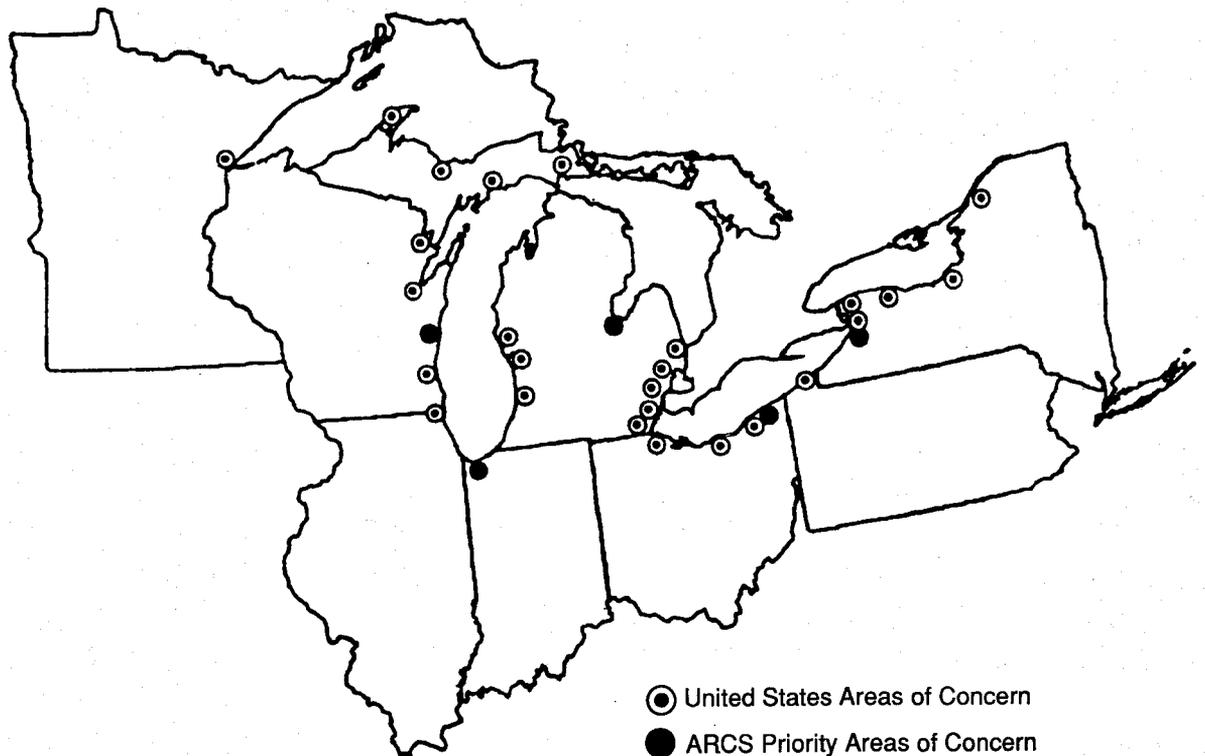




Assessment and Remediation Of Contaminated Sediments (ARCS) Program



BENCH SCALE EVALUATION OF ZIMPRO'S WET AIR OXIDATION PROCESS ON CONTAMINATED SEDIMENTS FROM THE GRAND CALUMET RIVER



**Bench-Scale Evaluation of
Zimpro's Wet Air Oxidation Process on
Contaminated Sediments from the Grand Calumet River**

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DISCLAIMER

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ABSTRACT

The Great Lakes National Program Office (GLNPO) leads efforts to carry out the provisions of Section 118 of the Clean Water Act (CWA) and to fulfill U.S. obligations under the Great Lakes Water Quality Agreement (GLWQA) with Canada. Under Section 118(c)(3) of the CWA, GLNPO was responsible for undertaking a 5-year study and demonstration program for the remediation of contaminated sediments. GLNPO initiated an Assessment and Remediation of Contaminated Sediments (ARCS) Program to carry out this responsibility. In order to develop a knowledge base from which informed decisions may be made, demonstrations of sediment treatment technologies were conducted as part of the ARCS Program. Bench-scale studies of the Zimpro Wet Air Oxidation Process, the subject of this report, took place at Zimpro Passavant Environmental Systems, Inc. (Zimpro) in Rothschild, WI on August 27 to 29, 1991. The primary objective for this effort was to determine the feasibility and cost-effectiveness of the Zimpro wet air oxidation process for treating and removing PAHs. The wet air oxidation process was not expected to treat PCBs, another known primary contaminant group detected in the sediments.

The Zimpro Wet Air Oxidation Process was tested using a sediment obtained from the Grand Calumet River. The concentrations of the contaminants of concern in the sediment were 11.9 mg/kg PCBs and 266 mg/kg PAHs. The PCB and PAH concentrations of 8.5 and <2.84 mg/kg, respectively, were found in the treated solids. This corresponds to PCB and PAH removals of 29 percent and >98.9 percent, respectively. Metals analyses were performed on the treated solids and untreated sediments. The feed sediments and treated solids were analyzed for percent moisture, oil and grease, total organic carbon (TOC), total volatile solids, and pH. Due to the sampling and analytical program for these tests, it was not possible to calculate a mass balance as part of this study.

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1.0 EXECUTIVE SUMMARY

The Wet Air Oxidation Process was tested using sediments obtained from the Grand Calumet River. The contaminants of concern in the sediments for these tests were polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Samples of the feed material and the treated solids produced using the Wet Air Oxidation Process were analyzed by Battelle Marine Sciences Laboratory for residual PAH and PCB contamination. The data from these analyses are presented in Tables 1 and 2.

Table 1. Summary of Total PAHs (mg/kg, dry)

Sample	Feed	Treated Solids	% Destruction
Total PAHs	266	>2.84	>98.9

As these data demonstrate, the PAH destruction efficiency for the Grand Calumet River sediment is about 99 percent. The data demonstrate the technical feasibility of the Zimpro Wet Air Oxidation Process for treating and removing PAHs.

Feed material and treated solids were also analyzed for residual PCB concentrations. Table 2 outlines the analytical results obtained by Battelle.

Table 2. Summary of Total PCBs (mg/kg, dry)

Sample	Feed	Treated Solids	% Destruction
Total PCBs	11.9	8.5	29

The destruction efficiency for PCBs was only 29 percent, but the wet air oxidation process was not expected to treat PCBs.

Metal analyses were performed on the treated solids and untreated sediments (see Section 4.2.1.3). The Battelle analyses demonstrate that the treatment process, as expected, had little effect on metals removal from the sediments.

The feed and treated solids were analyzed for percent moisture, oil and grease, TOC, total volatile solids, and pH (see Table 3). The percent moisture decreased. Ninety percent of the oil and grease was removed. TOC and treated volatile solids were reduced more than 50 percent. The pH dropped to 6.5.

Table 3. Characterization of Feed Sediments and Treated Solids (mg/kg, dry basis, unless otherwise specified)

	Feed Sediments	Treated Solids
Total PCBs	11.9	8.5
Total PAHs	266	<2.84
Moisture, % (as received)	55.0	43.3
Oil & Grease	9890	951
TOC, % weight	19.3	9.3
Total Volatile Solid, %	15.0	7.3
pH, S.U. (as received)	7.67	6.51

Because of the nature in which the organic material is oxidized, the TOC analysis shown in Table 11 was used to calculate the mass balance of the solids. The summation of the percent recovery results indicates that 90 percent of the material charged to the reactor was recovered after treatment. After correcting for the amount of sample oxidized during treatment and the amount known to be lost in Run Number 4, about 94 percent of the original sample was accounted for. Since all the species containing carbon and hydrogen in the sediment were not known and the organics were being oxidized to carbon dioxide and water, it was not possible to conduct a more detailed mass balance.

Small vials of the residuals from the treatability test were retained and given to the EPA Technical Project Manager for the GLNPO for "show" purposes. All quantities of the test products (solids and filtrate) from the treatability test were sent to the analytical laboratory, Battelle, for analysis. Due to the small quantities generated from the tests, none were retained and shipped to EPA for possible further treatability studies.

Zimpro has estimated the capital costs of units to treat 10,000, 40,000, and 100,000 yd³ of sediment at rates of 10 (60 TPD), 20 (120 TPD), and 40 gpm (240 TPD). These estimates are approximately \$4,500,000 for the 10 gpm unit; \$5,600,000 for the 20 gpm unit; and \$7,300,000 for the

40 gpm unit. The sediment would be treated at a rate of 60 to 240 tons per day using 10 to 40 gpm units operated on a 24 hour per day, 5 days per week, 50 weeks per year basis. The cost of treating the sediment is estimated to be \$329, \$203, and \$133/yd³ for the 10, 20, and 40 gpm units respectively. This estimate by Zimpro includes capital and operating costs but does not account for the costs associated with site excavation, civil work, applicable taxes, pre-screening needs, and overall site management and disposition of the residuals.

2.0 INTRODUCTION

The Great Lakes National Program Office (GLNPO) leads efforts to carry out the provisions of Section 118 of the Clean Water Act (CWA) and to fulfill U.S. obligations under the Great Lakes Water Quality Agreement (GLWQA) with Canada. Under Section 118(c)(3) of the CWA, GLNPO is responsible for undertaking a 5-year study and demonstration program for the remediation of contaminated sediments. Five areas were specified for priority consideration in locating and conducting demonstration projects: Saginaw River and Bay, Michigan; Sheboygan River, Wisconsin; Grand Calumet River/Indiana Harbor Canal, Indiana; Ashtabula River, Ohio; and Buffalo River, New York. In response, GLNPO initiated the Assessment and Remediation of Contaminated Sediments (ARCS) Program.

In order to develop a knowledge base from which informed decisions may be made, bench- and pilot-scale demonstrations of sediment treatment technologies were conducted as part of the ARCS Program. Information from remedial activities supervised by the U.S. Army Corps of Engineers and the Superfund program were also utilized. The Engineering/Technology (ET) Work Group was charged with overseeing the development and application of the bench- and pilot-scale tests.

Science Applications International Corporation (SAIC) was contracted to provide technical support to the ET Work Group. As part of this effort, SAIC was charged with conducting bench-scale treatability studies on designated sediments to evaluate the removal of specific organic contaminants. The bench-scale studies of the Zimpro Wet Air Oxidation Process, the subject of this report, took place at Zimpro Passavant Environmental Systems, Inc. (Zimpro) in Rothschild, Wisconsin on August 27 to 29, 1991. The primary objective for this effort was to determine the feasibility and cost-effectiveness of the Zimpro wet air oxidation process for treating and removing PAHs. The wet air oxidation process was not expected to treat PCBs, another known primary contaminant group detected in the sediments.

2.1 Background

SAIC and its subcontractors have conducted seven bench-scale tests for the ARCS Program on four different sediments using four treatment technologies: Wet Air Oxidation (Zimpro Passavant), B.E.S.T.™ Solvent Extraction Process (RCC), Thermal Desorption Technology (ReTeC), and Anaerobic Thermal Process Technology (SoilTech). This report summarizes the approach used and results obtained during treatability testing of the Zimpro Wet Air Oxidation Process. The sediments tested using this technology were obtained from the Grand Calumet River.

The primary objective of this portion of the study was to determine the feasibility and cost-effectiveness of the Zimpro Wet Air Oxidation Process for treating and removing PAHs from the Grand Calumet River sediment. Based upon previous tests performed by Zimpro, the bench scale tests were designed to provide data that closely simulate full-scale performance. Thus, data generated by these tests may be used to estimate treatment costs for full-scale operations and to evaluate process feasibility.

2.2 Sediment Descriptions

The sediments used during the treatability studies conducted by SAIC are typical of sediments in the Great Lakes and their tributaries. These sediments were obtained from the Grand Calumet River. They are representative of locations around the Great Lakes where future field demonstration projects may be conducted. The primary contaminants in the Grand Calumet River sediments for the purpose of this study are PCBs and PAHs.

2.2.1 Site Names and Locations for Each Sediment

GLNPO collected sediments for study from the following areas around the Great Lakes: Saginaw River, Michigan; Sheboygan River, Wisconsin; Grand Calumet River/Indiana Harbor Canal, Indiana; Ashtabula River, Ohio; and Buffalo River, New York. SAIC was contracted to treat four of the sediments (from the Grand Calumet River, Buffalo River, Ashtabula River, and Saginaw River) using four different technologies. Samples from the Grand Calumet River were treated using the Zimpro Wet Air Oxidation Process. A map is provided in Figure 1 which shows the ARCS Priority Areas of Concern. Specifics of the sample location for the Grand Calumet River are shown in Figure 2.

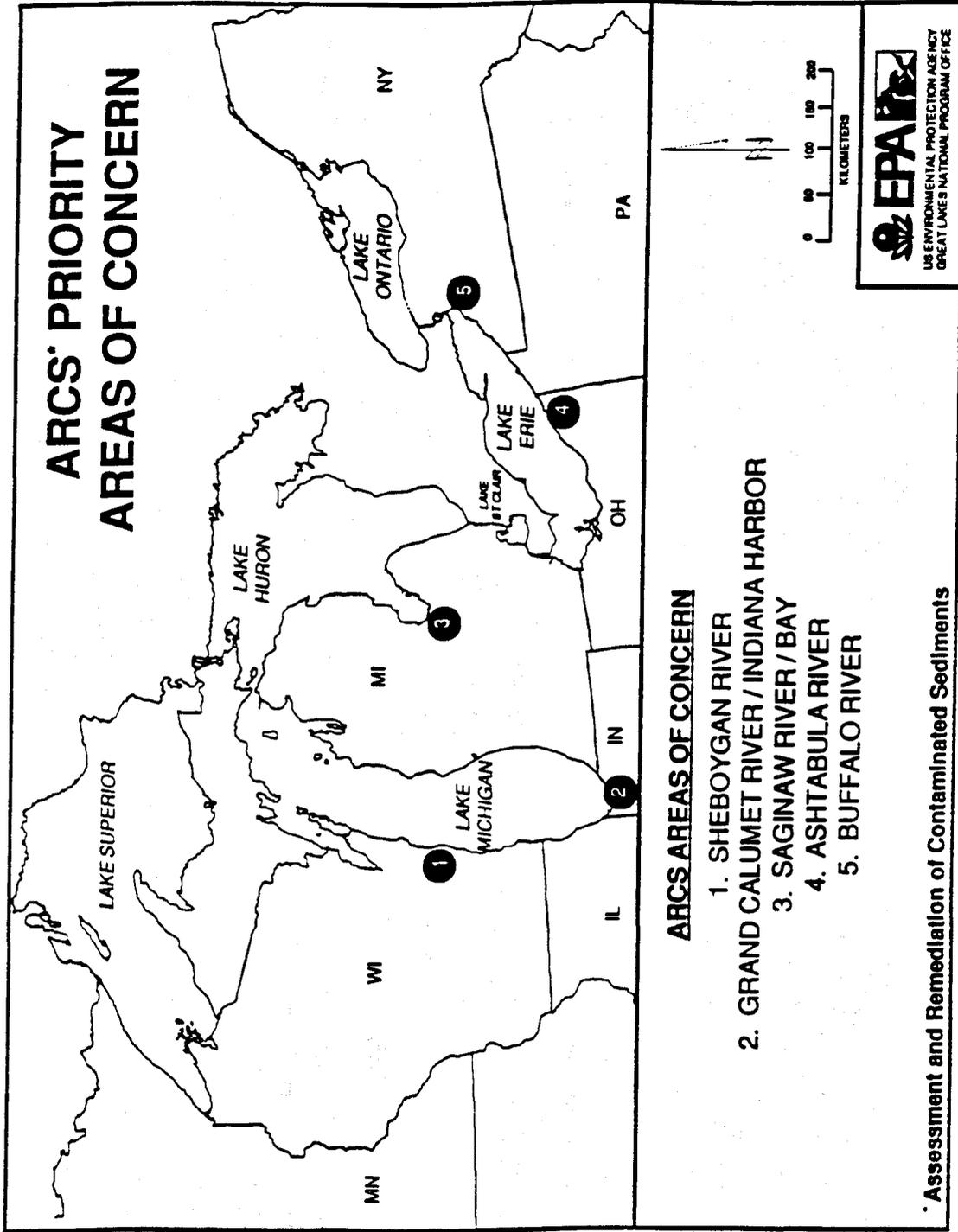


Figure 1. ARCS Priority Areas of Concern

2.2.2 Sediment Acquisition and Homogenization

Prior to conducting the bench-scale treatability study using the wet air oxidation technology, the GLNPO samples were homogenized and stored under refrigeration by the U.S. EPA Environmental Research Laboratory in Duluth, MN.

Approximately 1 gallon of the homogenized sediments were sent to SAIC by the Duluth laboratory. These sediment samples were then transferred by SAIC to Zimpro. Zimpro used these samples in Phase I to perform a series of standard tests commonly performed to determine if the waste sample was compatible with their process and to determine optimum testing conditions and procedures for the Phase II treatability study. The sediments used during the treatability studies also originated from this stock and were forwarded to Zimpro by SAIC.

2.3 Sediment Characterization

SAIC was responsible for the physical and chemical characterization of the raw sediment samples used during the tests. Under SAIC direction, the sediments and their residuals were analyzed by Battelle Marine Sciences Laboratory in Sequim, WA. Table 4 provides characterization data pertaining to the sediments. The results from the raw sediment samples analyzed by Battelle are shown in Table 4.

**TABLE 4. Battelle Analysis - Characterization of Feed Sediments
(mg/kg, dry basis, unless specified)**

	Grand Calumet River
Total PCBs	13.1
Total PAHs	266
Moisture, % (as received)	55.0
Oil & Grease	9890
TOC, % weight	19.3
Total Volatile Solid, %	15.0
pH, S.U. (as received)	7.67

2.4 Technology Description

Wet air oxidation is a process in which organic or inorganic substances are oxidized in the presence of water at elevated temperatures and pressures. The usual temperature range varies from

approximately 350 to 600°F (175 to 320°C). System pressures of 300 to well over 3000 psig are required. The reactor pressure is determined by the vapor pressure of the water and the amount of excess oxidant used in the reactor. Compressed air or pure oxygen is the source of oxygen that serves as the oxidizing agent in the wet air oxidation process. As the oxidation temperature is increased, a larger portion of the organic compounds is oxidized. A basic flow diagram for the Zimpro Wet Air Oxidation Process is shown in Figure 3.

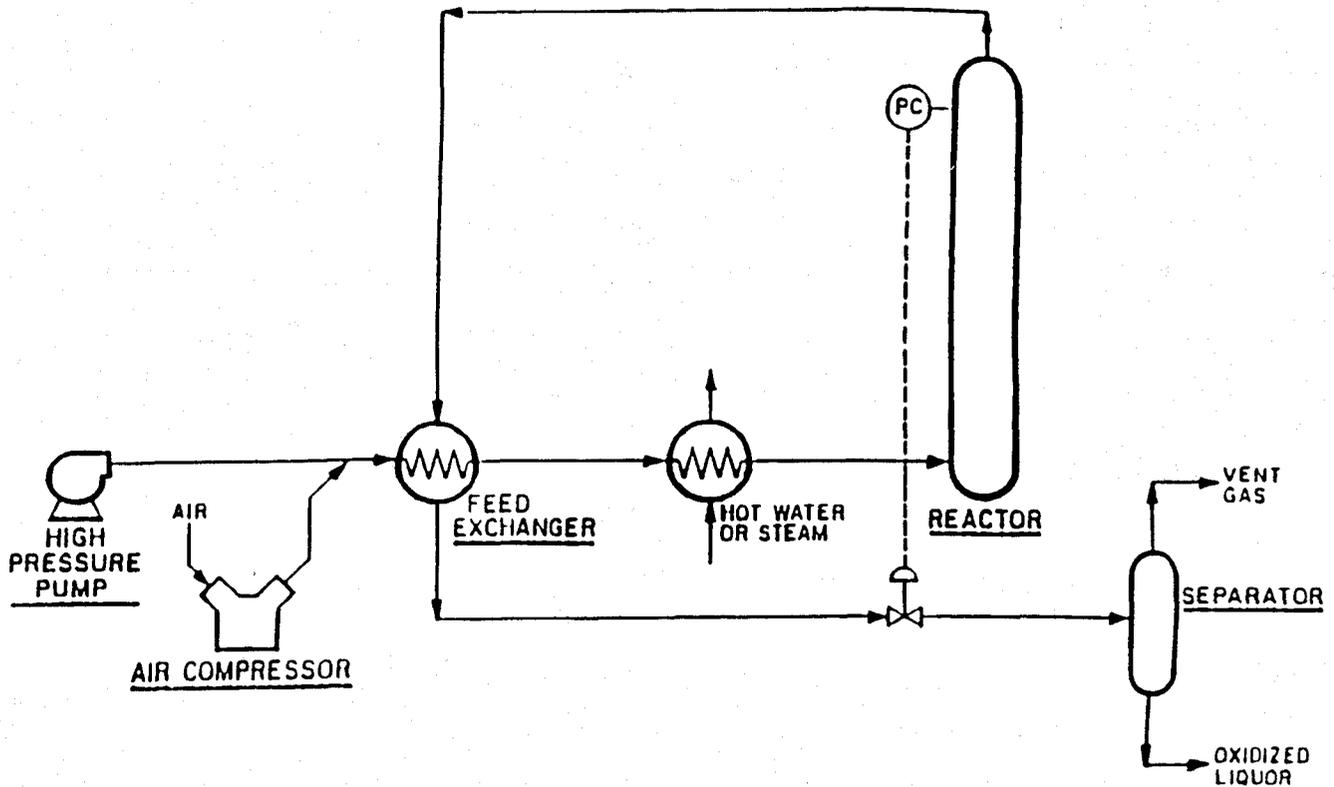


Figure 3. Flow Diagram for the Zimpro Wet Air Oxidation Process.
(Source: Zimpro Passavant Environmental Systems, Inc.)

In processing an aqueous waste, the waste stream containing the oxidizable material is first pumped to the system using a positive displacement, high pressure pump. The pressurized discharge from the high-pressure pump is combined with the air stream from the air compressor, forming a two-phase stream.

