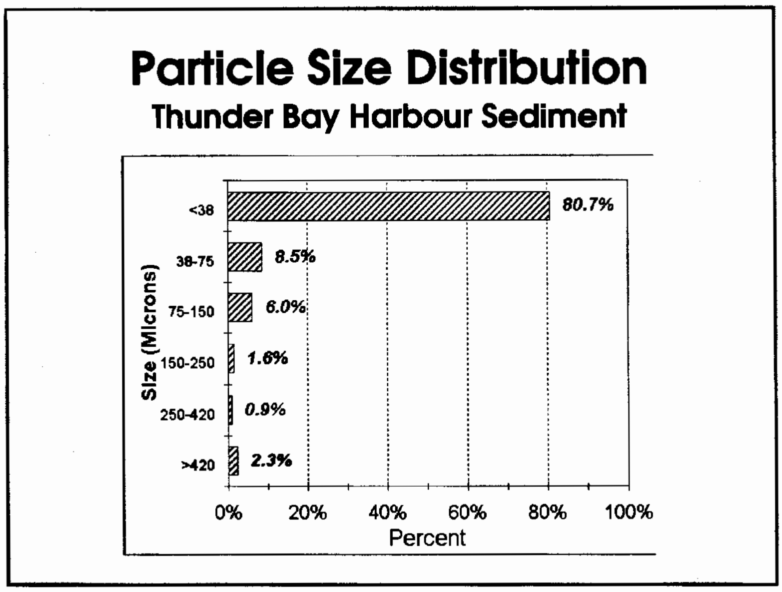

Figure 3. Thunder Bay Harbour sediment particle size distribution

Overall removal effectiveness of the BioGenesis washing process is illustrated in figure 4. Three wash cycles with about 5 minutes of total contact time in the washing unit resulted in 90-95% contaminant removal depending upon the test used. Oil &

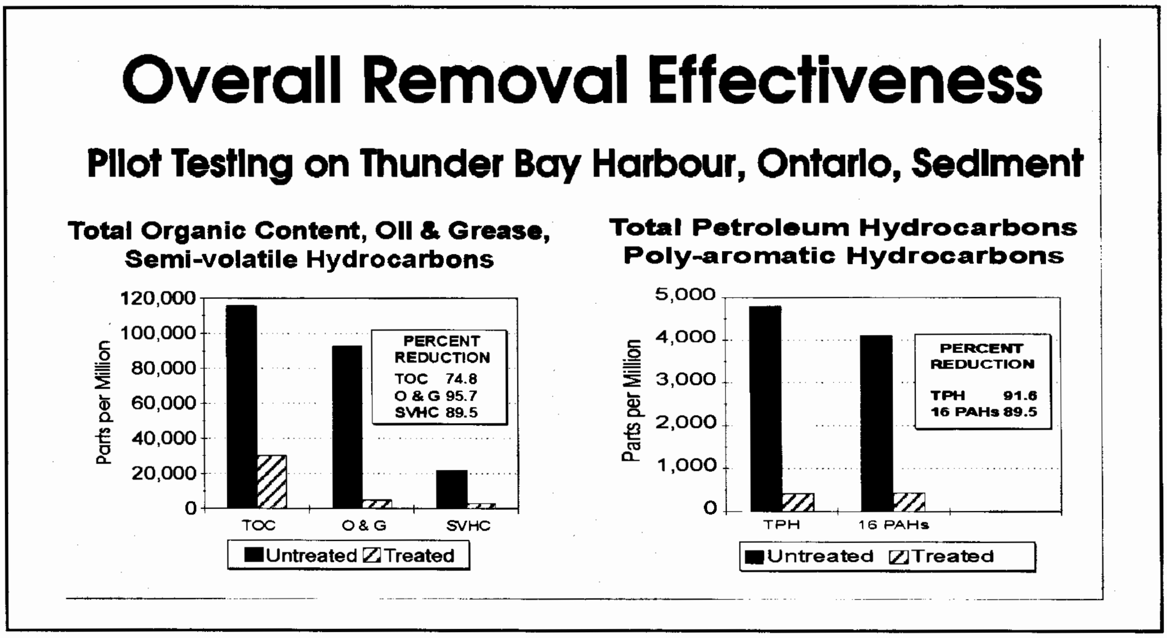

Figure 4. BioGenesis washing, overall removal effectiveness, Thunder Bay Harbour sediment

above expectations for the small pilot scale unit. Galson Laboratory noted that the results for SVHC (C_{12-23} as diesel), TPH, and GCMS results should not be confused since although each method assesses petroleum content, different analytical techniques are utilized and different types of contamination may respond differently to each of the techniques. Nevertheless, results from the principal tests performed by two different laboratories (Galson subcontracted SVHC analysis) correlate very well and give confidence to the overall removal percentages.