Next the air/waste stream passes through the feed/effluent heat exchanger, recovering heat from the hot, oxidized effluent. The heated mixture is then routed through an auxiliary heat exchanger, if needed. A vertical bubble-column is commonly used as the reactor to provide the required hydraulic detention time to effect the desired reaction. The reactor contents are mixed by the action of the gas phase rising through the liquid. As the gas phase rises and mixes with the liquid, oxygen is dissolved into the liquid. The reactor is sized to allow the oxidation reactions to proceed to the desired level. The desired reaction may range from a mild oxidation, which requires a few minutes, to total waste destruction, which requires an hour or more of detention time.

The oxidized liquid, oxidation product gases, and spent air leave the reactor and are routed through the shell side of the feed/effluent heat exchanger. A cooler can achieve additional cooling, if necessary. The cooled reactor effluent is throttled through a pressure control valve into the process separator where the reactor effluent is separated into a gaseous stream and a liquid stream. The gaseous stream from the process separator is routed through an off-gas cooler. The liquid stream is pumped beyond the treatment system's boundary limits. Further treatment of these oxidized liquids by a biological system may be required prior to discharge into the final receiving system (POTW, river, lake).

3.0 TREATABILITY STUDY APPROACH

3.1 Test Objectives and Rationale

SAIC has been contracted by the ARCS Program to test four technologies in removing organic contaminants (PCBs and PAHs) from sediments typical of locations around the Great Lakes. This treatability study has been done to determine the feasibility and cost-effectiveness of the Zimpro Wet Air Oxidation Process for destroying PCBs and PAHs in Grand Calumet River sediments. In order to accomplish this, this bench-scale test had the following objectives:

- To record observations and data to predict full-scale performance of the Zimpro Wet Air Oxidation Process
- To take samples during the treatability tests and conduct analyses sufficient to evaluate the solids and filtrate with respect to compounds of interest
- To calculate the destruction efficiency of target compounds
- To obtain treated solids (330 g dry basis) and filtrate for independent analysis.

Based upon previous tests performed by Zimpro, it is their experience that the data obtained from the bench test simulate full-scale operation. Ultimately, this data may be used to estimate both

the feasibility and treatment costs associated with a full-scale application of the technology. The ability to evaluate process feasibility from these tests was also reported in the Zimpro reports on the Phase I and Phase II tests (see Appendix A).

A two-phase approach was used during this study. During Phase I, SAIC sent a sample of the untreated sediment to Zimpro. The sample underwent a series of initial tests in order to determine the optimum conditions to be used during the actual treatability tests (Phase II). During Phase II, untreated sediment from the Grand Calumet River was sent to Zimpro. Samples of raw (untreated) sediments and the various end products generated during the treatability tests (Phase II) were obtained and analyzed by SAIC. The data generated by SAIC were primarily used to determine treatment efficiencies. Vendor-generated data are reported and commented on when available.

This study is only one part of a much larger program and is not intended to evaluate the treatment of the sediments completely. In order to ensure that the data obtained from this study can be objectively compared with data generated from the other studies performed in support of the ARCS Program, Battelle was subcontracted to perform all analyses for the different treatability studies performed by SAIC (seven treatability studies utilizing four technologies on four sediments). Assuming that the appropriate volumes of sediment and residuals were available, the same set of analyses described in Table 6 were applied during the characterization of each raw sediment and the end products from the different treatability tests. In addition, representatives from SAIC observed all Phase II treatability tests.

3.2 Experimental Design and Procedures

3.2.1 Phase I

Phase I was designed to allow Zimpro to explore a range of variables in order to set test parameters which would optimize the performance of the wet air oxidation technology for the bench-scale tests (Phase II). In order to accomplish this, a one-gallon sample of the Grand Calumet River sediment was sent to Zimpro by SAIC prior to bench-scale testing.

A factorial-design wet oxidation test with three levels of each variable was performed on the sediment to give an indication of the importance of the two experimental variables: residence time and oxidation temperature. Tests were run at the conditions shown in Figure 4.

320	X		X
300		X	
280	X		X
	30	60	90
	OXIDATION TIME (min)		

Figure 4. Conditions of Phase I Tests.

At 280°C typical test pressures were 2100 to 2200 psig; at 300°C typical test pressures were 2400 to 2500 psig; at 320°C typical test pressures were 2800 to 3000 psig. The Phase I wet air oxidation tests were performed in stainless steel laboratory autoclaves, each having a capacity of 0.75 L. The as-received waste sample was diluted with 3 parts distilled water to 1 part sediment (by volume) to reduce the total solids concentration and viscosity of the waste. The solids and water were slurried and put into the autoclaves with sufficient compressed air to result in an excess of oxygen following oxidation. The charged autoclaves were then placed in a heater/shaker mechanism, heated to the desired temperature, and held for the specified reaction time. Immediately following oxidation, the autoclaves were cooled to room temperature and depressurized.

Materials screening tests were also performed on the prepared sediment slurry. The tests were performed at 280°C for 100 hours. The following materials were tested, and all were found to have no localized corrosion and a general corrosion rate of < 1.0 MPY: 316-L stainless, Alloy 20cb-3, Alloy 625, Hastelloy C-276, and Titanium Grade 2. The results of these materials tests indicate that 316-L stainless steel would perform acceptably and be the most economical material of construction for a full-scale wet air oxidation system. A longer-term materials of construction test is recommended once the final wet air oxidation design conditions are determined.

3.2.2 Phase II

The experimental design for Phase II of the treatability program is presented in Appendix B and is summarized in this section.

The Phase II wet air oxidation tests were performed in titanium-stirred laboratory autoclaves, each having a capacity of 3.78 L. The autoclaves were equipped with a magnetic stirring device to help the

oxygen diffuse into the liquid and keep the solids in suspension. The stirrer remained on throughout the oxidation.

The as-received feed samples were removed from their jars and placed in a stainless-steel mixing bowl. A continuous mixer was used to stir the samples to obtain homogeneity. A glass beaker was used to remove aliquots and samples from the bowl, with the stirrer still in operation. The feed material was divided into seven portions for testing and two samples for the analysis of the raw feed. Separate stirred autoclave oxidations were performed using six of the seven samples. The samples were diluted, using HPLC grade water, to produce an autoclave feed sample with a suspended solids concentration of approximately 10 percent. Ten percent suspended solids was used to simulate the 10 to 20 percent concentrations that would be used in a commercial unit to allow the sediment to be pumped at pressure. This does not mean that all the additional water needs to be supplied as feed water; some can be recycled from the filtrate after treatment. Based on the Phase I test, a reactor temperature of 280°C and a hydraulic detention time of 90 minutes was selected for the Phase II tests. These conditions were selected to provide a balance between PAH destruction and process economics. Table 5 presents information on the feed samples charged to the stirred autoclave and the volume discharged.

Table 5. Wet Oxidation Feed

Run Number	Sample Number	Sample Charged	
		Sediment	Water
1	US02	253	597
2	US04	250	601
3	US01	225	626
4	US03	225	625
5	US05	128	627
6	US06	126	625

The autoclaves were charged with the sediment slurry and sufficient compressed air to result in excess oxygen remaining following oxidation. The charged autoclaves were then heated to the desired oxidation temperature by electrical heating bands and held at that temperature for the specified reaction time. Immediately following the oxidation, the autoclaves were cooled to room temperature by internal water cooling coils and then depressurized.

3.3 Sampling and Analysis

The Quality Assurance Project Plan is provided in Appendix C.

3.3.1 Sampling

At the beginning of the Phase II Treatability test, SAIC personnel observing Phase II packed and shipped a sample of the untreated Grand Calumet River sediment to SAIC's subcontract laboratory, Battelle, in accordance with written detailed instructions supplied to the SAIC on-site representative. The material was thoroughly mixed to achieve homogeneity of the solids and liquids in order to obtain a sample representative of the material treated in the Zimpro Wet Air Oxidation Process. There was no feed preparation other than mixing prior to sampling or testing.

After each of the six wet oxidation tests was complete, samples of the final filtrate and solid residuals were collected by SAIC for EPA and Zimpro. Samples from the six tests were composited to a single sample for analysis. The filtrate and solids were composited separately. As specified in the Quality Assurance Project Plan (QAPP) a minimum of 300 g dry basis of solid material was required in order for Battelle to be able to complete the necessary analyses of that material. The net weight of sample collected for Battelle was 394 g. Zimpro was provided with approximately 30 g of sample and two show vials with a small amount of solid material were collected for GLNPO.

3.3.2 Analysis

The analyses specified in Table 6 were conducted by SAIC's subcontracted laboratory, Battelle, on the sediments and the process by-products from Phase II. Zimpro conducted analyses for COD, BOD, total solids and ash, and pH. Battelle's data was used for the results presented in this report. Zimpro's data, where possible, is discussed to facilitate interpretation of the results of the treatability test.

3.3.2.1 Battelle Analyses

Following the Phase II treatability test, Battelle conducted analyses on the raw sediment and the end products. The number of analyses conducted on these sediments and their residuals are listed in Table 6. Descriptions of the analytical methods employed can be found in the QA Section of this report.

3.3.2.2 Zimpro Analyses

Zimpro analyzed the treated solids and filtrate for COD, BOD, total ash and solids, and pH. Table 7 shows the analyses performed by Zimpro. Details on the analytical methods used by Zimpro are presented in Appendix A.

Table 6. SAIC's Analysis Schedule For the Phase II Wet Air Oxidation of Grand Calumet River Sediments

Parameters	QC Sample and Method Blank	Untreated Sediment	MS	Tripli- cate	Treated Solids	MS	MSD	Tripli- cate	Water	MS	MSD	Tripli- cate	Oil	MS	Tripli- cate
Total Solids (Moisture)	(1) YES	(1) G		(2) G	(1) G			(2) G							
Volatile Solids	(1) YES	(1) G		(2) G	(1) G			(2) G	NA*			NA			
O & G	(1) YES	(1) G		(2) G	(1) G			(2) G	NA			NA			
Metals	(0) YES	(1) G	(1) G	(2) G	(1) G	(1) G		(2) G	NA	NA		NA			
PCBs	(0) YES	(1) G	(1) G	(2) G	(1) G	(1) G	(1) G	(2) G	(1) G	(1) G	(1) G		NA	NA	NA
PAHs	(0) YES	(1) G	(1) G	(2) G	(1) G	(1) G	(1) G	(2) G	(1) G	(1) G	(1) G		NA	NA	NA
TOC	(0) YES	(1) G	NA	NA	(1) G	NA	NA	NA	NA	NA		NA			
Total Cyanide	(0) YES	(1) G	NA	NA	(1) G	NA		NA	NA	NA		NA			
Total Phosphorus	(0) YES	(1) G	NA	NA	(1) G	NA		NA	NA	NA		NA			
pH	(0) YES	(1) G		NA	(1) G			NA	NA	NA		NA			
BOD	NA								NA						
Total Suspended Solids	NA								NA						
Conductivity	NA								NA						

* Not Analyzed
 (1) = Number of Analyses
 G = Grand Calumet River
 MS = Matrix Spike
 MSD = Matrix Spike Duplicate

Table 7. Zimpro Analyses

Matrix Sample	COD	BOD ₅	Total Solids	Total Ash	pH
Treated Solids	yes	no	yes	yes	no
Filtrate	yes	yes	yes	yes	yes

4.0 RESULTS AND DISCUSSION

4.1 Summary of Phase I Results

The principal objectives for the Phase I study were to ascertain the degree of destruction of PAHs and COD found in the sediment sludge. In addition, a preliminary materials of construction evaluation was conducted. Oxidations were performed in laboratory autoclaves at temperatures of 280, 300, and 320°C. The residence time for the oxidations ranged from 30 to 90 minutes. The conditions tested are illustrated in Figure 5, which indicates the destruction efficiency for PAHs. The Phase I study concluded that the PAH destruction was in the range of 94 to 99 percent and the COD destruction was in the range of 45 to 70 percent. The condition selected by Zimpro as optimum was a reactor temperature of 280°C and a hydraulic detention time of 90 minutes.

320	96.2%		98.8%
300		94.2%	
280	97.3%		95.7%
	30	60	90

OXIDATION TIME (min)

Figure 5. Percent Destruction of PAH in Solids as a Function of Operating Conditions.

4.2 Summary of Phase II Results

The concentrations of PAHs, PCBs, metals, total solids, volatile solids, and oil and grease present in the untreated sediments and treated solids were measured in this study. The following sections briefly address the analytical results obtained for contaminant concentrations present in the raw sediments and

the process residuals (i.e., treated solids and filtrate). The analytical data received from Battelle can be found in Appendix D.

Individual PAH compounds, PCB Aroclors, and metals were quantitated during sample analyses. In order to determine overall destruction efficiencies for each class, it was necessary to sum these individual results. In instances where all reported results were less than the analytical detection limits, total concentrations are reported as less than the sum of the individual detection limits. Where one or more individual components are above detection limits, total concentrations are reported as less than the sum of the detected components plus the sum of the detection limits of the undetected components.

4.2.1 Sediments/Treated Solids

4.2.1.1 PAHs

Feed material and treated solids were analyzed for PAHs. As shown in Table 8, total PAH concentrations of less than 2.84 mg/kg were found in the solids produced by treating the Grand Calumet River sediments. These values correspond to a destruction efficiency of greater than 98.9 percent. Some of the organics in the untreated sediment were destroyed during treatment, thereby reducing the volume of the sediments. Based on results for TOC (shown in Table 11), it appears that about 10 percent by weight of the sediment was destroyed by wet oxidation. Since the mass balance (Section 4.2.3) indicates that over 90 percent of the material charged to the reactor was recovered, the calculation for PAH destruction was based on the PAH concentrations in the solids before and after treatment.

4.2.1.2 PCBs

Samples of the feed material and the treated solids produced using the Zimpro Wet Air Oxidation Process were analyzed for PCB contamination. The data from these analyses are presented in Table 9.

A PCB concentration of 8.5 mg/kg was found in the treated solids generated from the Grand Calumet River sediment. This corresponds to a PCB destruction efficiency of 29 percent. However, the Wet Air Oxidation Process was not expected to treat PCBs since previous tests have shown that PCBs are too refractory for effective treatment by wet oxidation under these test conditions.

**Table 8. Feed and Treated Solids PAH Concentrations
(mg/kg, dry basis)**

Contaminant	Grand Calumet River		
	Feed ¹	Treated ²	% Destruction
Naphthalene	4.2	0.03	99.3
Acenaphthylene	3.1	<0.15	>95.2
Acenaphthene	4.4	<0.02	>99.5
Fluorene	4.9	<0.02	>99.6
Phenanthrene	15.9	0.17	98.9
Anthracene	6.4	0.04	99.4
Fluoranthene	33.3	0.11	99.7
Pyrene	33.0	0.18	99.5
Benzo(a)anthracene	21.4	0.24	98.9
Chrysene	29.4	0.84	97.1
Benzo(b)fluoranthene	25.0	0.29	98.8
Benzo(k)fluoranthene	16.3	<0.004	>99.9
Benzo(a)pyrene	27.6	0.27	99.0
Indeno(1,2,3-cd)pyrene	19.5	0.12	99.4
Dibenzo(a,h)anthracene	7.1	0.17	97.6
Benzo(g,h,i)perylene	14.4	0.19	98.7
Total PAH	265.9	<2.84	>98.9

1 Average of three analyses
2 Single analysis

**Table 9. Total PCBs
(mg/kg, dry)**

Sample	Feed ²	Treated Solids ³	% Destruction
Total PCBs ¹	11.9	8.5	29

1 Identified as Aroclors 1248 and 1254
2 Average of three analyses
3 Single analysis

4.2.1.3 Total Metals

The data in Table 10 highlight the results for the metal contaminants present in the untreated feed and the treated solids. As demonstrated by the fact the metals concentrations are higher in the treated solid than in the untreated sediment, the Wet Air Oxidation Process does not effectively remove metals. The increase is probably related to the 10 percent volume reduction for the subject sediment achieved from the destruction of the organics by the Wet Air Oxidation Process.

**TABLE 10. Metal Concentrations in the Feed and Treated Solids
(mg/kg, dry)**

Contaminant	Feed	Treated Solids
Arsenic	27.6	29.1
Barium	283	368
Cadmium	7.7	13.0
Chromium	1075	1437
Copper	254	350
Iron	173,000	227,000
Lead	746	1095
Manganese	1910	2677
Mercury	1.40	2.26
Nickel	115	138
Selenium	5.4	6.7
Silver	4.8	6.9
Zinc	3030	4290

4.2.1.4 Other Analyses

The feed sediments and treated solids were analyzed for percent moisture, oil and grease, TOC, total volatile solids, and pH as shown in Table 11. The oil and grease was reduced by 90 percent. The TOC was initially 19.3 percent by weight and was reduced to 9.3 percent by weight, including a 10 percent weight loss caused by destruction of the organics. The pH was reduced from about 7.5 to 6.5 in the treated solids.

**Table 11. Reduction Percentages for Other Parameters
(mg/kg, dry basis, unless specified)**

Contaminant	Feed	Treated Solids	Percent Reduction or Destruction
Total PAHs	266	<2.84	>98.9
Total PCBs	11.9	8.5	29
Moisture, % (as received)	55.0	43.3	
Oil & Grease	9890	951	90
TOC, % weight	19.3	9.3	52
Total Volatile Solids, %	15.0	7.3	51
pH, S.U. (as received)	7.67	6.51	

4.2.2 Filtrate

The concentrations of PAHs and PCBs in the filtrate from the wet oxidation reactor can be found in Tables 12 and 13. Individual PAH concentrations were mainly below the detection limits. The results indicate that the wet oxidation process destroys the PAHs and some of the PCBs, but does not extract large amounts into the water.

4.2.3 Mass Balance Calculations

Wet air oxidation is a process in which organic material is oxidized in the presence of water. Hydrocarbons are oxidized to water and carbon dioxide, while chlorine reacts to form HCl. Because of the interaction between the organic material and water, the sum of the solids and the water is used for the mass balance. Table 11 indicates that the TOC in the solids (Dry Basis) is reduced from 19.3 percent to 9.3 percent. This amounts to an 11 percent weight loss for the dry sediment, which is equivalent to a 5 percent weight loss for the wet sediment. This weight loss from reaction amounts to about 1.5 percent of the total weight of sediment and water charged to the reactor. An additional 100 to 150 g of sample were lost in a transfer procedure in Run Number 4. This represents 2 to 3 percent of the total mass of the six test runs. The summation of the percent recovery results shown in Table 14 indicates that 90 percent of the material charged to the reactor was recovered after treatment. Correcting for the amount of sample oxidized during treatment, and the amount known to be lost in Run Number 4, about 94 percent of the original sample was accounted for. Since all the species containing carbon and hydrogen in the sediment were not known and the organics were being oxidized to carbon dioxide and water, it is not possible to conduct a more detailed mass balance.

Table 12. PAH Concentrations in the Filtrate (ug/L)

Contaminant	Filtrate
Naphthalene	0.96
Acenaphthylene	<0.15
Acenaphthene	<0.22
Fluorene	<0.19
Phenanthrene	1.04
Anthracene	<0.14
Fluoranthene	0.16
Pyrene	0.14
Benzo(a)anthracene	<0.10
Chrysene	<0.10
Benzo(b)fluoranthene	<0.07
Benzo(k)fluoranthene	<0.06
Benzo(a)pyrene	<0.08
Indeno(1,2,3-cd)pyrene	<0.07
Dibenzo(a,h)anthracene	<0.09
Benzo(g,h,i)perylene	<0.07
Total PAHs	<3.64

Table 13. PCB Concentrations in the Filtrate (ug/L)

Contaminant	Filtrate
Aroclor 1242	<0.2
Aroclor 1248	<0.2
Aroclor 1254	<0.1
Aroclor 1260	<0.1

Table 14. Wet Oxidation Feed and Output (grams)

Run Number	Sample Number ¹	Sample Charged		Sample Removed		Percent Recovered ²
		Sediment	Water	Solids	Filtrate	
1	US02	253	597	88	682	91
2	US04	250	601	84	685	90
3	US01	225	626	108	703	95
4 ³	US03	225	625	66	545	84
5	US05	128	627	51	615	88
6	US06	126	625	43	657	93

1 Note that Table 1 in Appendix A, Phase II is based on Sample Number instead of Run Number.

2 Before accounting for weight loss by oxidation. Average of all six percentages is 90 percent.

3 Pump tubing leaked causing small loss of sample (100-150 ml). Sample was considered valid since the loss was small and sample appeared representative.

4.3 Summary of Vendor Cost Calculations

Zimpro and SAIC mutually developed three scenarios for the full-scale wet air oxidation of the Grand Calumet River sediments. The three scenarios involve the treatment of 10,000, 40,000, and 100,000 yd³ of all sediments; all at 40 percent solids. The Wet Air Oxidation Process designed can handle sediments at a solids concentration of 10 percent; therefore a 3 to 1 dilution, using water from the harbor that is being dredged, would be required. Wet air oxidation units of 10, 20 and 40 gallons per minute capacity would handle these volumes of sediment as shown in Table 15. The design parameters for the proposed systems are presented in Table 16.

Table 15. Time Required to Process Harbor Sediments as a Function of Unit Size

WAO Capacity, gpm	Time to Process Sediments, Yrs.		
	10,000 yd ³	40,000 yd ³	100,000 yd ³
10	2.25	6.75	22.50
20	1.12	3.38	11.25
40	0.56	1.69	5.62

Table 16. System Design Parameters Selected by Zimpro

Design Flow Rate (U.S. gpm)	10.0	System 1
	20.0	System 2
	40.0	System 3
Operating Schedule		24 hours/day 5 days/week 50 weeks/year
Normal Operating Mode		Autothermal
Reactor Hydraulic Detention Time (minutes)		90
COD Reduction (%)		83
Mechanical Design Temperature (°F)		570
Mechanical Design Pressure (psig)		2,000
Operating Temperature (°F)		536
Operating Pressure (psig)		1,500
Material of Construction for Waste Wetted Surfaces		316L

Detailed information on the equipment and the capital cost basis may be found in Appendix A. The estimated supply and installation cost for each of the systems is given in Table 17. Costs do not include provisions for the following items:

- Any applicable state, local, or federal taxes, permits, bonds, fees, or duties
- Design or supply of foundations, civil work, sumps, concrete lining, or sewers
- Design, supply, or installation of equalization tanks
- Design, supply, or installation of the post-treatment system
- Equipment storage necessitated due to action of the purchaser
- Any operational spare parts other than spare rotating equipment specified by Zimpro
- Any piping or wiring beyond the proposed system boundary limits.

Table 17 also includes the estimated utility requirements.

Table 17. Capital Cost and Estimated Utility Requirements

	System 1	System 2	System 3
Capital Cost (\$)	4,500,000	5,600,000	7,300,000
Natural Gas @1000 BTU/scf - startup only (scfm)	3	10	36
Cooling Water @ 65°F (U.S. gpm)	135	275	550
Operating Power (kWh/hr)	130	265	530

Table 18 provides information on the operating costs for the wet air oxidation units.

4.4 Quality Assurance/Quality Control

The conclusions and limitations of data obtained during the evaluation of Zimpro's wet air oxidation process are summarized in the following paragraphs.

Upon review of all sample data and associated QC results, data generated for the Zimpro treatability study has been determined to be of acceptable quality. In general, QC results for accuracy and precision were good and can be used to support technology removal efficiency results.

Refer to Appendix E for the analyses related to Quality Assurance/Quality Control.

Table 18. Annual Operating and Maintenance Costs for Treating Dredged Sediments

	System 1	System 2	System 3
Energy			
Natural Gas @ \$5.00/MBTU 8 hr/day, 5 day/wk, 50 wk/yr	360	1200	4320
Power @ \$0.05/kwh	39,000	79,500	159,000
Water and Chemicals			
Cooling Water @\$0.50/1000 gal	24,300	49,500	99,000
Labor			
Operation @ \$20.00/hr 24 hr/day, 5 day/wk, 50 wk/yr	120,000	120,000	120,000
Maintenance @ \$20.00/hr 24 hr/day, 5 day/wk, 50 wk/yr	24,000	24,000	24,000
Supervision @ \$30.00/hr 8 hr/day, 5 day/wk, 50 wk/yr	60,000	60,000	60,000
Maintenance			
Materials @ 2% of Capital	90,000	112,000	146,000
Waste Disposal			
Supernatant and Filtrate @ 3750 mg/l BOD POTW Sewer Chg \$0.15/lb BOD	17,000	34,000	68,000
Annual Capital Cost¹ Amortized over 10 yr @ 10%	732,354	911,374	1,188,041
Taxes @ 4% of Capital Cost	180,000	224,000	292,000
Overhead Charges @ 60% of Labor and Maintenance	176,400	189,600	210,000
Total Annual O&M Costs	\$1,463,414	\$1,805,174	\$2,370,361
Sediment Processed (yd ³ /yr)	4,444	8,889	17,778
Volume Processed (gal/yr)	3,600,000	7,200,000	14,400,000
Cost (\$/gal)	0.406	0.251	0.163
Cost (\$/yd ³)	329.30	203.10	133.33

1 It is assumed that the system will be used for other purposes after completion of remediation. Therefore a 10-year lifetime is assumed for uniformity.

APPENDIX A

BENCH-SCALE SHAKING AUTOCLAVE RESULTS FOR
WET AIR OXIDATION SYSTEM TREATMENT
OF INDIANA HARBOR SEDIMENT SLUDGE
SCIENCE APPLICATIONS INTERNATIONAL CORPORATION
PHASE I
SAIC SUBCONTRACT NO. 16-920034-51

SEPTEMBER 18, 1991

1.0 INTRODUCTION

Laboratory wet air oxidation tests were performed on sediment sludge from the Indiana harbor. The test work was performed for Science Applications International Corporation (SAIC) under contract with the U.S. EPA. The principal objectives for this Phase I study were to ascertain the degree of destruction of poly-aromatic hydrocarbons (PAHs) and chemical oxygen demand (COD) found in the sediment sludge.

Oxidations were performed in laboratory autoclaves at temperatures of 280, 300, and 320°C. The residence time for the oxidations ranged from 30 to 90 minutes. Data from this report will provide the basis for evaluation of wet air oxidation for treatment of the sediment sludge.

2.0 WET AIR OXIDATION PERFORMANCE

The initial sediment sample contained approximately 48 percent total solids and contained approximately 140 g/l of COD. The sample was not size classified and did contain some particles over 1/16 inch. The "as received" sample had to be diluted to reduce the total solids concentration and viscosity of the solution. A dilution of 3 parts distilled water to 1 part sediment (by volume) was mixed. The analysis of this autoclave feed sample is presented in Table 1. The autoclave feed mixture contained 33.7 g/l of COD. The total solids of the feed was measured at 119.2 g/l. The total PAHs concentration was measured at 2761.6 ug/l.

A 2^2 factorial wet air oxidation test was performed on the sediment sludge. The factorial test will give an indication of the importance of the two experimental variables: residence time, and oxidation temperature. A diagram of the 2^2 factorial test can be seen in Figure 1. The reductions of COD (Y_{COD}) and of total PAHs (Y_{PAHs}) obtained by the wet air oxidation testing were fitted to a first order model:

and
$$Y_{\text{COD}} = b_0 + b_1X_1 + b_2X_2$$

$$Y_{\text{PAHs}} = b_0 + b_1X_1 + b_2X_2$$

where:

$$X_1 = \frac{\text{Temperature} - 300^\circ\text{C}}{20^\circ\text{C}}$$

$$X_2 = \frac{\text{Time} - 60^\circ\text{C}}{30 \text{ minutes}}$$

$$b_0 = \frac{\sum Y}{N}$$

where N = 5 experimental points

$$b_1 = 0.5(Y_H - Y_L)$$

where Y_H is the average of the results at the high temperature and Y_L is the average of the low temperature results.

Likewise:

$$b_2 = 0.5(Y_H - Y_L)$$

where Y_H is the average of the results at the high time and Y_L is the average of the low time results.

Certain assumptions must be made to determine the values for the first order models since suspended solid concentration in the oxidized effluents were not measured. First we assume that the ash content of the influent and oxidized effluent are equal and that the effluent ash content is divided between suspended ash and soluble ash, which was measured. Therefore the suspended ash content is given by the equation:

$$\text{Suspended Ash (SAS)} = \text{Total Ash}(119.2 \text{ g/l}) - \text{Soluble Ash} \quad (1)$$

in addition:

$$\text{Total Solids (TS)} = \text{SAS} + \text{Volatile Solids (VS)} \quad (2)$$

where:

$$\text{VS} = \text{COD}/1.8 \quad (3)$$

Where the COD is given as a fraction (mg/g) of the total solids (f*TS). By combining and rearrangement of (2) and (3) the total solids is obtained as follows:

$$TS = SAS/(1-f/1.8)$$

Assuming the density of the suspended solids is 1.2 then the volume of filtrate obtained for each oxidized effluent can be calculated using the relationship:

$$\text{Volume of filtrate} = 1.0 \text{ liters} - TS/1.2$$

Using the above relationships: the concentration of suspended solids, the COD and total PAHs concentrations in the effluents, and the volumes of filtrate for each oxidation condition can be determined. These calculated values are reported in Tables 1 and 2 under the calculated values heading.

COD REDUCTION

The first order coefficients for the COD reduction (see Table 1) are determined as follows:

$$b_0 = 59.28$$

$$b_1 = 0.5(69.3 - 55.15)$$

$$b_2 = 0.5(61.8 - 62.65)$$

The first order model for COD reduction is then given as:

$$Y_{\text{COD}} = 59.28 - 7.08X_1 - 0.42X_2$$

The first order model for the COD reduction shows a strong dependency on the temperature (X_1) and a negative dependency on time (X_2). These results are slightly misleading, in most cases COD destruction should increase with respect to time. One possible explanation for

the results is analytical error of the COD values. The measured COD of the autoclave feed was 33.7 g/l and the oxygen uptake for the 280°C oxidation at 30 minutes was calculated at 33.8 g/l. By adding 33.8 g/l to the remaining COD in the oxidized effluent at the same condition (14.8 g/l) one would estimate the feed COD at 48.6 g/l and not the measured value of 33.7 g/l. The oxidation process could have partially destroyed some organic compound that did not completely respond to the feed COD test, thus yielding additional COD in the oxidized effluents.

The reductions in COD obtained by wet air oxidation ranged from 56.1 percent at 280°C for 30 minutes to 69.4 percent at 320°C for 90 minutes. The COD remaining after wet air oxidation appears to be very biodegradable as indicated by the BOD₅/COD ratios. The BOD₅/COD ratios in the filtered effluents were greater than 0.5. The remaining COD is most likely partially oxidized organic compounds in the form of low molecular weight organic acids.

PAHs REDUCTION

The first order model for PAHs reduction can also be calculated in the same manner and is given as:

$$Y_{\text{PAH}} = 96.4 - 0.5X_1 + 0.25X_2$$

The first order model for the PAHs destruction indicates only a slight dependency on both temperature (X_1) and time (X_2). Excellent reduction of the total PAHs was obtained by wet air oxidation. For the conditions tested, reduction of the total PAHs concentration ranged from 94.2 to 98.8 percent. The PAHs data is somewhat misleading in that the 300°C oxidation has a slightly lower reduction than at the 280°C, 30 minutes sample. Analytical error in the PAHs analysis of the filtered effluent appears to be the source of the discrepancy. A limitation of sediment sample prevented a repeat of this wet air oxidation run.

Using the data obtained from the shaking autoclave study, parameters for the demonstration testing in a stirred autoclave (Phase II) were set. It was recommended that additional testing would be performed at 280°C for 90 minutes. This recommendation is based on PAHs

destruction which showed only slight improvement by increasing the temperature to 320°C.

3.0 MATERIALS OF CONSTRUCTION EVALUATION

Materials screening tests were performed on the diluted sediment sludge. The test was performed at 280°C for 100 hours. The objective of the screening test was to identify types of alloys which could be considered candidate materials of construction for a full scale wet air oxidation system.

The alloys selected for the screening were 316-L, Alloy 20, 625, C-276, and titanium grade 2. A list of the alloy's nominal chemical compositions can be found in Table 3. These materials were selected for their known corrosion resistance in the wet air oxidation environment.

The results indicate that all the alloys tested would be acceptable materials. The general corrosion rates were less than 1.0 mpy (0.001 inches per year). The results from the testing are presented in Table 4. None of the alloys showed signs of pitting or transgranular stress corrosion cracking (TGSCC). The low chloride levels and near neutral pH of the sediment sludge make it non-aggressive to these alloys at the elevated temperature. The results of this materials test indicate that 316-L would perform acceptably and be the most economical material of construction for a full scale wet air oxidation system. A longer term materials of construction test is recommended once the final wet air oxidation design conditions have been determined.

4.0 EXPERIMENTAL PROCEDURES

4.1 Wet Air Oxidation Testing

All wet air oxidation tests were performed in laboratory stainless steel autoclaves each having a capacity of 750 mls. Autoclaves were charged with the waste and sufficient compressed air to result in excess residual oxygen following oxidation. The charged autoclaves were then placed in a heater/shaker mechanism, heated to the desired oxidation temperature and held for the specified reaction time.

Immediately following oxidation, the autoclaves were cooled to room temperature and depressurized.

All analyses included as a part of the oxidation testing were performed by the Zimpro/Passavant analytical laboratory, Enviroscan, according to Standard Methods¹ or EPA Methods for the Chemical Analysis of Water and Waste².

4.2 Materials of Construction Testing

Materials screening testing was performed in a 500 ml capacity titanium shaking autoclave similar to that used in the wet air oxidation testing. The coupons that were utilized in testing were welded u-bends fabricated from commercial sheet stock of various alloys. The u-bend coupons were not annealed after welding and bending. Therefore, the test coupons were in a plastically strained and residually stressed metallurgical state. The placement of the coupons in the autoclave was facilitated through use of a threaded rod and nuts. Teflon washers were placed between the coupons and retaining nuts to produce a crevice area for monitoring of crevice corrosion.

Prior to and after testing, the alloy coupons were cleaned in 10% nitric acid, weighed and measured to determine a general corrosion rate. Visual and microscopic examinations were performed after testing to identify the presence of any localized corrosion.

5.0 ZIMPRO[®] WET AIR OXIDATION SYSTEMS

Thermal oxidation is a widely accepted approach to waste treatment.³ Wet air oxidation (WAO) is a process that combines the effectiveness of thermal oxidation with fuel economy when handling aqueous streams and slurries.⁴ With the exception of a few polysubstituted halogenated organic compounds (kepone, PCB), WAO can destroy most organic compounds.

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Environmental Systems, Inc.

The wet air oxidation process is based on the discovery that many chemicals will oxidize (burn) in the aqueous phase at relatively low temperatures. The reaction mechanisms involve a family of related oxidation and hydrolysis reactions. The enhanced solubility of oxygen in aqueous solution at elevated temperature and pressure provides a strong driving force for oxidation. The source of oxygen for the process is usually compressed air. High pressure pure oxygen may also be used.

ZIMPRO's Wet air oxidation treatment technology has been applied to waste liquors, slurries, and aqueous streams for over forty years.⁵ The Wet Air Oxidation process is simple, exceptionally adaptable to variations in feed characteristics, and is applicable to a wide variety of oxidizable materials.

In most current applications, wet air oxidation is used to treat hazardous wastewaters which are prohibited from land disposal by new USEPA restrictions.⁶ Wet air oxidation has been specified as Best Demonstrated Available Technology (BDAT) by USEPA for some hazardous waste classes restricted by the Resource Conservation and Recovery Act (RCRA).

A basic flow diagram for the ZIMPRO Wet Air Oxidation system is shown in Figure 2. According to the flow scheme, a stream containing oxidizable material is pumped to the system using a positive displacement, high pressure pump. In the wet air oxidation process elevated pressures are required to keep water in the liquid state.

The feed stream is preheated by heat exchange with hot oxidized effluent. Air or oxygen is introduced at the high pressure pump discharge or injected directly into the wet air oxidation reactor. The reactor provides liquid retention time, during which oxidation reactions occur. Liquid water "catalyzes" oxidation so that reactions proceed at relatively lower temperatures than would be required if the same materials were oxidized in open flame combustion. The retention time varies from a few minutes to several hours depending on the type of wastewater and the treatment objectives. The heat of oxidation raises the reactor temperature to

the desired operating level. Water moderates oxidation rates, providing a medium for heat transfer and removing excess heat by evaporation.

Oxidation takes place at temperatures of 175 to 320°C (347 to 608°F) and at pressures of 2,069 to 20,690 kPa (300 to 3,000 psig). Injection of steam into the reactor or external heating may be used to maintain the operating temperature for systems not generating enough heat from the oxidation process.

Effluent from the oxidation reactor is cooled by heat exchange with the feed before the pressure is reduced through a control valve. The liquid and non-condensable gases are disengaged in a separator drum and released separately. The aqueous stream is discharged or is treated further.

Wet oxidation is intrinsically energy conservative. The heat that is released in the oxidation process can be harnessed to produce steam or hot water. Wet oxidation consumes far less fuel than other forms of thermal oxidation.

TABLE I
 WWT AIR OXIDATION OF INDIANA HARBOR SLUDGE
 FOR SCIENCE APPLICATIONS INTERNATIONAL CORPORATION

ANALYTICAL NO.	54594		54595		54600		54597		54602		54598		54596		54601	
	AUTOCCLAVE PRD	FILTRATE CAKE														
OXIDATIONS TEMP. C	-	280	200	200	200	200	300	300	300	100	320	320	320	320	320	320
TIME AT TEMPERATURE, MIN.	-	30	30	90	90	90	60	60	60	60	30	30	30	90	90	90
COD	33.7	5.99	90.6 mg/g	6.05	95.9 mg/g	5.5	120.0 mg/g	5.13	57.2 mg/g	4.32	62.6 mg/g	4.32	62.6 mg/g	4.32	62.6 mg/g	4.32
T BOD	2.0	3.6	-	3.5	-	2.9	-	3.1	-	2.6	-	2.6	-	2.6	-	2.6
T BOD/COD	0.06	0.60	-	0.58	-	0.53	-	0.60	-	0.60	-	0.60	-	0.60	-	0.60
pH	7.23	4.95	-	4.93	-	5.01	-	5.17	-	5.14	-	5.14	-	5.14	-	5.14
SOL. CHLORIDE	mg/l	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TOTAL SOLIDS	g/l	4.95	51.6 g	5.19	54.4 g	4.3	52.4 g	5.13	55.3 g	4.15	54.9 g	4.15	54.9 g	4.15	54.9 g	4.15
TOTAL ASH	g/l	2.67	90.3 g	2.66	90.9 g	2.5	92.8 g	4.46	92.6 g	2.52	93.6 g	2.52	93.6 g	2.52	93.6 g	2.52
OILS/GREASE	mg/l	30.7	485 mg/g	33.8	519 mg/g	18.9	375 mg/g	15.1	332 mg/g	10.4	231 mg/g	10.4	231 mg/g	10.4	231 mg/g	10.4
CALCULATED VALUES																
BEFORE FILTRATION OF EFFLUENT																
SUSPENDED SOLIDS	g/l	102.91	-	103.24	-	104.94	-	99.09	-	99.09	-	99.09	-	101.41	-	101.41
SUSPENDED ASH	g/l	97.73	-	97.74	-	97.9	-	95.98	-	95.98	-	95.98	-	97.68	-	97.68
AFTER FILTRATION OF EFFLUENT																
VOLUME FILTERED	ml/l	914.2	-	914.0	-	912.5	-	917.4	-	917.4	-	917.4	-	915.5	-	915.5
COD	g/l	5.48	9.32	5.53	9.90	5.02	12.60	4.71	5.67	3.95	6.35	3.95	6.35	3.95	6.35	3.95
TOTAL COD DESTRUCTION, %	-	56.1	54.2	54.2	47.5	69.2	69.2	69.2	69.2	69.2	69.2	69.2	69.2	69.2	69.2	69.2
OFF GAS ANALYSES																
CO2	%	57.3	52.9	52.9	62.7	60.4	60.4	60.4	60.4	60.4	60.4	60.4	60.4	60.4	60.4	60.4
O2	%	29.6	35.9	35.9	25.1	27.2	27.2	27.2	27.2	27.2	27.2	27.2	27.2	27.2	27.2	27.2
N2	%	30.9	4.4	4.4	5.7	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
CO	%	4.7	3.1	3.1	1.7	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
THC	PPM	926	794	794	311	550	550	550	550	550	550	550	550	550	550	550
OFF GAS VOLUME, liters	liters	8.03	9.6	9.6	9.72	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
OXYGEN CONSUMED, g/l	g/l	33.8	29.0	29.0	33.5	32.6	32.6	32.6	32.6	32.6	32.6	32.6	32.6	32.6	32.6	32.6

TABLE 2
 WWT AIR OXIDATION OF INDIANA HARBOR SLUDGE
 FOR SCIENCE APPLICATIONS INTERNATIONAL CORPORATION

EPA METHOD 610

ANALYTICAL NO.	OXIDATIONS TEMP. C	TIME AT TEMPERATURE, MIN.	54594		54595		54600		54597		54602		54593		54596		54601		
			FILTRATE	CARE	FILTRATE	CARE	FILTRATE	CARE	FILTRATE										
ACENAPHTHYLENE	ug/l	< 20	< 1.0	< 10 ng/g	< 1.0	< 1.0	479 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g
ANTHRACENE	ug/l	< 20	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g								
BENZO(A) ANTHRACENE	ug/l	85.2	< 1.0	117 ng/g	< 1.0	117 ng/g	1.1	31.6 ng/g	< 1.0	133 ng/g	< 1.0	133 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g
BENZO(A) PYRENE	ug/l	204	< 1.0	101 ng/g	< 1.0	79.6 ng/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	100 ng/g	< 1.0	58.4 ng/g	< 1.0	58.4 ng/g	
BENZO(B) FLUORANTHENE	ug/l	114	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	176 ng/g	< 1.0	176 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g
BENZO(GHI) PERYLENE	ug/l	283	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
BENZO(K) FLUORANTHENE	ug/l	146	< 1.0	16.2 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	103 ng/g	< 1.0	103 ng/g	< 1.0	< 1.0	362 ng/g	< 1.0	17.3 ng/g	< 1.0	17.3 ng/g
CURYSENE	ug/l	< 20	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
DIBENZO(A,H) ANTHRACENE	ug/l	92.8	< 1.0	155 ng/g	< 1.0	68.4 ng/g	< 1.0	199 ng/g	< 1.0	199 ng/g	< 1.0	199 ng/g	< 1.0	< 1.0	157 ng/g	< 1.0	14.8 ng/g	< 1.0	14.8 ng/g
FLUORANTHENE	ug/l	1113	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
FLUORENE	ug/l	158	< 1.0	70.8 ng/g	< 1.0	< 10 ng/g	< 1.0	75.4 ng/g	< 1.0	215 ng/g	< 1.0	215 ng/g	< 1.0	< 1.0	82.2 ng/g	< 1.0	57.4 ng/g	< 1.0	57.4 ng/g
INDENO(1,2,3-CD) PYRENE	ug/l	< 20	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	16.8 ng/g	< 1.0	16.8 ng/g	< 1.0	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g	< 1.0	< 10 ng/g
NAPHTHALENE	ug/l	51.6	4.18	37.8 ng/g	< 1.0	< 10 ng/g	< 1.0	< 1.0	< 1.0	76.5	70 ng/g	70 ng/g	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
PHENANTHRENE	ug/l	229	1.26	61.8 ng/g	1.93	66.6 ng/g	8.84	196 ng/g	8.84	196 ng/g	1.22	70.6 ng/g	1.22	70.6 ng/g	1.0	31.2 ng/g	1.0	31.2 ng/g	
PYRENE	ug/l	281	< 1.0	71.2 ng/g	< 1.0	73.8 ng/g	< 1.0	222 ng/g	< 1.0	222 ng/g	< 1.0	222 ng/g	< 1.0	< 1.0	89.2 ng/g	< 1.0	20.8 ng/g	< 1.0	20.8 ng/g

CALCULATED VALUES

TOTAL PAHS	ug/l	2761.6	5.44	73.26	1.93	117.68	92.82	161.28	1.22	104.88	1.0	33.88	96.2	98.8
PERCENT REDUCTION OF PAHS, %														

TABLE 3
 MATERIALS OF CONSTRUCTION
 FOR THE
 WET AIR OXIDATION PROCESS

ALLOY	NOMINAL CHEMICAL COMPOSITION					
	Fe	Cr	Ni	Mo	C	Cu
316-L STAINLESS	bal	18	13	2.25	0.03	-
20 cb-3	bal	20	34	2.5	0.03	3.5
625	3	22	bal	9	0.05	-
HASTELLOY C-276	5	16	bal	16	0.02	-
TITANIUM - 2	COMMERCIALY PURE TITANIUM				0.01	

TABLE 4
MATERIAL TESTING
280°C for 100 hours

ALLOY	GENERAL RATE MPY	COMMENTS
316-L	<1.0	NO LOCALIZED CORR.
20cb-3	<1.0	NO LOCALIZED CORR.
625	<1.0	NO LOCALIZED CORR.
C-276	<1.0	NO LOCALIZED CORR.
TI-2	NIL	NO LOCALIZED CORR.