Washing removal effectiveness for individual PAH contaminants varied between 83.3% and 94.8%. This can be observed visually in figure 5 where the extraction end points for contaminants with beginning concentrations greater than 100 ppm are all very similar. About 15% of contamination is removed during the first wash cycle. A further 75% is removed in cycles 2 and 3. Whether the additional removal is due to dwell time in the presence of the chemical, or to additional physical scrubbing in the collision chamber and collision scrubber is undetermined at this time.

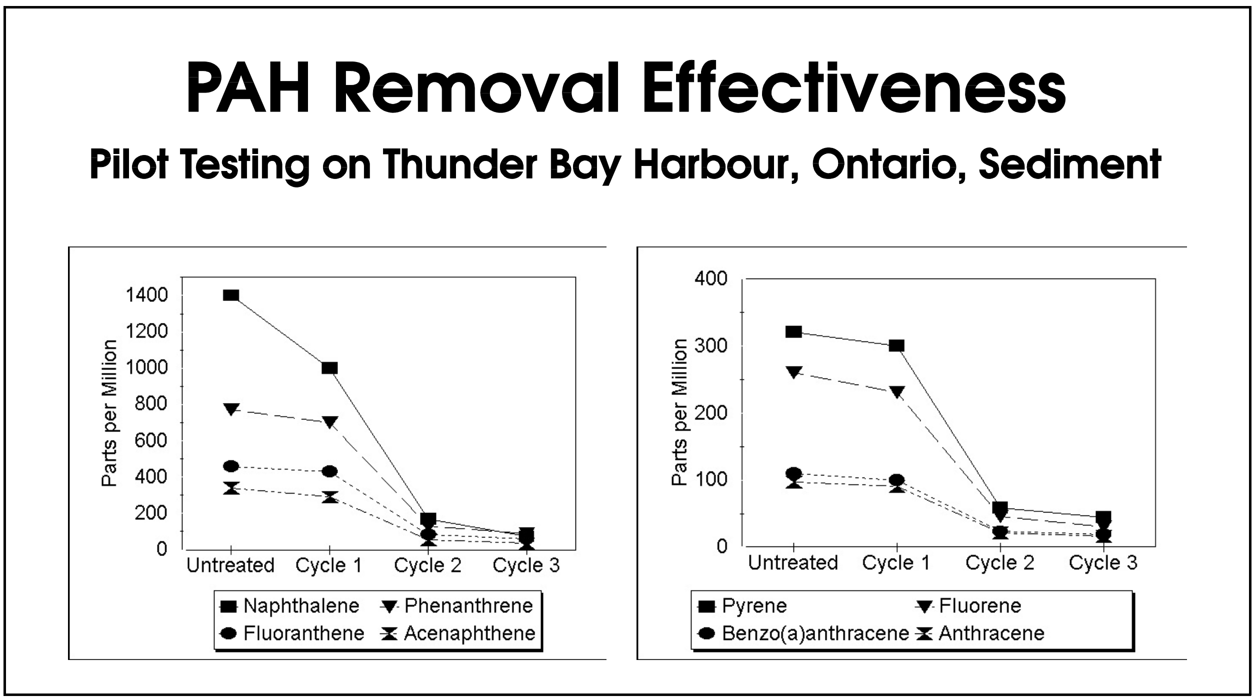

Figure 5. BioGenesis washing, PAH removal effectiveness, higher concentration pollutants, Thunder Bay Harbour sediment

Likewise figure 6 shows much the same picture for PAH compounds having initial concentrations below 100 ppm.