Figure 1
2² Factorial Testing

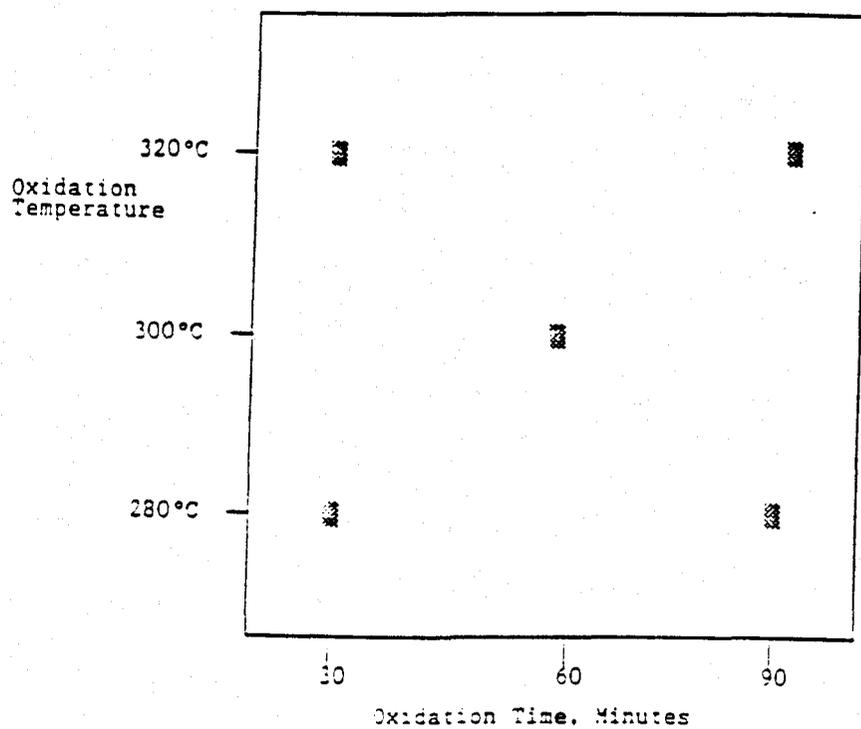
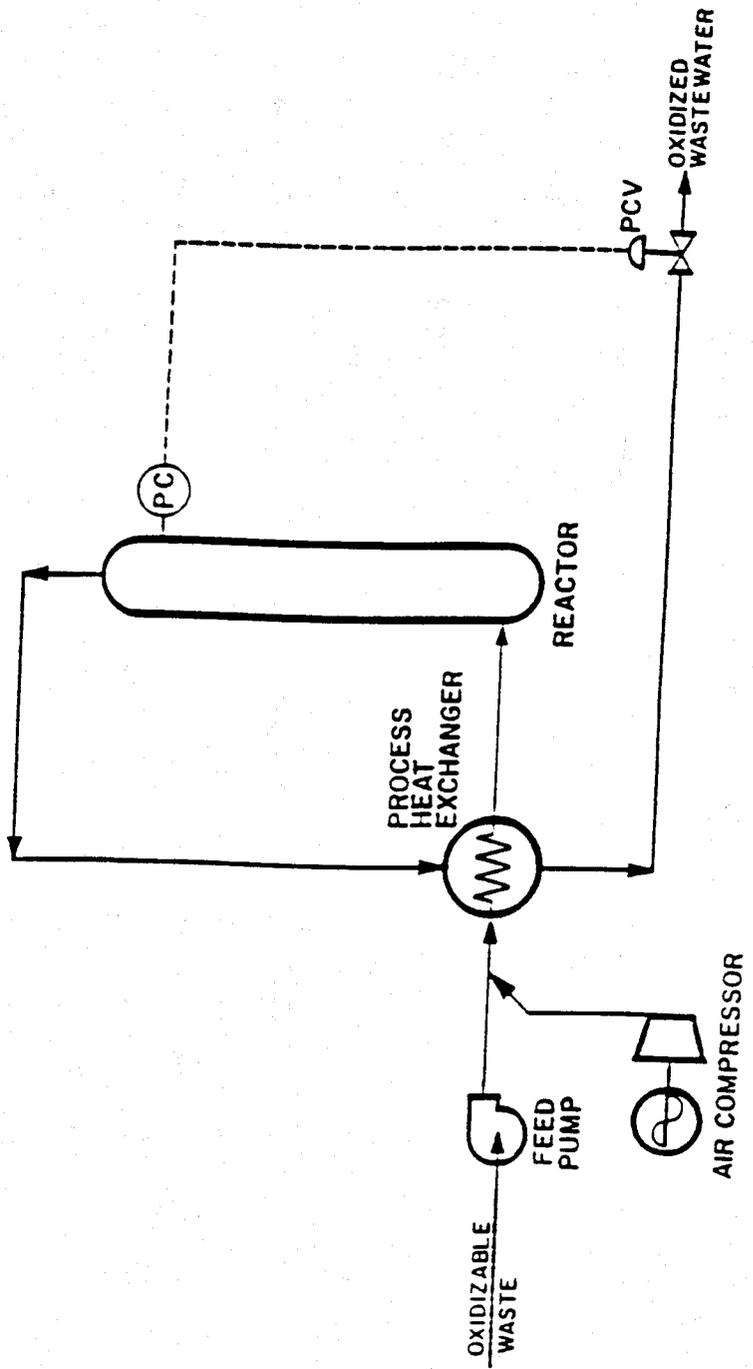


Figure 2

WET AIR OXIDATION
GENERAL FLOW DIAGRAM



REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., APHA, AWWA, WPCF, 1985.
2. Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EPA-600/4-79-020, March, 1979.
3. Flynn, B.L., "Wet Air Oxidation of Waste Streams," Chemical Engineering Progress. April, 1979, pp. 66-69
4. Copa, W.M., et. al.. "Simultaneous Sludge Disposal and Carbon Regeneration," presented at the AIChE National Meeting, New York, 1987
5. Force, J.M. ed., "Wet Air Oxidation - A Rediscovered Technology," REACTOR. No. 65, May 1989, p.4
6. Dietrich, M.J., et. al.. "Wet Air Oxidation of Hazardous Organics in Wastewater," Environmental Progress. Vol.4, No. 3, August, 1985, p. 171

BENCH SCALE STIRRED AUTOCLAVE
WET AIR OXIDATION DEMONSTRATION
ON INDIANA HARBOR SEDIMENT SLUDGE
FOR
SCIENCE APPLICATION INTERNATIONAL CORP.
PHASE II

SAIC SUBCONTRACT NO. 16-920034-51

September 27, 1991

**ZIMPRO
PASSAVANT**

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I. INTRODUCTION

Zimpro Passavant Environmental Systems, Inc. (ZIMPRO) performed laboratory wet air oxidation tests on dredged sediments from the Indiana harbor. The test work was performed for Science Applications International Corporation (SAIC) under contract with the U.S. EPA. The principal objectives for this Phase II study were to produce a volume of oxidized samples at the optimal operating conditions. The operating conditions were determined by a series of shaking autoclave tests performed under the Phase I study. The Phase I study concluded that the optimal condition was a reactor temperature of 280°C and a hydraulic detention time of 90 minutes. The oxidized effluent from Phase II shall be analyzed by others. The results from the testing are to be presented to the EPA for evaluation of the wet air oxidation technology for treatment of the sediment sludge.

This report includes the procedures used and analytical results obtained from the Phase II wet air oxidation testing of the sediment sludge.

II. WET AIR OXIDATION PERFORMANCE

The "as received" feed samples were well mixed and divided out into eight (8) portions. Separate stirred autoclave oxidations were performed using six (6) of the eight (8) samples. The samples were diluted using HPLC grade water. The dilutions were made to produce an autoclave feed sample with a suspended solids concentration of approximately ten percent (10%). A list of the feed samples charged to the stirred autoclave and the volumes discharged is reported in Table 1.

TABLE 1: STIRRED AUTOCLAVE OXIDATION INFORMATION

Sample Number	SAMPLE CHARGED		SAMPLE REMOVED		OFF GAS ANALYSES, %				
	Sediment Grams	Water Grams	Solids Grams	Filtrate Grams	CO ₂	O ₂	N ₂	CO	THC ppm
1	225	625	66	545*	13.1	3.7	82.0	nd	173
2	253	597	88	682	14.3	2.1	82.1	0.5	229
3	225	625	107	703	13.8	2.0	82.6	nd	150
4	250	601	84	685	13.4	2.8	82.3	nd	197
5	125	650	51	615	11.1	6.4	78.6	nd	170
6	125	650	43	657	9.2	8.4	79.2	nd	190

* Pump tubing leaked causing some loss of sample
nd = not detected

Following the oxidation, effluent samples were decanted from the stirred autoclave using a peristaltic pump with silicon tubing. The samples were then vacuum filtered using Whatman #1 filter paper. The mass of both filtrate and filter cake was individually measured. The filter cake samples were placed in a glass bottle and the filtrate was pumped into a Tedlar bag. Blending of all the filtrate samples, and cake samples, was performed on completion of the stirred autoclave testing. Sampling of the blended filter cake and blended filtrate samples was performed by SAIC.

Analyses were performed on the oxidized filter cake and filtrate by Enviroscan Corporation. The tabulation of the obtained data is located in Table 2. Comparing the results from Phase I to Phase II, the testing indicates that the filtrates had equivalent CODs. The remaining 6,136 mg/l of COD in the filtered effluent would have to be reduced further. The remaining COD appears to be very biodegradable. The filtrate had a BOD₅/COD ratio of 0.55, indicating that biological treatment may be acceptable as a polishing step. The filter cake sample had a higher COD when compared to the Phase I results (187 mg/g verses 96 mg/g). Little more can be said about the samples due to the limited scope of the analyses. A more complete analytical evaluation of the effluents will be performed by SAIC once they have obtained the results from their outside laboratory.

TABLE 2: ANALYTICAL RESULTS FROM PHASE II

	<u>Filtrate</u>	<u>Cake</u>
Analytical No.	56,617	56,518
Oxidation Temperature, °C	280	280
COD	6,136 mg/l	187 mg/g
BOD ₅	3,372 mg/l	—
pH	5.2	—
Total Solids	4,668 mg/l	56.8%
Total Ash	2,544 mg/l	90.2%

III. EXPERIMENTAL PROCEDURES

All wet air oxidation tests were performed in laboratory titanium stirred autoclaves each having a capacity of 3,780 mls. The autoclaves are equipped with a magnetic stirring device which helps diffusion of oxygen into the liquid and keeps the solids in solution. The stirring mechanism is on continuously throughout the oxidation. The autoclaves were charged with the waste and sufficient compressed air to result in excess residual oxygen following oxidation. The charged autoclaves were then heated to the desired oxidation temperature by electric heating bands and held for the specified reaction time. Immediately following oxidation, the autoclaves were cooled to room temperature by internal water cooling coils and then depressurized.

All analyses included as part of the oxidation testing were performed by the ZIMPRO analytical laboratory, Envirosan Corp., according to Standard Methods¹ or EPA Methods for the Chemical Analysis of Water and Waste².

IV. PROCESS DESCRIPTION

Wet air oxidation is an aqueous phase oxidation of organic and inorganic compounds by dissolved molecular oxygen at elevated temperatures and pressures. The oxygen is typically supplied to the system as compressed air; however, pure gaseous oxygen has also been used in specific applications. Depending on the overall desired treatment level, the oxidation reactions will occur at moderate temperatures (400 - 600°F) and at pressures ranging from 300 to over 3000 pounds per square inch. As the oxidation temperature is increased, a larger portion of the organic compounds will be oxidized which will correspond to a higher overall chemical oxygen demand (COD) reduction. The wet air oxidation process will oxidize simple organic compounds to carbon dioxide and water while some complex compounds are partially oxidized to simpler compounds, such as acetate, which are more readily biodegradable.

Figure 1 presents the basic wet air oxidation system process flow scheme. The proposed flow scheme recommends the utilization of an equalization tank to provide short term storage during maintenance shutdowns and to dampen out the effects of periodic changes in waste characteristics. The waste is transferred from the equalization tank to a high pressure diaphragm pump by means of a centrifugal low pressure pump. The pressurized discharge from the high pressure pump is combined with the air stream from the process air compressor thereby forming a two-phase stream.

A B C D E F G H I J K

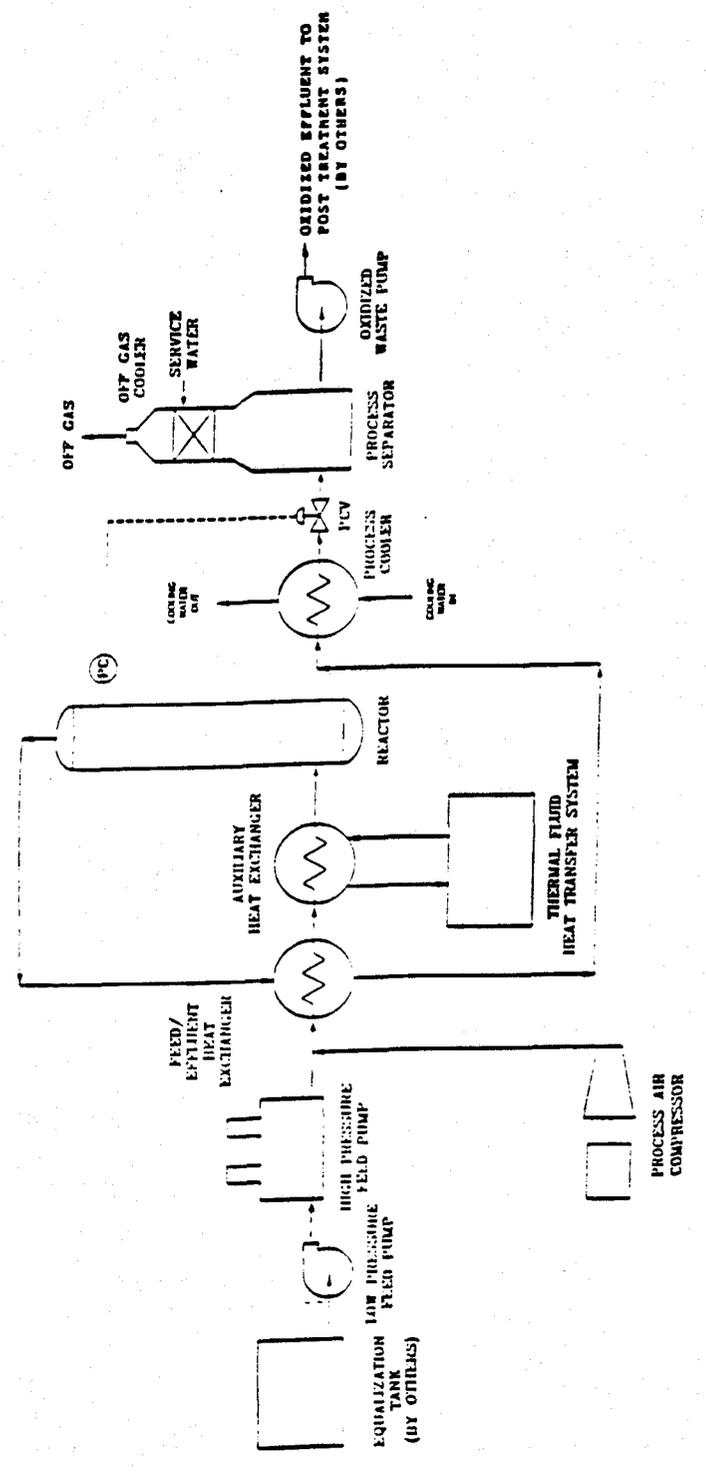


		FIGURE 1	
PRELIMINARY WET AIR OXIDATION SYSTEM PROCESS FLOW DIAGRAM			
<small> This diagram is a preliminary process flow diagram for the Wet Air Oxidation System. It is intended for informational purposes only and is not to be used for design or construction. The system is subject to change without notice. </small>			
<small> The process flow diagram shows the flow of materials and energy through the system. The process starts with the Equalization Tank (by others) and the Low Pressure Feed Pump. The feed then passes through the Feed/Effluent Heat Exchanger and the High Pressure Feed Pump into the Reactor. The reactor is part of the Thermal Fluid Heat Transfer System, which includes the Auxiliary Heat Exchanger and the Process Cooler. Cooling water enters the process cooler, and cooling water exits. The reactor effluent goes to the Process Separator, which has the Off Gas Cooler and Service Water input. The separator outputs Oxidized Effluent to the Post Treatment System (by others) and Oxidized Waste Pump. A Process Air Compressor is also shown. </small>			

The two-phase air/waste stream passes through the tube-side of the feed/effluent heat exchanger. The feed/effluent is used to transfer the sensible heat from the oxidized effluent to the unreacted waste and air mixture. The heated mixture is then routed through an auxiliary heat exchanger. The auxiliary heat exchanger is used, when necessary, to supplement the thermal energy transferred to the air/waste mixture. The supplemental thermal energy is supplied by a thermal fluid heat transfer system which may be either fuel-fired or electrically heated. The thermal fluid heat transfer system is used to initially bring the system up to operating temperature.

The heated air/waste mixture is then introduced in the process reactor vessel. The reactor vessel is a vertically-oriented column type pressure vessel. The reactor contents are mixed by the action of the gas phase rising through the liquid. As the gas phase rises and mixes with the liquid, oxygen is dissolved into the liquid. The dissolved oxygen is then available to take part in the oxidation reactions. The reactor is sized to provide sufficient hydraulic detention time to allow the oxidation reactions to proceed to the desired level.

The oxidized liquid, oxidation product gases, and spent air leave the process reactor and are routed through the shell side of the previously mentioned feed/effluent heat exchanger. A substantial cooling of the reactor effluent is achieved in the feed/effluent heat exchanger; additional cooling is accomplished by the process cooler. In the process cooler, additional sensible heat energy is transferred from the reactor effluent to a cooling water stream. It should be mentioned that the system is still at an elevated pressure at this point.

The cooled reactor effluent is throttled through a pressure control valve, thereby depressurizing the flow, into the process separator. The reactor effluent is separated into a gaseous stream and a liquid stream by the process separator.

The gaseous stream from the process separator is routed through the process off-gas cooler. The off-gas cooler is a vertically oriented packed column. The process gases enter the base of the column and flow counter-current to a flow of service water. The service water cools the process gases causing some higher boiling point constituents to condense out and exit the off-gas cooler with the service water; the liquids leaving the off-gas cooler are discharged into the process separator.

At this point in the flow scheme, the process separator liquids are pumped beyond the treatment system's boundary limits; typically another treatment process receives these liquids. The receiving process varies depending on the chemical characteristics of the oxidized liquids (COD, BOD, pH, suspended solids, etc.). Typically, liquids with a high suspended solids are sent through a clarifier to settle out particulate matter. It should be noted that the oxidized liquid may still contain a relatively high concentration of biological nutrients. Further treatment of these oxidized liquids by a biological system may be required prior to discharge to the final receiving system (lake, river, POTW).

V. DESIGN BASIS

ZIMPRO and SAIC mutually developed three scenarios for the full scale wet air oxidation of the dredged sediments. These scenarios were based on the laboratory findings that the wet air oxidation process could adequately handle sediments at a solids concentration of approximately ten percent (10%). The dredged sediment is produced at a solids concentration of approximately forty (40) percent. Therefore, the sediment would require a three (3) to one (1) dilution using water from the harbor that is being dredged. The three scenarios involve the treatment of total dredgings of 10,000; 40,000; and 100,000 yd³ (all at forty percent (40%) total solids). It was determined that wet air oxidation units of ten (10), twenty (20), and forty (40) gallons per minute [at ten percent (10%) total solids] capacity would be adequately sized to process these volumes of dredgings as shown in the following table.

WAO Capacity, gpm	TIME TO PROCESS DREDGING, YRS		
	10,000 yd ³	40,000 yd ³	100,000 yd ³
10	2.25	6.75	22.50
20	1.12	3.38	11.25
40	0.56	1.69	5.62

Each of the three (3) proposed wet air oxidation systems covered under these scenarios was designed based on ZIMPRO's experience in the construction of similar systems. Each proposed system shall be constructed to the standards of ZIMPRO and all applicable national codes.

The waste to be treated is to be a slurried harbor sediment with characteristics as listed in Table 3.



TABLE 3: WASTE CHARACTERISTICS

Average COD, [g/l]:	40.0
Total Suspended Solids, [wt %]:	10.0
pH:	7
Chlorides, [ppm]:	12

The design parameters for the proposed systems are presented in Table 4.

TABLE 4: SYSTEM DESIGN PARAMETERS

Design Flowrate, [U.S. GPM]:	10.0	SYSTEM 1
	20.0	SYSTEM 2
	40.0	SYSTEM 3
Operating Schedule:	24 hours/day	
	5 days/week	
	50 weeks/year	
Normal Operating Mode:	Autothermal	
Reactor Hydraulic Detention Time, [minutes]:	90	
COD Reduction, [%]:	83	
Mechanical Design Temperature, [°F]:	570	
Mechanical Design Pressure, [psig]:	2,000	
Operating Temperature, [°F]:	536	
Operating Pressure, [psig]:	1,500	
Material of Construction for Waste Wetted Surfaces:	316L	

VI. SCOPE OF OFFERING

ZIMPRO proposes to provide all engineering, design, equipment supply and start-up services necessary to complete and install the wet air oxidation system to the extent described herein.



The proposed major equipment pieces and/or system components to be furnished and installed by ZIMPRO for each system and included in the proposed price, as stated hereafter, are listed in Table 5.

TABLE 5: MAJOR EQUIPMENT LIST

Item	Quantity	Alloy Material of Construction - If Applicable
1. Low Pressure Feed Pump	2 (1 standby)	316L SS Wetted Parts
2. High Pressure Feed Pump	1	316L SS Wetted Parts
3. Process Air Compressor	1	
4. Feed/Effluent Heat Exchanger	1	316L SS
5. Auxiliary Heat Exchanger	1	316L SS Tube/CS Shell
6. Thermal Heat Transfer System	1	
7. Thermal Fluid Recirculation Pump	2 (1 standby)	
8. Process Reactor	1	316L SS Clad CS
9. Process Cooler	1	316L SS Tube/CS Shell
10. Pressure Control Valve/Pot	2	
11. Process Separator	1	316L SS
12. Off-gas Cooler	1	316L SS
13. Separator Bottoms Pump	2 (1 standby)	316L SS
14. Instrument Air Compressor	1	
15. Interconnecting Pipe	1 lot	As Required
16. Valves	1 lot	As Required
17. Motor Control Center	1	
18. Instrumentation	1 lot	As Required

The majority of the equipment listed above shall be pre-piped and wired on equipment skids to facilitate field erection and/or installation of the system by ZIMPRO. Other equipment shall be provided as individual items. Skids and individual equipment items, as provided, are designed to be erected on concrete foundations provided by the PURCHASER. Table 6 is a listing of the equipment skids which are anticipated to be provided for the proposed system.

TABLE 6: EQUIPMENT SKIDS

SYSTEM 1 - 10 GPM			
	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
1. Air Compressor Skid	1	17 x 10	21,500
2. Equipment Skid	1	10 x 11	30,000
3. High Pressure Pump Skid	1	14 x 8	25,000
4. Thermal Fluid Heat Transfer System Skid	1	7 x 8	7,000

SYSTEM 2 - 20 GPM			
	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
1. Air Compressor Skid	1	23 x 10	36,000
2. Equipment Skid	1	15 x 10	35,000
3. High Pressure Pump Skid	1	14 x 8	25,000
4. Thermal Fluid Heat Transfer System Skid	1	7 x 8	7,000

SYSTEM 3 - 40 GPM			
	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
1. Air Compressor Skid	1	23 x 10	37,000
2. Equipment Skid	1	16 x 12	40,000
3. High Pressure Pump Skid	1	14 x 10	27,000
4. Thermal Fluid Heat Transfer System Skid	1	7 x 8	7,000



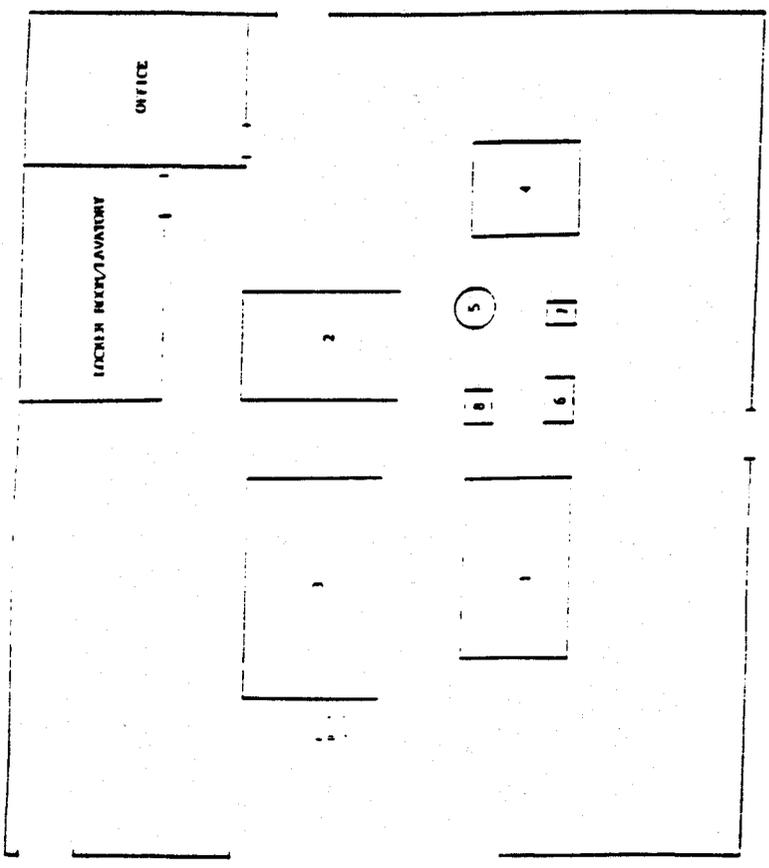
Individual equipment items and/or system components such as the reactor, feed/effluent heat exchanger, auxiliary heat exchanger, process cooler, field valves, and field instrumentation will be fabricated and shipped to the project site for installation, erection and/or independent mounting by ZIMPRO on separate concrete foundations to be provided by the PURCHASER. Table 5 lists major individual equipment items being offered for the proposed wet air oxidation systems which will require independent mounting and/or installation. Figures 2-A, 2-B, and 2-C are preliminary plot plans showing the suggested equipment layout and building size. ZIMPRO will also supply all pipe required to make interconnections between skids and free-standing equipment.

TABLE 5: FREE-STANDING EQUIPMENT

SYSTEM 1 - 10 GPM			
	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
Process Reactor	1	3 (diam.)	27,000
Feed/Effluent Heat Exchanger	1	3.5 x 2.0	7,500
Process Cooler	1	2.5 x 2.0	4,100
Auxiliary Heat Exchanger	1	1.5 x 2.0	1,000
SYSTEM 2 - 20 GPM			
	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
Process Reactor	1	4 (diam.)	53,000
Feed/Effluent Heat Exchanger	1	3.0 x 2.0	21,100
Process Cooler	1	4.0 x 2.0	10,300
Auxiliary Heat Exchanger	1	2.5 x 2.0	7,100

2 5 3

File No.	Equipment
1	PUMP SKID
2	EQUIPMENT SKID
3	PROCESS AIR COMPRESSOR SKID
4	THERMAL FLUID HEAT TRANSFER SYSTEM
5	REACTOR VESSEL
6	FEED/RETURN HEAT EXCHANGER
7	AUXILIARY HEAT EXCHANGER
8	PROCESS COOLER

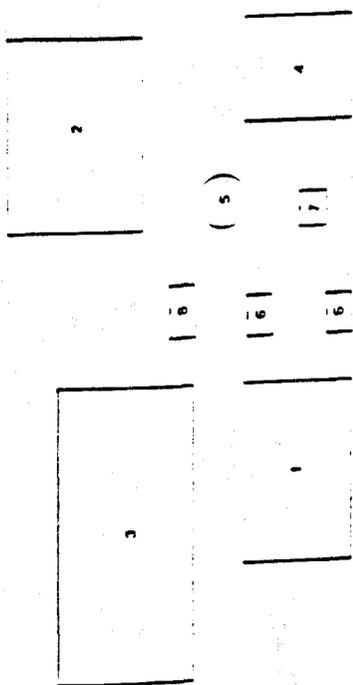
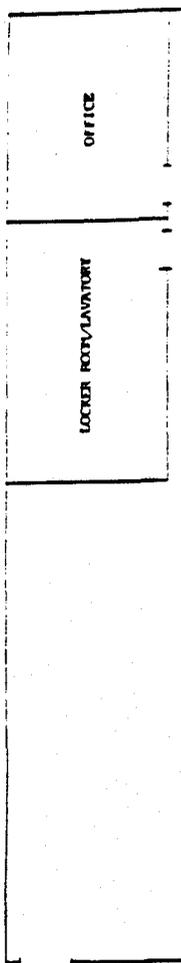


SCALE: 1/8" = 1'

<p>WET AIR OXIDATION SYSTEM PRELIMINARY PLOT LAYOUT</p>		<p>10 GPM SYSTEM</p>	
<p>ZIMPRO PASSAVANI PROCESSING SOLUTIONS</p>		<p>FIGURE 2-A</p>	

J K L

Item No.	Equipment
1	PUMP SKID
2	EQUIPMENT SKID
3	PROCESS AIR COMPRESSOR SKID
4	THERMAL FLUID HEAT TRANSFER SYSTEM
5	REACTOR VESSEL
6	FEED/EFFLUENT HEAT EXCHANGER
7	AUXILIARY HEAT EXCHANGER
8	PROCESS COOLER

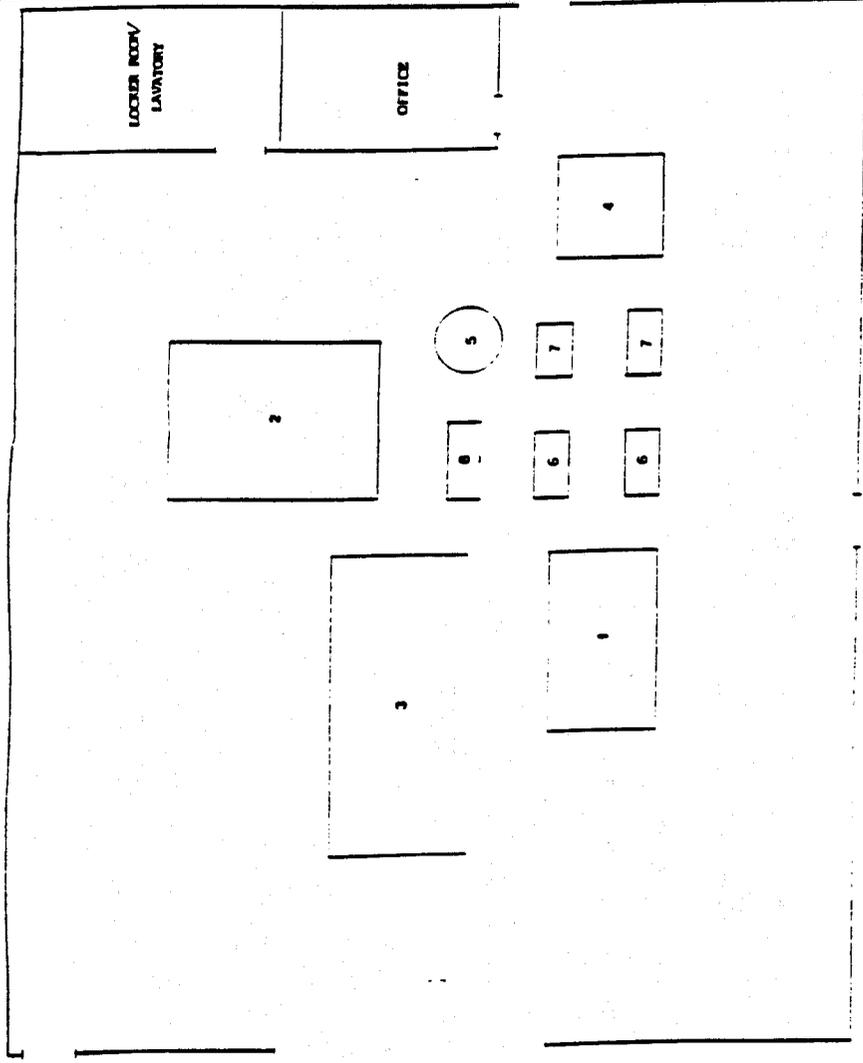


SCALE: 1/8" = 1'

MIT AIR ORIENTATION SYSTEM
 PNEUMATIC FLUID LAYOUT
 20 GIN SYSTEM

ZIMPRO
 PASSAVANT
 INVESTIGATIONAL SERVICES
 FIGURE 2-B

Item No.	Equipment
1	PUMP SKID
2	EQUIPMENT SKID
3	PROCESS AIR COMPRESSOR SKID
4	THERMAL FLUID HEAT TRANSFER SYSTEM
5	REACTOR VESSEL
6	FEED/FERTILIZER HEAT EXCHANGER
7	AUXILIARY HEAT EXCHANGER
8	PROCESS COOLER



SCALE: 1/8" = 1'

		FIGURE 2-C	
WET AIR OXIDATION SYSTEM PRELIMINARY PILOT LAYOUT 40 GPM SYSTEM		J K L	
E F G H		I J K L	
A B C D		E F G H	

SYSTEM 3 - 40 GPM

	Qty.	Approximate Dimension each (L x W) in feet	Approximate Weight each lbs.
Process Reactor	1	4.5 (diam.)	104,000
Feed/Effluent Heat Exchanger	2	5.0 x 2.5	27,000
Process Cooler	1	6 x 2.5	24,000
Auxiliary Heat Exchanger	1	4.0 x 2.5	24,000
	1	5.0 x 2.5	26,000

Please note that the dimensions and weights given are approximations only and are subject to change.

Instrumentation and valves associated with the skid mounted equipment will be installed and pre-piped on the appropriate skids to the extent practical. Skid mounted instruments and start-stop stations shall be pre-wired to skid mounted terminal strips/boxes. ZIMPRO shall supply a control panel for each proposed wet air oxidation system and perform all wiring necessary to provide a complete system. The control panel shall be mounted on an equipment skid.

ZIMPRO has included the cost of a building in each of the proposed systems. Costs not included with the building are: foundations, pilings, site preparation, site dewatering, or equipment pads.

The PURCHASER shall be required to supply utility connections at a point not greater than a one (1) foot distance from the building wall. Utilities to be supplied by the PURCHASER shall include: 480 Volt, 3 Phase electrical service; 120 Volt, 1 Phase electrical service; conditioned cooling water at 65°F; service water; and natural gas. Table 6 is a listing of major system components and the required utility services.

 ZIMPRO
PASSAVANT

TABLE 6: REQUIRED UTILITY SERVICES

Item	Required Utility Services
1. Air Compressor Skid	480 Volt 3 ϕ Electrical, 65°F (max.) Cooling Water
2. Equipment Skid	480 Volt 3 ϕ Electrical, 120 Volt 1 ϕ Electrical, 65°F (max) Cooling Water, Service Water
3. High Pressure Pump Skid	480 Volt 3 ϕ Electrical, 65°F (max) Cooling Water
4. Thermal Fluid Heat Transfer System Skid	480 Volt 3 ϕ Electrical, Natural Gas
5. Process Cooler	65°F (max) Cooling Water

VII. ESTIMATED UTILITIES

ZIMPRO estimates that the proposed wet air oxidation systems will require the utility duties presented in Table 7. Please note that these are estimates only and are subject to change.

TABLE 7: ESTIMATED UTILITY DUTIES

	SYSTEM 1	SYSTEM 2	SYSTEM 3
Natural Gas - Start-up Only @1000 BTU/SCF, (scfm):	3	10	36
Cooling Water at 65°F, (U.S. gpm):	135	275	550
Operating Power, (kWh. Hr):	130	265	530

VIII. PRICING

The budgetary price for the supply and installation of the proposed wet air oxidation systems as defined above is:

SYSTEM 1 - 10 GPM: Four Million Five Hundred Thousand and 00.00 Dollars (\$4,500,000).



SYSTEM 2 - 20 GPM: Five Million Six Hundred Thousand and 00/100 Dollars (\$5,600,000) .

SYSTEM 3 - 40 GPM: Seven Million Three Hundred Thousand and 00/100 Dollars (7,300,000).

These prices do not include provisions for the following items:

1. Any applicable state, local, or federal taxes, permits, bonds, fees or duties.
2. Design or supply of foundations, civil work, sumps, concrete lining, or sewers.
3. Design, supply, or installation of equalization tanks.
4. Design, supply, or installation of the post-treatment system.
5. Equipment storage necessitated due to action of the PURCHASER.
6. Any operational spare parts other than the spare rotating equipment previously listed.
7. Any piping or wiring beyond the proposed system boundary limits.

REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., APHA, AWWA, WPCF, 1985.
2. Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EPA-600/4-79-020, March, 1979.

APPENDIX B

**EXPERIMENTAL DESIGN - ZIMPRO PASSAVANT'S
WET AIR OXIDATION TREATMENT TECHNOLOGY**

FOR

**GLNPO - ASSESSMENT AND REMEDIATION OF CONTAMINATED
SEDIMENT TECHNOLOGY DEMONSTRATION SUPPORT**

May 1991

Submitted to:

U.S. Environmental Protection Agency
Great Lakes National Program Office
230 S. Dearborn
Chicago, Illinois 60604

Submitted by:

Science Applications International Corporation
635 West Seventh Street, Suite 403
Cincinnati, Ohio 45203

EPA Contract No. 68-C8-0061, Work Assignment No. 2-18
SAIC Project No. 1-832-03-207-40

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APPENDIX A - ENVIROSCAN Environmental and Analytical Services Brochure

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SECTION 1

1.0 TECHNOLOGY DESCRIPTION

Wet air oxidation is a process that accomplishes an aqueous phase oxidation of organic or inorganic substances at elevated temperatures and pressures. The usual temperature range varies from approximately 350° to 600° F (175° to 320° C). System pressures of 300 psig to well over 3000 psig may be required. However, testing has been done at temperatures exceeding the critical point for water to limit the amount of evaporation of water, depending on the desired reaction temperature. Compressed air or pure oxygen is the source of oxygen that serves as the oxidizing agent in the wet air oxidation process.

The basic flow diagram for a conventional wet air oxidation process is shown in Figure 1-1. In processing an aqueous waste, the wastestream containing the oxidizable material is first pumped into the system using a positive displacement, high pressure pump. Next, the waste is preheated in a heat exchanger with the hot oxidized effluent. The compressed air or oxygen is injected into the wastestream either at the discharge of the high pressure pump or at the inlet to the reactor. A vertical bubble column is commonly used as the reactor which provides the required hydraulic detention time to effect the desired reaction. The desired reaction may range from a mild oxidation, which requires a few minutes, to total waste destruction, which requires an hour or more detention time. Exothermic heat of oxidation is released to the wastestream during oxidation. This heat release usually raises the temperature of the wastestream to the desired level in the reactor. The hot, oxidized effluent exits the reactor and is cooled in the process heat exchangers. The cooled effluent then exits the system through a pressure control valve. The oxidized liquid and non-condensable offgases are separated in a separator tank and discharged through separate lines.

The products of wet air oxidations vary with the degree of oxidation that is accomplished. For low degrees of oxidation, oxidizable organic matter is converted to low molecular weight organic compounds such as acetic acid. For high degrees of oxidation, oxidizable organic matter is chiefly converted to carbon dioxide and water. Organic or inorganic sulfur is converted to sulfate. Organic nitrogen is converted primarily to ammonia. The halogens in halogenated organics are converted to inorganic halides.

The commercial applications of wet air oxidation are chiefly in the disposal of aqueous wastes. However, some applications employ wet air oxidation for recovery of chemicals and energy production, simultaneously with waste disposal.

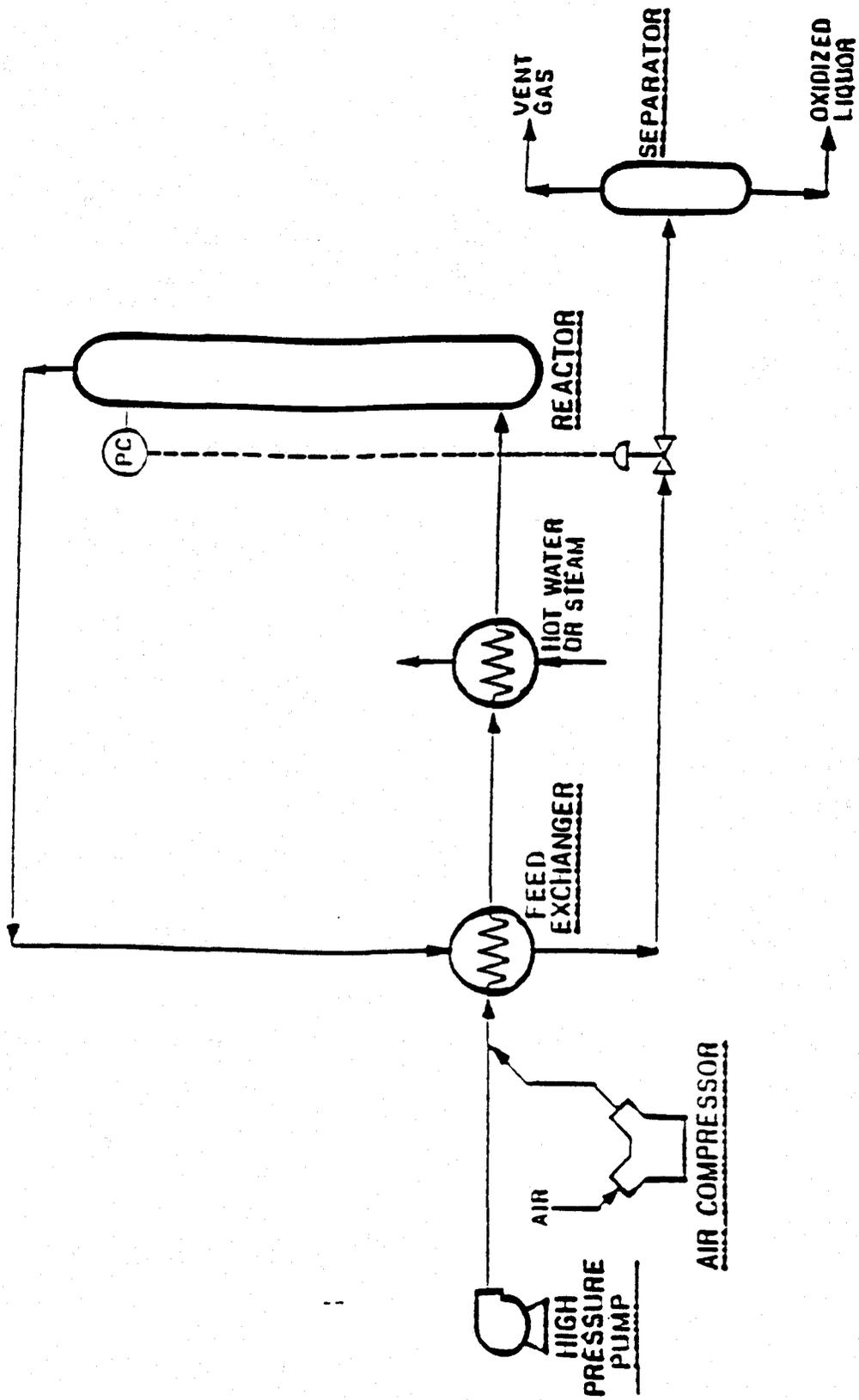


Figure 1-1. Wet Oxidation Flow Diagram (Source: Zimpro Passavant)

SECTION 2

2.0 TEST PLAN

2.1 Purpose

The primary objective of these tests is to determine the feasibility and cost effectiveness of Zimpro Passavant's Wet Air Oxidation process for treating and removing polyaromatic hydrocarbons (PAH's) from sediments. The Great Lakes National Program Office (GLNPO) has obtained and homogenized sediments collected for the Indiana Harbor near Gary, Indiana. The wet air oxidation process is not expected to treat polychlorinated biphenols (PCBs), another known primary contaminant group detected in the sediments.