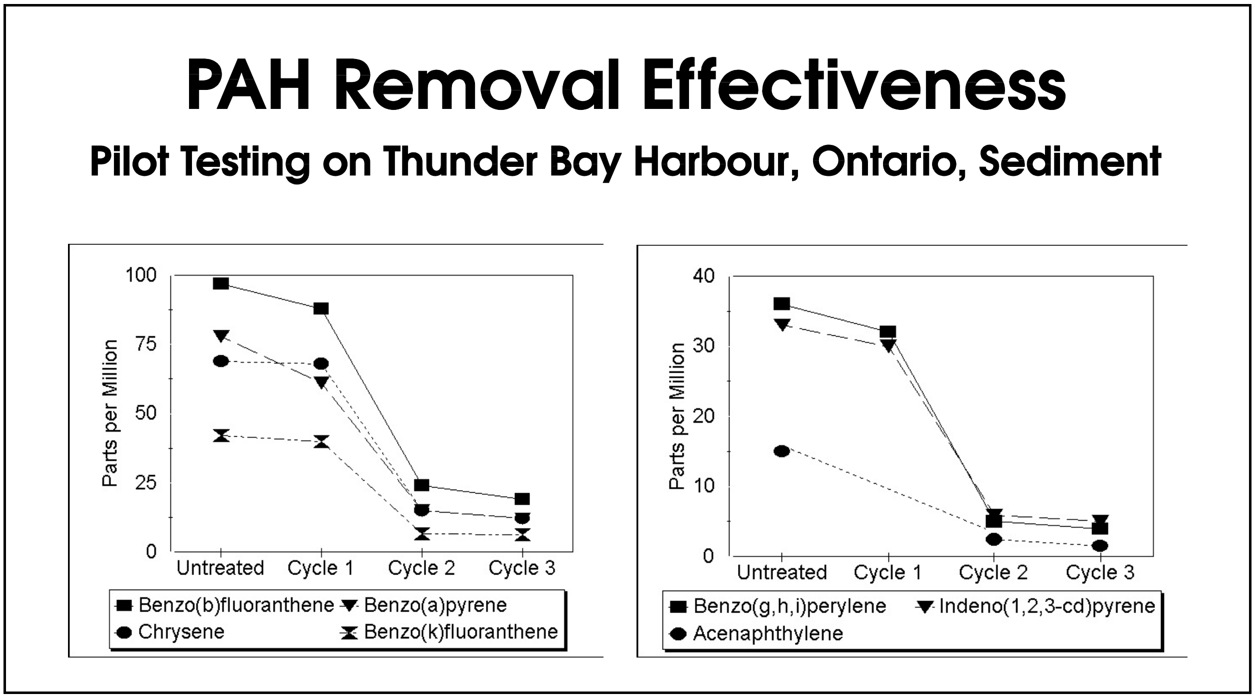

Figure 6. BioGenesis washing, PAH removal effectiveness, lower concentration pollutants, Thunder Bay Harbour sediment

VI. Conclusions, Technology Extensions, and Recommendations

A. Conclusions

For the first time known to BioGenesis Enterprises, Inc., PAH and hydrocarbon contamination has been effectively extracted from sediments in a continuous process. This is a major advance in the state-of-the-art for sediment remediation. It effectively makes obsolescent, if not completely obsolete, the previous concept of washing technology as a pretreatment technique which leaves large residue needing further treatment.

The testing for this project used prototype, pilot scale equipment. Extraction efficiency was 90-95%. The test proved that BioGenesis sediment washing technology can physically/chemically extract relatively high levels of oil & grease, TPH, SVHCs, and PAHs from harbour sediment which was 81% medium silt and smaller.

B. Technology Extensions

The sediment washing equipment used in the June 1993 testing was the initial, proof-of-principal prototype. It worked. Second generation equipment capable of processing 5 to 7 cubic yards per hour is under construction with the intent to be able to demonstrate at full pilot scale in December 1993. Design revisions being incorporated in the new equipment are projected to raise extraction efficiency to the 97 to 99% range for three processing cycles. Extraction efficiencies above 99% may be achievable with multiple processing units in series.

Levels of PCBs, phenols, and dioxins were too low in the Thunder Bay Harbour sediment to calculate an extraction efficiency. But considering hydrocarbon similarities, it is reasonable to expect similar removal efficiencies on these substances. Pesticides also fall in this category.

The washing operation achieved a collateral effect of removing 30 to 40% of the metals present despite optimization of the chemical cleaner for hydrocarbons and PAHs. It is reasonable to expect that a chemical optimized for metals together with improvements in the cleaning machine will lead to substantially increased rates of metals extraction.

Given the performance on hydrocarbons, PAHs, and metals, it seems possible to design a sequential treatment train which first extracts hydrocarbons and then, with a different chemical, extracts metals. The ability to use the same equipment to clean different contaminants leads to the expectation that sediment washing will evolve to be an effective, economical, rapid means of treating multi- and mixed contaminant sediments.

C. Recommendations

BioGenesis recommends that WTC consider further testing of both the scope and range of application of the sediment washing technology.

As to scope--BioGenesis has begun construction of a pilot unit with capacity of 5 to 7 cubic yards per hour. This unit will be ready for use after December 1993. As the next step in Thunder Bay remediation, it seems reasonable to proceed to pilot scale remediation as early as the weather and funding will permit in 1994. The pilot work should be carefully designed to answer all technical uncertainties related to full scale remediation at Thunder Bay and to provide reasonable assurance of cost and production parameters.

As to technology range--washing using BioGenesis sediment technology seems applicable to a broad range of contaminants including PCBs, dioxins, phenols, and pesticides. These need testing in a similar way to that done for Thunder Bay PAHs for proof-of-principal, followed by pilot testing when successful.

Appendix A: Galson Laboratory Test Report Data Sheets

FINAL REPORT

BENCH SCALE STUDIES OF THUNDER BAY HARBOUR SEDIMENT

BIOGENESIS WASHING PROCESS

Appendix B: Galson Laboratory Test Report Data Sheets with Mass Spectra for Semi-volatiles

(BOUND SEPARATELY)

Submitted to:	Wastewater Technology Centre (WTC) 867 Lakeshore Road Burlington, Ontario L7R 4A6
Date:	August 31, 1993
WTC Contract:	No. 2-6020, December 7, 1992