The bench scale treatability tests of the treatability study are designed to provide data that closely simulates full scale performance. The data generated by the tests allows Zimpro Passavant and EPA to evaluate feasibility of the process and to estimate treatment costs for full scale performance.

The Bench Scale Treatability Test objectives are:

- To record observations and data to predict full-scale performance of Zimpro Passavant's wet air oxidation process.
- Take samples during the oxidation tests and conduct analysis sufficient to allow for calculation of mass balances for oil, water, solids and other compounds of interest.
- To calculate the oxidation efficiency of target compounds, specifically determining the level of destruction of organic contaminants, principally PAHs. PCBs, the other primary organic contaminant group in the sediments are not expected to be treated by the wet air oxidation technology.
- To supply GLNPO with treated solids (300 grams dry basis), and filtrate (water), for independent analysis.

2.2 Approach

In order to accomplish the test objectives a two phased approach will be used. Phase I is a preliminary phase conducted by Zimpro Passavant to determine the optimum conditions to be used during Phase II. Phase II is the treatability test at optimum conditions and GLNPO, through its contractor Science Applications International Corporation (SAIC), will obtain samples of the untreated sediments and treated residuals for analysis by an independent laboratory. All analyses for this treatability study program (consisting of seven treatability studies utilizing four technologies on four sediments) will be conducted by the same laboratory. This arrangement will eliminate interlaboratory variation from the comparison of the performance of these technologies. In addition representatives of both GLNPO and SAIC are scheduled to observe the conduct of Phase II of each treatability study.

2.3 Phase I

2.3.1 Procedures

In Phase I, Zimpro Passavant will analyze the Indiana Harbor sediment for the parameters shown below in Table 2-1. This Phase I analyses will be conducted by Zimpro Passavant since this initial phase serves as an optimization step for their wet air oxidation process.

Table 2-1. Zimpro Passavant's Analysis Schedule for the Phase I Wet Air Oxidation of Indiana Harbor Sediment

<u>Analysis</u>	<u>Feed Slurry</u>	<u>Oxidized</u>		<u>Total No. of Samples</u>
		<u>Filtrate</u>	<u>Solids</u>	
COD	1	5	5	11
BOD	1	5	-	6
Total Solids and Ash	1	5	5	11
Suspended Solids and Ash	1	-	-	1
pH	1	5	-	6
Oil/Grease	1	5	5	11
PAHs	1	5	5	11
Chloride	1	0	0	1

Zimpro Passavant will conduct the Phase I wet air oxidation treatability study in a shaking autoclave at temperatures ranging from 280° C to 320° C using reactor residence times of 30 to 90 minutes. The batch shaking autoclaves are fabricated from various corrosion resistant alloys, including 316 stainless steel, nickel, Inconel 600 and 625, Hastelloy C-276, and titanium. The shaking autoclaves have total volumes of 0.5 liters and 0.75 liters.

Each wet air oxidation test will be conducted by placing approximately one hundred (100) ml of slurried sediment in the shaking autoclave. The autoclave will be closed and pressurized with air so that an amount of oxygen equivalent to 125 percent of Chemical Oxygen Demand (COD) is charged to the autoclave. The autoclave will then be placed in a heater shaker mechanism and heated to the desired reactor temperature. The autoclave will be held at temperature for the desired reaction residence time, after which, it will be cooled to room temperature. The non-condensable gas will be analyzed for oxygen, nitrogen, carbon dioxide, carbon monoxide, total hydrocarbons, and methane. After completing the offgas

analysis, the autoclave will be de-pressurized and opened. The oxidized effluents from each oxidation condition will be composited. The composite samples will be filtered using a laboratory vacuum filter funnel and collection flask. The feed sediment slurry, oxidized filtrates, and solids will be analyzed by Zimpro Passavant according to the analysis schedule presented in Table 1-1, Section 1.3.

The feed sediment slurry will be prepared by diluting the sediment that is provided to approximately ten (10) percent solids, using distilled water.

2.3.2 Test Conditions, Process Variables and Schedule

Zimpro Passavant will require approximately 500 grams of sediment solids (dry weight basis) to complete Phase I, which is equivalent to approximately 1300 grams of wet Indiana Harbor sediment (the Indiana Harbor sediment has a reported moisture content of approximately 39%).

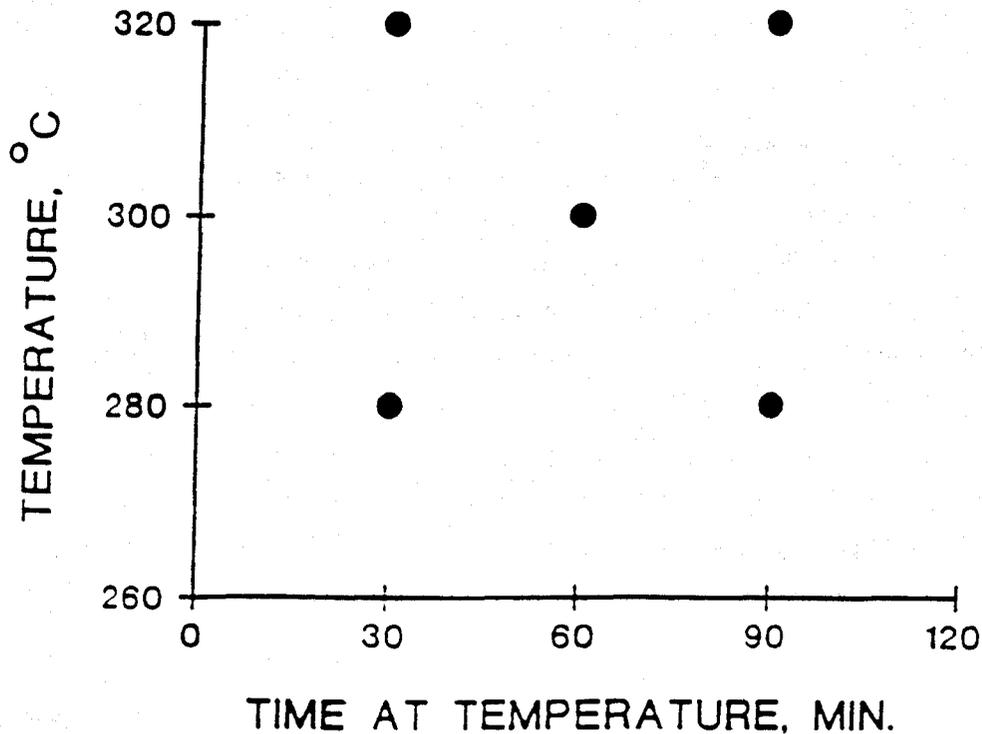
The Phase I test plan consists of a 2² factorial experimental design which will determine the effect of temperature and time at temperature on the destruction of organic contaminants in the sediment. The test plan will consist of the following autoclave oxidation conditions:

<u>Temperature °C</u>	<u>Time at Temperature, Minutes</u>
280	30
280	90
300	60
320	30
320	90

A temperature-time diagram of the experimental plan is shown in Figure 2-1. It is estimated by Zimpro Passavant that five oxidations will be conducted at each condition to obtain sufficient samples which will be used for analysis purposes.

The Phase I work, including sample analysis, can be completed in approximately six (6) weeks after receipt of the sediment solids. The Phase I work can be initiated within two (2) weeks after receipt of contract and notification to proceed.

Figure 2-1. 2² Factorial Experimental Design for Wet Air Oxidation of Indiana Harbor Sediment



The process variables for Phase I test plan include the following:

- Temperature (280° - 320° C)
- Time at Temperature (0.5 hours - 1.5 hours)

Note: Percent solids for feed (2 to 20 percent or maximum pumpable slurry concentration) was not included as a test variable because the destruction of organic contaminants is not concentration dependent. Also, pressure (300 to 3000 psig) is not included as a test variable because the destruction of organic contaminants is not dependent on the system pressure, provided excess oxygen is present.

2.3.3 Report

At the completion of Phase I, a letter report specifying the wet air oxidation conditions required for Phase II testing will be prepared and sent to SAIC. These would include, but would not necessarily be limited to reaction temperature(s) and reactor residence time(s), and will reflect those conditions (process variables) that produced the maximum destruction of target compounds, as determined in Phase I.

2.4 Phase II

2.4.1 *Procedures*

Zimpro Passavant will conduct Phase II of the wet air oxidation treatability study in stirred autoclaves. The stirred autoclaves are fabricated from 316 stainless steel and titanium. The one-gallon capacity of the stirred autoclave will facilitate the production of larger quantities of oxidized effluents. Zimpro Passavant proposes to conduct the stirred autoclave test using the wet air oxidation conditions that produce the maximum destruction of the polynuclear aromatic hydrocarbons, as determined in Phase I.

In Phase II, the stirred autoclave will be charged with approximately two (2) liters of slurried sediment (10 percent suspended solids). The stirred autoclave would be charged with sufficient air to provide an amount of oxygen equivalent to 125 percent of the COD. The stirred autoclave will then be heated to the desired temperature and kept at temperature for the desired length of time. After completion of the reaction time, the stirred autoclave will be cooled and the non-condensable gas will be analyzed for oxygen, nitrogen, carbon dioxide, carbon monoxide, total hydrocarbons, and methane. After completion of the gas analysis, the stirred autoclave will be de-pressurized. The oxidized effluent will be withdrawn and saved for analysis by SAIC and Zimpro Passavant. It is anticipated that two (2) stirred autoclave oxidations will be conducted using the chosen wet air oxidation conditions. The combined oxidation effluent will produce approximately four (4) liters of filtrate and 400 grams of solids. Zimpro Passavant will require approximately 250 ml of filtrate and 10 grams of solids for analytical purposes.

2.4.2 *Test Conditions and Process Variables*

Zimpro Passavant will require approximately 500 grams of sediment solids (dry weight basis) to complete Phase II as described herein.

The Phase II work can be completed in three (3) weeks, approximately four (4) working days for preparation of equipment and one (1) working day for conducting the stirred autoclave tests. The remaining two (2) weeks will be required to complete the sample analyses, develop cost information, and report all of the wet air oxidation test results to SAIC.

The process variables for the Phase II test plan include oxygen content (equivalent to 125% of the COD), the percent solids used, the pressure of the stirred autoclaves, a specified temperature, and a desired length of time. The latter two variables will be determined from the Phase I test.

2.4.3 *Sediment Sample Characterization and Analyses*

There will be two separate analytical matrices conducted on the Indiana Harbor sediment during Phase II, one by Zimpro Passavant and one by SAIC's subcontract laboratory, Battelle. Zimpro Passavant will conduct analyses on the treated sediment according to the analytical matrix shown in Table 2-2.

**Table 2-2. Zimpro Passavant Analysis Schedule for the Phase II
Wet Air Oxidation of Indiana Harbor Sediment**

<u>Analysis</u>	<u>Feed Slurry</u>	<u>Oxidized</u>		<u>Total No. of Samples</u>
		<u>Filtrate</u>	<u>Solids</u>	
COD	1	1	1	3
BOD	1	1	-	2
Total Solids and Ash	1	1	1	3
Suspended Solids and Ash	1	-	-	1
pH	1	1	-	2

At the beginning of the Phase II treatability test, SAIC personnel observing Phase II will pack and ship untreated Indiana Harbor sediment per written detailed instructions supplied to the SAIC on-site representative. This sample will be obtained from a separate unopened container of the sediments sent for Phase II. The analyses to be conducted on these sediments through SAIC's subcontract laboratory are listed in Table 2-3.

Following the Phase II treatability test, SAIC's subcontract laboratory will conduct analysis on the untreated sediments and end products. The number of analyses conducted on the anticipated residuals are also outlined in Table 2-3.

2.4.4 *Quality Assurance (QA)*

Zimpro Passavant will conduct their portion of this study according to the quality assurance/quality control procedures of their subsidiary laboratory, ENVIROSCAN, Inc. (Wisconsin Department of Natural Resources Certification No. 737 053 130). ENVIROSCAN's QA program includes the following internal controls.

- Sample protocols
- Sample handling procedures
- Chain of Custody
- Sample receipt, preservation, and storage
- Analytical procedures
- Reporting results
- Laboratory quality control programs
- On-going employee training

Table 2-3. SAIC's Analysis Schedule for the Phase II Wet Air Oxidation of Indiana Harbor Sediment

Parameters	QC Sample () and Method Blank	Untreated Sediment	MS	Tripli- cate	Treated Solids	MS	MSD	Tripli- cate	Water	MS	MSD	Tripli- cate	Oil	MS	Tripli- cate	
Total Solids (Moisture)	(1) YES	(1) I		(2) I	(1) I			(2) I								
Volatile Solids	(1) YES	(1) I		(2) I	(1) I			(2) I	NA*						NA	
O & G	(1) YES	(1) I		(2) I	(1) I			(2) I	NA						NA	
Metals	(0) YES	(1) I	(1) I	(2) I	(1) I	(1) I		(2) I	NA	NA					NA	
PCBs	(0) YES	(1) I	(1) I	(2) I	(1) I	(1) I	(1) I	(2) I	(1) I	(1) I	(1) I			NA	NA	NA
PAHs	(0) YES	(1) I	(1) I	(2) I	(1) I	(1) I	(1) I	(2) I	(1) I	(1) I	(1) I			NA	NA	NA
TOC	(0) YES	(1) I	NA	NA	(1) I	NA	NA	NA	NA	NA	NA			NA	NA	NA
Total Cyanide	(0) YES	(1) I	NA	NA	(1) I	NA	NA	NA	NA	NA	NA	NA		NA	NA	NA
Total Phosphorous	(0) YES	(1) I	NA	NA	(1) I	NA	NA	NA	NA	NA	NA	NA		NA	NA	NA
pH	(0) YES	(1) I		NA	(1) I			NA	NA							
BOD	NA															
Total Suspended Solids	NA															
Conductivity	NA															

* Not Analyzed
 (1) = Number of Analyses
 I = Indiana Harbor Sediment
 MS = Matrix Spike
 MSD = Matrix Spike Duplicate

SAIC has developed and GLNPO has approved a QA project plan for this project. This QA project plan is available as a separate document. Additional information on Zimpro Passavant's analytical laboratory (ENVIROSCAN) is included in the ENVIROSCAN brochure (Appendix A).

SECTION 3

3.0 RESIDUAL MANAGEMENT

The anticipated residuals from the wet air oxidation treatability studies are of very small quantity (estimated at approximately 400 grams of dry solids and 4 liters of filtrate). A portion of the Zimpro Passavant complex is a permitted hazardous/toxic waste storage, treatment, and disposal facility (WI/EPA Registration No., WID044393114). The pilot plant facilities, where the treatability tests will be conducted, are within the same complex, thus Zimpro Passavant has in-house residual management capabilities.

SECTION 4

4.0 FINAL REPORT

Upon completion of the bench scale treatability program, Zimpro Passavant will prepare a Final Report. The Final Report will contain the following:

- Zimpro Passavant's wet air oxidation process description, test procedures, operating parameters, sampling locations and frequencies
- Test results discussion with analytical data
- Mass balance calculations, if applicable
- Projected full scale system configuration and operating parameters that would be used to treat site waste materials
- Treatment cost estimates in dollars per unit volume of soil for the Indiana Harbor type soil, based on the lowest cleanup level which can reasonable be achieved
- The following data will be presented in tabular form:
 - Initial contaminant concentrations; along with the moisture contents and pH values and other relevant data
 - Final analytical results for all streams generated from the extracts of each sample
 - Percentages of individual contaminants extracted for each sample, as well as a calculation of total PAHs oxidized
 - Oxidation efficiency for each contaminant
- Log books and chromatograms if generated.

APPENDIX C

**QUALITY ASSURANCE PROJECT PLAN
FOR
GLNPO - ASSESSMENT AND REMEDIATION OF
CONTAMINATED SEDIMENT TECHNOLOGY
DEMONSTRATION SUPPORT**

Revision II

February 15, 1991

Submitted to:

U.S. Environmental Protection Agency
Great Lakes National Program Office
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Submitted by:

Science Applications International Corporation
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EPA Contract No. 68-C8-0061, Work Assignment No. 2-18
SAIC Project No. 1-832-03-207-50

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QUALITY ASSURANCE PROJECT PLAN APPROVALS

QA Project Plan Title: GLNPO Assessment and Remediation of Contaminated Sediment Technology Demonstration Support

Prepared by: Science Applications International Corporation (SAIC)

QA Project Category: II

Revision Date: January 9, 1990

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1.0 INTRODUCTION

The Great Lakes National Program Office (GLNPO) leads efforts to carry out the provisions of Section 118 of the Clean Water Act (CWA) and to fulfill U.S. obligations under the Great Lakes Water Quality Agreement (GLWQA) with Canada. Under Section 118(c)(3) of the CWA, GLNPO is responsible for undertaking a 5-year study and demonstration program for contaminated sediments. Five areas are specified for priority consideration in locating and conducting demonstration projects: Saginaw Bay, Michigan; Sheboygan Harbor, Wisconsin; Grand Calumet River, Indiana (aka: Indiana Harbor); Ashtabula River, Ohio; and Buffalo River, New York. In response, GLNPO has initiated an Assessment and Remediation of Contaminated Sediments (ARCS) Program. The ARCS Program will be carried out through a management structure including a Management Advisory Committee consisting of public interest, Federal and State agency representatives, an Activities Integration Committee which is made up of the chairpersons of the technical work groups, and technical work groups.

In order to obtain the broadest possible information base on which to make decisions, the ARCS Program will conduct bench-scale and pilot-scale demonstrations and utilize opportunities afforded by contaminated sediment remedial activities by others, such as the Corps of Engineers and the Superfund program, to evaluate the effectiveness of those activities. These bench-scale and pilot-scale tests will be developed and conducted under the guidance of the Engineering/Technology (ET) Work Group for ARCS.

SAIC has been contracted to supply technical support to the ET Work Group. The effort consists of conducting bench-scale treatability studies on designated sediments to evaluate the removal of specific organic contaminants.

Sediments have been obtained by GLNPO from various sites and represent the type of material that would be obtained for onsite treatment. The primary contaminants of these sediments are polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs). Analyses to date show PCB concentrations are less than 50 ppm. These sediments have been homogenized and packaged in smaller containers by EPA.

2.0 PROJECT DESCRIPTION

2.1 Background

SAIC and its subcontractors will conduct seven (7) bench-scale (several liters) tests on wet contaminated sediments using four treatment technologies.

The seven treatability tests (as currently planned) will utilize sediments from 4 sites (Saginaw River, Buffalo River, Indiana Harbor Canal, and Ashtabula River). Five sediments have been collected from these sites by GLNPO. These samples have been homogenized by the U.S. EPA and are being stored under refrigeration in 5 gallon containers by EPA in Duluth, MN.

These five sediments are currently being analyzed in the U.S. EPA, Environmental Research Laboratory in Duluth. The Duluth Laboratory is analyzing the sediments for total organic carbon/total inorganic carbon (TOC/TIC), particle size, density of dry material, total sulfur, acid volatile sulfide, oil and grease (O & G), total PCBs, PAHs (10), and metals including mercury. Table 2-1 is a summary of the data received to date.

A portion (small vial) of each residual of each treatability test may be retained and sent to the GLNPO office for "show" purposes. If available, sub-regulated quantities of the solid and oil residuals from each test treatability study may also be retained and shipped to EPA for possible further treatment studies.

The following is a list of technologies and the proposed number of sediment samples to be tested by each technology:

- a. B.E.S.T.TM Extraction Process on three samples (Buffalo River, Indiana Harbor, Saginaw TRP 6)
- b. Low Temperature Stripping (RETEC) on one sample (Ashtabula River)
- c. Wet Air Oxidation (Zimpro Passavant) on one sample (Indiana Harbor)
- d. Low Temperature Stripping (Soil Tech) on two samples (Buffalo River and Indiana Harbor)

Summaries of these technologies are included in Appendix A.

TABLE 2-1a. Preliminary Analytical Results on ARCS Sediments

Description	Concentration (Mg/kgm)(a)											Concentration (%) (a)	
	Total PCB	Total PAH	Cu	Cd	Ni	Fe (%)	Cr	Zn	Pb	TOC	O & G	Moisture (b)	
Saginaw 221	0.6	1.2	33	0.9	76	1.4	140	240	30	1.4	0.1	40.3	
Saginaw TRP6	6.0	3.1	81	4.7	110	0.9	200	200	47	1.2	0.3	31.1	
Ashtabula River	C	C	55	3.0	96	3.7	550	240	48	2.6	1.7	52.9	
Indiana Harbor	0.2	96	320	9.4	150	16	540	3300	780	21	5.8	61.0	
Buffalo River	0.4	5.6	85	1.9	57	3.9	110	200	94	2.0	0.5	41.5	

(a) Concentration in ppm and dry weight basis unless otherwise indicated.
 (b) As received basis.

TABLE 2-1b. Preliminary Particle Size Distribution (%)

Description	Particle Size (a)					Median Diameter, u
	> 50 u	50-20 u	20-5 u	5-2 u	2-0.2 u	
Buffalo River	19.8	12.1	29.0	11.8	24.3	9.3
					0.2-0.08 u	< 0.08 u
					2.4	0.6

(a) u microns

2.2 Testing Program for Chemical Characterization

SAIC shall be primarily responsible for the physical and chemical characterization of both the sediment samples prior to testing and the residuals created during the tests. Analyses conducted by the vendors or subcontractors will not be depended on, but such data shall be reported whenever available.

Two different sets of chemical analyses will be conducted during the performance of the treatability tests: optimization test analyses and performance evaluation analysis. The Phase I optimization test analyses will be conducted by the subcontractor or vendor during the series of initial technology tests. The Phase II performance evaluation analyses will be conducted by SAIC (or its analytical subcontractor) on the raw sediment sample prior to the treatability test run at optimum conditions and on the end products produced by that particular test. These tests are described further in this section.

In order to assure objectivity and consistency of data obtained from multiple vendors running different technology tests, SAIC shall conduct analyses as described in Table 2-2 for characterization of the sediments and the end products of the treatability tests at optimum conditions (Phase II).

The analyses described for the solid fraction in Table 2-2 shall be performed by SAIC's analytical subcontractor once on a subsample taken from each sample sent to each vendor or subcontractor for treatability tests (Phase II). This subsample will be taken at the same time that the sample for the Phase II treatability study is taken by the vendor. This data will serve as the measure of the raw sediment quality for comparison to analyses of treated end products from each technology test that may be conducted on sediments from a particular area of concern.

Each bench-scale technology test may actually involve the performance of multiple laboratory simulations. During the initial tests (Phase I), any analyses performed by the

vendor or subcontractor shall be reported, as available. For the tests run at optimum conditions (Phase II), SAIC shall conduct the full suite of analyses, as detailed in Table 2-2, on the end products if sufficient quantities are produced by the technology. Quotes solicited for each technology specified that a minimum 300 grams dry basis of treated solid had to be produced for SAIC's analyses. Table 2-3 shows the apportionment of the 300 grams for the solid analyses. The quantity of water is depended on the sediments and the individual technologies. To do all the analyses listed in Table 2-2, and associated QC, approximately 10 liters of water are required. Table 2-4 listed specified sample volumes for each analysis, and gives a priority to each analysis. It is possible that only the PCB and PAH analysis and associated QC will be performed on the water samples. If any oil residue is produced, it will be analyzed by dilution with appropriate sample cleanup steps for PCBs and PAHs.

The data generated by SAIC's analyses of the untreated sediment and the treated end products from the test at optimum conditions will be primarily relied upon to determine treatment efficiencies. Vendor- or subcontractor-generated data will not be relied upon but shall be reported when available.

2.3 Required Permits

Because of the small quantities of sediments required for the bench-scale treatability tests, SAIC anticipates that no formal permits will be required to conduct these tests. If this is not the case and permits (such as TSCA, RD&D or RCRA permits) are required, the subcontractor will notify SAIC and the TPM will be notified to obtain approval for acquisition of the permit(s).

All unused sediment samples requested by SAIC for the treatability test and all testing residuals, except those requested by the TPM for "show" purposes and those requested by the TPM for possible further testing, will be properly disposed of per federal and state regulations.

TABLE 2-2

Parameters and Detection Limits for Analysis of ARCS Technologies

<u>Parameter</u>	<u>Solid</u> ¹	<u>Water</u> ²	<u>Oil</u> ³
TOC/TIC	300	1000	
Total Solids ⁴	1000		
Volatile Solids ⁴	1000	1000	
Oil & Grease ⁴	10	1000	
Total Cyanide	0.5	10	
Total Phosphorus	50	10	
Arsenic ⁴	0.1	1	
Barium ⁴	0.2	2	
Cadmium ⁴	0.4	4	
Chromium ⁴	0.7	7	
Copper ⁴	0.6	6	
Iron (total) ⁴	0.7	7	
Lead ⁴	5	50	
Manganese ⁴	0.2	2	
Mercury ⁴	0.1	0.01	
Nickel ⁴	2	20	
Selenium ⁴	0.2	1	
Silver ⁴	0.7	7	
Zinc ⁴	0.2	2	
PCBs (total & Aroclors) ⁴	0.02	0.07	0.1
PAHs (16) ^{4,5}	0.2	2	0.1
pH	full range	full range	
BOD ₅		1000	
Total Suspended Solids ⁴		1000	
Conductivity		full range	

NOTES:

- ¹ Detection limits for solids are ppm (mg/kg dry weight). The D.L.'s for metals should be obtainable by ICP except for As, Se, and Hg. If GFAA is used, the D.L.'s will be 2 mg/kgm except Hg, Cd, and Ag which will be 0.1 mg/kgm.
- ² Detection limits for water are ppb (ug/l). The D.L.'s for metals should be obtainable by ICP except for As, Se, Hg. If GFAA is used D.L.'s will be 1 ug/L except Hg which will be 0.01 ug/L.
- ³ Detection limits for oil are ppm (mg/l).
- ⁴ Parameters tentatively identified for QC analyses.
- ⁵ Polynuclear aromatic hydrocarbons to be analyzed are the 16 compounds listed in Table 5-2.

TABLE 2-3

Solid Sample Quantities for Analyses

<u>Parameter</u>	<u>Initial Sample (g)</u>	<u>QC (g)</u>	<u>Total (g)</u>	<u>QC Approach</u>
TOC/TIC	15	--	15	None ¹
Total + Volatile Solids	5	10	15	Triplicate/Control
Oil & Grease	20	40	60	Triplicate/Control
Total Cyanide	10	--	10	None ²
Total Phosphorous	5	--	5	None ²
Metals (except Hg)	5	15	20	MS/Triplicate
Hg	1	3	4	MS/Triplicate
PCBs + PAHs	30	90(60) ³	90	(3)
pH	20	--	20	None ⁴
Subtotals	111	158(128)	269(239)	
Reserve	--	--	31(61)	
TOTAL	--	--	300	

¹ For sample set II that does not have such a limited quantity of solid, The QC described in footnote 3 will be implemented.

² For sample set II, MS/triplicate QC will be implemented.

³ Quality control for untreated solids is Triplicate and spike and for treated solids matrix spike and matrix spike duplicate.

⁴ For sample set II, Triplicate/Control sample QC will be implemented. The control sample may be an EPA QC check sample, an NBS - SRM, a standard laboratory reference solution, or other certified reference material.

TABLE 2-4

Sample Volumes Required and Priority Ranking for Water Analyses

<u>Parameter</u>	<u>Priority</u>	<u>Analysis Volume, ml</u>	<u>QC Volume, ml</u>	<u>QC Approach</u>
TOC/TIC	7	25	--	None (e)
Volatile Solids	5	d	d	Triplicate/Control
Oil & Grease	6	1000	2000	Triplicate/Control
Total Cyanide	7	500	--	None (f)
Total Phosphorus	7	50	--	None (f)
Arsenic	4	100	300	MS/Triplicate
Barium	2	100	300	MS/Triplicate
Cadmium	2	b	b	MS/Triplicate
Chromium	2	b	b	MS/Triplicate
Copper	2	b	b	MS/Triplicate
Iron (total)	2	b	b	MS/Triplicate
Lead	2	b	b	MS/Triplicate
Manganese	2	b	b	MS/Triplicate
Mercury	3	100	300	MS/Triplicate
Nickel	2	b	b	MS/Triplicate
Selenium	4	c	c	MS/Triplicate
Silver	2	b	b	MS/Triplicate
Zinc	2	b	b	MS/Triplicate
PCBs (total & Aroclors)	1	1,000	2,000	MS/MSD
PAHs (16)	1	a	a	MS/MSD
pH	7	25	--	None (f)
BOD	7	1,000	--	None (f)
Total Suspended Solids	5	200	400	Triplicate/Control
Conductivity	7	100	--	None (f)

Note:

- a) same aliquot as PCBs
 b) same aliquot as Barium
 c) same aliquot as Arsenic
 d) same aliquot as Total Suspended Solids
 e) see footnote 2, Table 2-3
 f) see footnote 4, Table 2-3

2.4 Purpose of Phase I Experimental Design

The purpose of the Phase I technology experimental design is for each subcontractor to establish a range of variables best suited for feasibly implementing their technology on a full-scale basis (Phase II). SAIC will send a quantity (specified by the vendor) of each sediment to the vendor to accomplish this. All data generated by the vendor during Phase I will be supplied to SAIC for inclusion in the report for that technology. This information will include the operating conditions/parameters, the input/output data for the contaminants of interest to show the range of effectiveness associated with various operating conditions, and the quantities of the input material and the various residuals resulting from the test. The optimum set of conditions to be used for Phase II will be reported to SAIC along with appropriate revisions to the Phase I experimental design to make it applicable to Phase II.

2.5 Purpose of Phase II Treatability Test

SAIC will send another container of sediment(s) to the vendor (quantity to be specified by the vendor). This container will not be opened until a representative of SAIC arrives for the scheduled treatability test(s). Other observers from U.S. EPA, COE and/or the GLNPO may also be present during the Phase II treatability test(s).

The new sample will be homogenized and a sample equivalent to a minimum of 300 gm of dry solids will be set aside for characterization analyses (Table 2-2) by SAIC. SAIC will observe the treatability tests and obtain samples of process residuals for analyses (Table 2-2). The bench-scale test(s) must produce enough solid residual for all vendor requirements and a quantity equivalent to 300 gm of dry solids for SAIC analyses. SAIC can utilize up to 10 liters of water for analysis and 25 ml of the oil residual. The actual quantities of water and oil that will be produced are dependent on the initial sediment and the technology. All technologies except wet air oxidation are expected to produce an oil residual. Also, if additional solid and/or oil residue is available, EPA may ask for these materials to be sent to them for storage for possible future evaluation.

All data generated by the vendor during Phase II is to be supplied to SAIC for inclusion in the report for that technology. The vendor must stipulate in their work plan, prior to conducting the test(s), the process locations to be sampled, the frequency and the information being obtained.

All other residuals from both phases of the treatability study, including any untreated sediment, will be properly disposed of by the vendor.

SAIC shall oversee the treatability test assessment(s) by vendors or subcontractors, including all QA/QC aspects, monitoring and analysis. SAIC shall ensure compliance with the specific experimental design during the tests conducted by vendors or subcontractors. SAIC will make specific notes regarding the equipment being used, any pretreatment of the sediment(s), the operation of the equipment, and any post treatment of the residuals. SAIC personnel will pack the untreated sediment sample and the end product samples from the Phase II test for each technology in an appropriate fashion for shipment from the vendor or subcontractor to the laboratory SAIC is using for the analysis. Proper chain-of-custody procedures will be developed in the QAPjP and strictly followed by SAIC personnel.

SAIC plans to take photos of the equipment while at the vendor's location for inclusion in the report.

SAIC shall perform limited interpretation of technology test results, specifically the development of material and energy balances. No test of air or fugitive emissions will be done. For material balances, estimates of the mass distribution of the analytes of interest (Table 2-2) among the residuals will be made. The term *energy balance* is interpreted to mean an estimation by the vendor of the energy input into the process at a pilot- or full-scale.

SAIC shall collect any information available from the vendor or subcontractor concerning the actual or estimated costs of constructing and operating full-scale versions of the technology tested.

The purpose of this project is to test five technologies for removing organic contaminants (PCBs and PAHs) from sediments typical of locations around the Great Lakes. GLNPO is specifying the technologies and the sediment(s) to be treated by each technology. This study is only one part of a much larger program, and it is not necessarily intended to evaluate the complete treatment of these sediments. Other aspects or treatment options are being evaluated by a number of agencies, contractors, etc.

Therefore, this study is based on the following assumptions:

- The percent removal of the PCBs and PAHs from the solid residual is the most important object of this study.
- The untreated sediments and solid residuals are the most important matrices.
- If water and oil residuals are generated by a technology, the existence of an appropriate treatment or disposal option for these residuals is assumed. PAHs and PCBs will be determined in these residuals as a cross check of their fate in treating the solids.

Based on the intents of this study, the critical measurements are PAHs, PCBs, metals, total solids, volatile solids, and oil and grease in the untreated and treated solids.

2.6 Organization and Responsibilities

A project organization and authority chart is shown in Figure 2-1. The Environmental Monitoring Systems Laboratory (EMSL) is cooperating with GLNPO and SAIC on this evaluation. Mr. Thomas Wagner is the SAIC Work Assignment Manager and is responsible for the technical and budgeting aspects of this work assignment. Mr. Clyde Dial is QA Manager and is responsible for QA oversight on this work assignment.

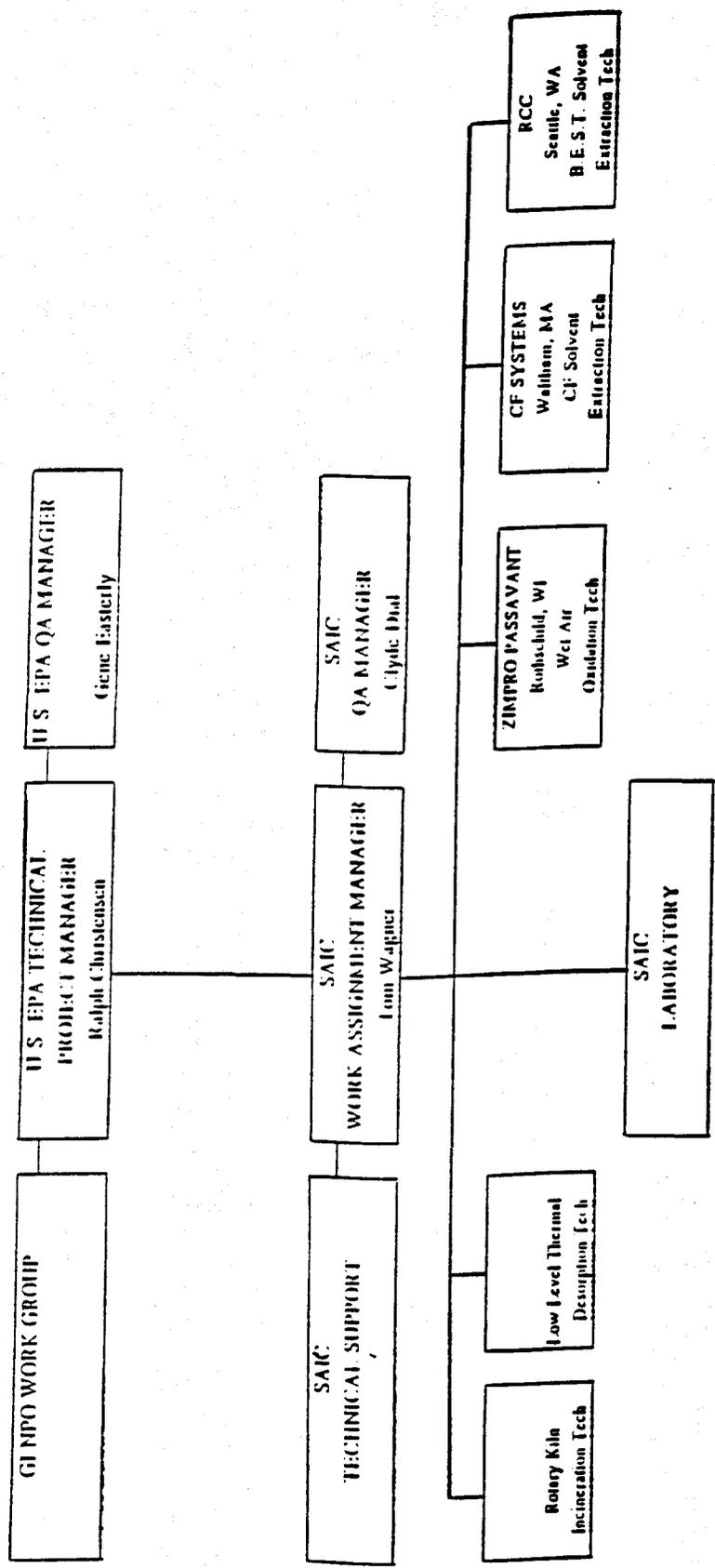


Figure 2-1. Project Organization

2.7 Schedule

The Phase I experimental designs are scheduled for mid to late February 1990, and the Phase II Treatability Tests are scheduled for March and April 1991.

3.0 QUALITY ASSURANCE OBJECTIVES

3.1 Precision, Accuracy, Completeness, and Method Detection Limits

Objectives for accuracy, precision, method detection limits, and completeness for the critical measurements of solids are listed in Table 3-1. Accuracy (as percent recovery) will be determined from matrix spike recovery for PAHs, PCBs and metals, and from laboratory control samples (certified reference material- CRM) for the remaining analyses. Precision (as relative standard deviation) will be determined from the results of triplicate analyses for PAHs, PCBs, solids (total, volatile and/or suspended), oil and grease, and metals. Matrix spike and matrix spike duplicate analyses will be used for treated solids for PCBs and PAHs. The completeness will be determined from the number of data meeting the criteria in Table 3-1 divided by the number of samples that undergo performance evaluation analyses.

3.2 Representativeness and Comparability

Representativeness and Comparability are qualitative parameters. The sediment samples have already been collected and have been reported to be representative of the areas to be remediated. The data obtained in this program will be comparable because all the methods are taken from a standard EPA reference manual and all the analyses will be conducted at the same laboratory. Reporting units for each analysis are specified in Section 6 of this document and are consistent with standard reporting units in this program.

3.3 Method Detection Limits

The target detection limits (TDLs) were specified by GLNPO (Table 2-2). Based on the analytical methods appropriate for the analyses and the amount of samples specified in the methods, the detection limits listed in Table 3-1 should be achievable. Generally the instrument detection limits are defined as 3 times the standard deviation of 15 blanks or standards with a concentration within a factor of 10 of the IDL.

**TABLE 3-1. Quality Assurance Objectives for Critical Measurements
(Sediments and Treated Solids)**

Parameter	Method (a)	Accuracy (b) (as % recovery)	Precision (c) %	Method Detection Limit (d) (mg/kgm)	Completeness %
Total Solids	160.3	80-120	20	1000	90
Volatile Solids	160.4	80-120	20	1000	90
Oil & Grease	9071	80-120	20	10	90
Arsenic	3050/7060	85-115	20	0.1	90
Barium	3050/6010	85-115	20	0.2	90
Cadmium	3050/6010	85-115	20	0.4	90
Chromium	3050/6010	85-115	20	0.7	90
Copper	3050/6010	85-115	20	0.6	90
Iron (total)	3050/6010	85-115	20	0.7	90
Lead	3050/6010	85-115	20	5	90
Manganese	3050/6010	85-115	20	0.2	90
Mercury	7471	85-115	20	0.1	90
Nickel	3050/6010	85-115	20	2	90
Selenium	3050/7740	85-115	20	0.2	90
Silver	3050/6010	85-115	20	0.7	90
Zinc	3050/6010	85-115	20	0.2	90
PCBs (total & Aroclors (e))	3540 or 3550/8080	70-130	20	0.02	90
PAHs (Table 5-2)	3540 or 3550/ 8270 or 8100	70-130	20	0.2	90

(a) References are to "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020 or "Test Methods for Evaluating Solid Waste", SW-846, 3rd. Ed.

(b) Determined from MS or MS/MSD analyses for metals, PAHs, and PCBs; others determined from laboratory control samples.

(c) Determined as relative percent standard deviation of triplicate analyses, except PAHs and PCBs in treated solids where MS/MSD will be used.

(d) See Footnotes 1 and 2 of Table 2-2

(e) Detection limits based on extraction of 30 gram samples.

4.0 SAMPLE TRANSFER AND PREPARATION PROCEDURES

As described in Section 2, SAIC will receive a number of 5 gallon containers of previously homogenized sediments from the U. S. EPA in Duluth, Minnesota. The number of containers of each sediment is dependent on the final determination by GLNPO of which sediments will be tested by the various technologies. Only if smaller portions of sediments are requested by the vendors will these containers be opened by SAIC. If smaller portions are required, SAIC will resuspend the solids and water within an individual container by rolling, tumbling, and stirring of the contents. The final stirring will be in the original containers using a metal stirrer as would be used to mix a 5 gallon container of paint. The metal stirrer is appropriate because metals are not the primary constituents of concern in these treatability tests.

The *Chain of Custody Record* shown in Figure 4-1 will be completed for each cooler shipped to the subcontractor or vendor that will conduct the optimization and performance evaluation tests. The samples obtained from the vendor for analysis will be labeled as shown in Figure 4-2. The labels will document the sample I.D., time and date of collection, and the location from where the sample was taken. The amount/type of preservative that was added will also be recorded.

SAIC personnel will pack and ship the untreated sediment and the end product samples (residuals) from the optimum conditions test for each technology. The amount of preservative will be recorded. Samples will be labeled (see Figure 4-2) and shipped by overnight delivery service to the laboratory in coolers containing ice. If "blue ice" is used in the coolers, samples will be initially cooled with regular ice prior to being packed in the coolers with blue ice. The *Chain of Custody Record* (Figure 4-1) will be completed for each cooler shipped to the laboratory.

Solid, sediment and oil samples require no preservative other than cooling to 4° C. The appropriate types of containers (solid and liquids), holding times, and preservatives for water samples are listed in Table 4-1.

TABLE 4-1. Sample Containers, Preservation and Holding Times

<i>Parameter</i>	<i>Container</i>	<i>Preservation of Water Samples</i>	<i>Holding Time</i>
TOC	P,G	Cool 4° C, H ₂ SO ₄ to pH < 2	28 days
Solids (Total, Volatile & Suspended)	P,G	Cool 4° C	7 days
Oil and Grease	G	Cool 4° C, H ₂ SO ₄ to pH < 2	28 days
Total Cyanide	P,G	Cool 4° C, NaOH to pH > 12 0.6g Ascorbic acid	14 days
Total Phosphorous	P,G	Cool 4° C, H ₂ SO ₄ to pH < 2	28 days
Metals (except Cr VI)	P,G	HNO ₃ to pH < 2	6 months except Hg (Hg 28 days)
Cr (VI)	P,G	Cool 4° C	24 hours
PAHs & PCBs	G teflon lined cap	Cool 4° C, store in dark	Extract within 7 days Analyze within 40 days
BOD ₅	P,G	Cool 4° C	48 hours
pH	P,G		Performed immediately
Conductivity	P,G	Cool 4° C	28 days



635 W. 7th Street, Suite 403, Cincinnati, OH 45203

Sample No.: _____

Sample Location/Date/Time: _____

Project Location/No.: _____

Analysis: _____

Collection Method: _____ *Purge Volume:* _____

Preservative: _____

Comments: _____

Collector's Initials _____

Figure 4-2. Example Sample Label

5.0 ANALYTICAL PROCEDURES AND CALIBRATION

Analytical procedures for all critical measurements are referenced in Table 3-1. The non-critical measurements are for any residual water and oil remaining after the performance evaluation tests and some additional analyses on the solid samples. The EPA procedures are specified in Table 5-1.

The required calibration for all analyses are specified in the methods and will be followed. All instruments will be calibrated as specified in the methods prior to performing any analysis of the samples. Internal QC checks, including initial calibration and continuing calibration checks, for the critical measurements are listed in Table 7-1.

Table 5-2 contains the minimum list of the sixteen PAHs that must be determined by either analytical method. Additional compounds may be included, but none of these sixteen may be deleted from the target list.

The laboratory is responsible for maintaining a preventive maintenance program consistent with manufacturers recommendations for all instruments required for this program. In addition, they are responsible for having a sufficient supply of routine spare parts necessary for the operation of the analytical equipment in order to complete the analysis in a timely fashion.

TABLE 5-1
Analytical Methods for Critical and Non-critical Measurements

<i>Parameter</i>	<i>Methods^a</i>		
	<i>Solid</i>	<i>Water</i>	<i>Oil</i>
TOC	9060	9060	NA
Total Solids	160.3	NA	NA
Volatile Solids	160.4	160.4	NA
Oil and Grease	9071	413.1	NA
Total Cyanide	9010	9010	NA
Total Phosphorous	365.2	365.2	NA
Arsenic	3050/7060	7060	NA
Mercury	7471	7470	NA
Selenium	3050/7740	7740	NA
Other Metals	3050/6010	3010/6010 (7760 Ag)	NA
PCBs	3540 or 3550/8080	3510 or 3520/8080	3580/8080
PAHs	3540 or 3550/ 8270 or 8100 ^b	3510 or 3520/ 8270 or 8100 ^b	3580/8270
pH	9045	9040	NA
BOD	NA	405.1	NA
Total Suspended Solids	NA	160.2	NA
Conductivity	NA	9050	NA

(a) References are to "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020 or "Test Methods for Evaluating Solid Waste", SW-846, 3rd. Ed.

(b) Where options for methods are given, -Either is acceptable if the detection limits given in Table 2-2 can be achieved.

NA - Not analyzed

TABLE 5-2
List of PAHs^a

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Inden(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(k)fluoranthene	Phenanthrene
Benzo(ghi)perylene	Pyrene

^a PAH analyses must determine these 16 compounds at a minimum.

6.0 DATA REDUCTION, VALIDATION AND REPORTING

Data will be reduced by the procedures specified in the methods and reported by the laboratory in the units also specified in the methods. The work assignment manager or his designer will review the results and compare the QC results with those listed in Table 3-1. Any discrepancies will be discussed with the QA Manager.

All data will be reviewed to ensure that the correct codes and units have been included. All organic and inorganic data for solids will be reported as mg/kgm except TOC, oil & grease (O&G), moisture and iron that will be reported as percent and pH that will be reported in standard pH units. All metals and organics in water samples will be reported as ug/l. TOC, solids (suspended and volatile), O&G, cyanide, phosphorus, and BOD will be reported as mg/l. Conductivity will be reported as umhos/cm and pH as standard pH units. After reduction, data will be placed in tables or arrays and reviewed again for anomalous values. Any inconsistencies discovered will be resolved immediately, if possible, by seeking clarification from the sample collection personnel responsible for data collection, and/or the analytical laboratory.

Data Tables in the report will be delivered in hard copy and on discs. The discs will be either in Lotus files or WordPerfect 5.1 files.

7.0 INTERNAL QUALITY CONTROL CHECKS

The internal QC checks appropriate for the measurement methods to be utilized for this project are summarized in Table 7-1. These items are taken from the methods and the QC program outlined in Section 3 of this QAPjP.

For the GLNPO program, the following QC measures and limits are employed:

- | | |
|-----------------------------|--|
| on-going calibration checks | <ul style="list-style-type: none">- beginning, middle, and end of sample set for metals, pH, TOC/TIC, total cyanide, and total P- mid-calibration range standard- $\pm 10\%$ limit unless otherwise stated- ± 0.1 pH unit for pH- ± 10 umhos/cm for conductivity at 25° C |
| | <ul style="list-style-type: none">- beginning, every 12, and end of sample set for PCBs and PAHs- mid calibration range standard- $\pm 10\%$ limit |
| method blanks | <ul style="list-style-type: none">- one per sample set for PCBs and PAHs- < MDL limit unless otherwise stated- beginning, middle and end for metals, TOC/TIC, total P, total cyanide, and pH- beginning, middle and end for conductivity with acceptance limits of < 1 umho/cm |
| matrix spikes | <ul style="list-style-type: none">- one per sample set- 1 to 1.5 times the estimated concentration of sample- $\pm 15\%$ limit for metals; $\pm 30\%$ for PCBs and PAHs |
| replicates | <ul style="list-style-type: none">- triplicate analyses- RSD $\leq 20\%$ unless otherwise stated- one per sample set- ± 0.1 pH unit for pH- ± 2 umhos/cm for conductivity |

- QC sample (CRM) - - minimum of one per sample set
- $\pm 20\%$ of known CRM
- ± 0.1 pH unit for pH
- ± 1 umhos/cm for conductivity

- surrogate spikes (PCBs and PAHs only) - added to each sample
- $\pm 30\%$ recovery

The surrogate for PCB analysis is tetrachlorometaxylene and the internal standard is 1,2,3-trichlorobenzene.

Table 7-2 shows an analytical matrix that will be completed for each technology tested. For example, consider the case of a bench scale treatability test of (1 kilogram) Indiana harbor sediment by low temperature stripping. Based on the data presented in Table 2-1a and assuming complete separation and recovery of oil, water, and solid, a 1 kilogram sample of untreated sediment will produce 58 grams of oil, 610 ml of water, and 332 grams of dry treated solids. For the purpose of this program, this sample set consists of 1 untreated solid, 1 treated solid, and the water and oil generated by the process. Table 7-3 is a completed analytical matrix for this test. Table 7-3 is based on Tables 2-2 and 2-4 and the QC approach described in this QA plan. The analysis of the water sample in this example is severely limited by the relatively small amount of sample obtained.

Table 7-4 is a matrix summarizing the anticipated samples to be analyzed for this project. The sets for each technology (see section 2.1) are:

- I B.E.S.T.
- II ReTec
- III Wet Air Oxidation
- IV Soil Tech

The Soil Tech process will process treated soils at two distinct points. Therefore, four treated solids are produced from the two untreated sediments.

TABLE: 7-1. Internal QC Checks for Measurements

Parameter	Method (a)	Initial Calibration	Calibration Checks	Method Blank	MS/MSD	Triplicate Sample Analysis	QC Sample	Surrogate Spikes
Solids (Total & Volatile)	160.3	Balance (Yearly)	Balance Each Day	Yes	NA	Yes	Yes	NA
	160.4							
Oil & Grease	9071	See Above	See Above	Yes	NA	Yes	Yes	NA
Metals	6010	2 points	Every 10th Sample	Yes	MS only	Yes	Yes	NA
	7000 series	4 points	Every 10th Sample	Yes	MS only	Yes	Yes	NA
PCBs (b)	8080	5 points	Every 10th Sample	Yes	Yes (treated) MS only (untreated)	NA (treated) Yes (untreated)	Yes	Yes
		5 points	Every 12 Hours	Yes	Yes (treated) MS only (untreated)	NA (treated) Yes (untreated)	Yes	Yes
PAHs	8270 or 8100	5 points	Every 12 Hours	Yes	Yes (treated) MS only (untreated)	NA (treated) Yes (untreated)	Yes	Yes

(a) References are to "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020 or "Test Methods for Evaluating Solid Waste", SW-846, 3rd. Ed.
 (b) Second column confirmation of positive results is required.
 NA - Not Applicable

TABLE 7-1. Internal QC Checks for Measurements (continued)

Parameter	Method (a)	Initial Calibration	Calibration Checks	Method Blank	MS/MSD	Triplicate Sample Analysis	QC Sample	Surrogate Spikes
pH	9045/9040	2 points	Every 10th Sample	NA	NA	NA	Yes	NA
Conductivity	9050	1 point	Every 15th Sample	NA	NA	NA	Yes	NA
Cyanide	9010	7 points	Every 15th Sample	Yes	NA	NA	Yes	NA
Phosphorous	365.2	9 points	Every 15th Sample	Yes	NA	NA	Yes	NA
TOC/TIC	9060	3 points	Every 15th Sample	Yes	NA	NA	Yes	NA

(a) References are to "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020
 or "Test Methods for Evaluating Solid Waste", SW-846, 3rd. Ed.
 NA - Not Applicable

TABLE 7-2. Analytical Matrix

Parameters	QC Sample and Method Blank	Untreated Sediment	MS	Tripli- cate	Treated Solids	MS	MSD	Tripli- cate	Water	MS	MSD	Tripli- cate	Oil	MS	Tripli- cate
Total Solids (Moisture)															
Volatile Solids															
O & G															
Metals															
PCBs															
PAHs															
TOC															
Total Cyanide															
Total Phosphorous															
pH															
BOD															
Total Suspended Solids															
Conductivity															

TABLE 7-3. Example

Parameters	QC Sample and Method Blank	Untreated Sediment	MS	Tripli- cate	Treated Solids	MS	MSD	Tripli- cate	Water	MS	MSD	Tripli- cate	Oil	MS	Tripli- cate	
Total Solids (Moisture)	Yes	I		X	I			X				X				
Volatile Solids	Yes	I		X	I			X				X				
O & G	Yes	I		X	I			X				X				
Metals	Yes	I	X	X	I	X		X				X				
PCBs	Yes	I	X	X	I	X	X	X	I			X	I	X	X	X
PAHs	Yes	I	X	X	I	X	X	X	I			X	I	X	X	X
TOC	Yes	I			I											
Total Cyanide	Yes	I			I											
Total Phosphorous	Yes	I			I											
pH	Yes	I			I											
BOD																
Total Suspended Solids																
Conductivity																

TABLE 7-4. Analytical and QC Sample Matrix for GLNPO Treatability Studies (numbers of samples)

SAMPLE SET	TOC/TIC		TOTAL SOLIDS		VOL SOLIDS		O & G		TOTAL CYANIDE		TOTAL PHOS		METALS		PCBs		PAH		pH		BOD		TSS		COND		
	S(a)	QC(b)	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	S	QC	
SET I																											
Untreated S.	3	-	3	3	3	3	3	3	-	-	3	3	3	3	3	3	3	3	3	-	-	-	-	-	-	-	-
Treated S.	3	-	3	2	3	2	3	2	3	3	3	3	2	3	2	3	2	3	2	3	-	-	-	-	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SET IV																											
Untreated S.	2	-	2	3	2	3	2	3	2	-	2	3	2	3	2	3	2	3	2	-	-	-	-	-	-	-	-
Treated S.	4	-	4	2	4	2	4	2	4	-	4	3	4	2	4	2	4	2	4	-	-	-	-	-	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SET II																											
Untreated S.	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3	-	-	-	-	-	-	-
Treated S.	1	2	1	2	1	2	1	2	1	3	1	3	1	3	1	2	1	2	1	2	-	-	-	-	-	-	-
Water	1	3	-	-	-	-	-	-	-	3	1	3	1	3	1	2	1	2	1	2	-	-	-	-	-	-	-
Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SET III																											
Untreated S.	1	-	1	3	1	3	1	3	1	-	1	3	1	3	1	3	1	3	1	-	-	-	-	-	-	-	-
Treated S.	1	-	1	2	1	2	1	2	1	-	1	3	1	3	1	2	1	2	1	-	-	-	-	-	-	-	-
Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
TOTALS																											
Solids	16	5	16	20	16	20	16	20	16	6	16	24	16	20	16	20	16	20	16	5	16	16	20	16	16	16	16
Water	1	3	-	-	1	3	1	3	1	3	1	3	7	6	7	6	7	6	7	3	1	3	1	3	1	3	1
Oil	-	-	-	-	-	-	-	-	-	-	-	-	6	9	6	9	6	9	-	-	-	-	-	-	-	-	-

(a) Number of original samples.
 (b) Number of quality control samples. A "3" represents two additional replicates (triplicate determination) and a spike or control sample analysis resulting in an additional three QC analyses. A "2" represents matrix spike/matrix spike duplicate analysis scheme resulting in an additional two QC analyses. A "1" indicates a blank spike or other control sample analysis resulting in one additional QC analysis.
 (c) Treated and untreated solids does not apply, and only one control sample per set will be analyzed.

8.0 PERFORMANCE AND SYSTEM AUDITS

The laboratory will perform internal reviews by the QA officer or a designee. These reviews should include, as a minimum, periodic checks on the analysts to assess whether they are aware of and are implementing the QA requirements specified in the ARCS QA program.

The laboratory will be prepared to participate in a systems audit to be conducted by the SAIC QA Officer or his designee and/or ARCS QA Officer.

The vendors of the various technologies have all been advised that a number of representatives from SAIC, GLNPO, and other organizations will be present during Phase II of the treatability studies. Thus the ARCS QA officer can be present during Phase II of any or all of the treatability studies.

9.0 CALCULATION OF DATA QUALITY INDICATORS

9.1 Accuracy

Accuracy for PAHs, PCB and metals will be determined as the percent recovery of matrix spike samples. The percent recovery is calculated according to the following equation:

$$\% R = 100\% \times \frac{C_i - C_o}{C_t}$$

where

- %R = percent recovery
- C_i = measured concentration in spiked sample aliquot
- C_o = measured concentration in unspiked sample aliquot
- C_t = actual concentration for spike added

Accuracy for the other critical measurements will be determined from laboratory control samples according to the equation:

$$\% R = 100\% \frac{C_m}{C_t}$$

where

- %R = percent recovery
- C_m = measured concentration of standard reference material
- C_t = actual concentration for standard reference material

9.2 Precision

Precision will be determined from the difference of percent recovery values of MS and MSDs for PAHs and PCBs or triplicate laboratory analyses. The following equations will be used for all parameters:

When 2 values are available:

$$\text{RPD} = \frac{[C_1 - C_2] \times 100\%}{[C_1 + C_2] / 2}$$

where

- RPD = Relative percent difference
 C_1 = The larger of two observed values
 C_2 = The smaller of the two observed values

When more than 2 values are available:

$$S = \sqrt{\frac{\sum_{i=1}^N X_i^2 - \frac{1}{N} \left(\sum_{i=1}^N X_i \right)^2}{N - 1}}$$

where

- S = standard deviation
 X_i = individual measurement result
 N = number of measurements

Relative standard deviation may also be reported. If so, it will be calculated as follows:

$$\text{RSD} = 100 \frac{S}{\bar{X}}$$

where

RSD = relative standard deviation, expressed in percent

\underline{S} = standard deviation

\underline{X} = arithmetic mean of replicate measurement.

9.3 Completeness

Completeness will be calculated as the percent of valid data points obtained from the total number of samples obtained.

$$\% \text{ Completeness} = \frac{\text{VDP}}{\text{TDP}} \times 100$$

where

VDP = number of valid data points

TDP = total number of samples obtained.

10.0 CORRECTIVE ACTION

Corrective actions will be initiated whenever quality control limits (e.g., calibration acceptance criteria) or QA objectives (e.g., precision, as determined by analysis of duplicate matrix spike samples) for a particular type of critical measurement are not being met. Corrective actions may result from any of the following functions:

- Data Review
- Performance evaluation audits
- Technical systems audits
- Interlaboratory/interfield comparison studies

All corrective action procedures consist of six elements:

- Recognition that a Quality Problem exists
- Identification of the cause of the problem
- Determination of the appropriate corrective action
- Implementation of the corrective action
- Verification of the corrective action
- Documentation of the corrective action

For these treatability studies after initial recognition of a data quality problem, the data calculation will be checked first. If an error is found, the data will be recalculated and no further action will be taken. If no calculation error is found, further investigation will be conducted. Depending on the cause and the availability of the appropriate samples, reanalysis or flagging of the original data will be utilized.

All corrective action initiations, resolutions, etc. will be implemented immediately and will be reported in Sections One and Two (Difficulties Encountered and Corrective Actions Taken, respectively) in the existing monthly progress reporting mechanisms established between SAIC, EPA-RREL, GLNPO, AND THE ARCS QA officer and in the QA section of the final report. The QA Manager will determine if a correction action has resolved the QC problem.

11.0 QA/QC REPORTS TO MANAGEMENT

This section describes the periodic reporting mechanism, reporting frequencies, and the final project report which will be used to keep project management personnel informed of sampling and analytical progress, critical measurement systems performance, identified problem conditions, corrective actions, and up-to-date results of QA/QC assessments. As a minimum, the reports will include, when applicable:

- Changes to the QA Project Plan, if any.
- Limitations or constraints on the applicability of the data, if any.
- The status of QA/QC programs, accomplishments and corrective actions.
- Assessment of data quality in terms of precision, accuracy, completeness, method detection limit, representativeness, and comparability.
- The final report shall include a separate QA section that summarizes the data quality indicators that document the QA/QC activities that lend support to the credibility of the data and the validity of the conclusions.

For convenience, any QA/QC reporting will be incorporated into the already well-established monthly progress reporting system between SAIC and EPA-RREL for all TESC Work Assignments. In addition, copies of monthly reports will be sent to the ARCS QA officer. Any information pertaining to the above-listed categories will be reported under Sections One through Three (Difficulties Encountered, Corrective Actions Taken, and Current Activities, respectively) in the monthly reports.

GLNPO - QAPjP

Section No.: Appendix A

Revision No.: 1

Date: Jan. 9, 1991

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APPENDIX A
TECHNOLOGY SUMMARIES

B.E.S.T.TM Process Description

The B.E.S.T.TM process is a patented solvent extraction technology utilizing triethylamine as the solvent. Triethylamine is an aliphatic amine that is produced by reacting ethyl alcohol and ammonia. The key to success of the B.E.S.T.TM process is triethylamine's property of inverse miscibility. At temperatures below 65°F, triethylamine is completely soluble with water. Above this temperature, triethylamine and water are only partially miscible. The property of inverse miscibility can be utilized since cold triethylamine can simultaneously solvate oil and water.

The B.E.S.T.TM process produces a single phase extraction solution which is a homogeneous mixture of triethylamine and the water and oil (containing the organic contaminants, such as PCBs, PNAs, and VOCs) present in the feed material. In cases where the extraction efficiencies of other solvent extraction systems are hindered by emulsions, which have the effect of partially occluding the solute (oil containing the organic contaminants), triethylamine can achieve intimate contact at nearly ambient temperatures and pressures. This allows the B.E.S.T.TM process to handle feed mixtures with high water content without penalty in extraction efficiency. This process is expected to yield solid, water, and oil residuals.

Low Temperature Stripping

Low-temperature stripping (LTS) is a means to physically separate volatile and semivolatile contaminants from soil, sediments, sludges, and filter cakes. For wastes containing up to 10% organics or less, LTS can be used alone for site remediation.

LTS is applicable to organic wastes and generally is not used for treating inorganics and metals. The technology heats contaminated media to temperatures between 200-1000°F, driving off water and volatile contaminants. Offgases may be burned in an afterburner, condensed to reduce the volume to be disposed, or captured by carbon adsorption beds. For these treatability studies, only processes that capture the contaminants driven off will

be considered. The process (for these treatability studies) is expected to yield solid, water, and oil residuals.

Wet Air Oxidation

Wet air oxidation is a process that accomplishes an aqueous phase oxidation of organic or inorganic substances at elevated temperatures and pressures. The usual temperature range varies from approximately 350 to 600°F (175 to 320°C). System pressures of 300 psig to well over 300 psig may be required. However, testing has been done at temperatures exceeding the critical point for water to limit the amount of evaporation of water, depending on the desired reaction temperature. Compressed air or pure oxygen is the source of oxygen that serves as the oxidizing agent in the wet air oxidation process. This process is expected to yield only solid and water residuals.

APPENDIX D

SAIC-GLNPO (CF #361)

ZIMPRO

CONVENTIONALS IN UNTREATED SEDIMENT

MSL Code MDL	Sponsor ID	% Moisture 0.01%	pH	% Volatile 0.00%	Total Solid	Oil & Grease (mg/kg)	TOC % weight	Total Cyanide (mg/kg)	Total Phosphorus (mg P/kg)
361-26/27, Rep 1	I-US-ZP, Rep 1	54.97	7.67	14.73	9811	19.25	22.3	2919	
361-26/27, Rep 2	I-US-ZP, Rep 2	55.12	NA	15.28	10016	NA	24.9	NA	
361-26/27, Rep 3	I-US-ZP, Rep 3	NA	NA	15.12	9851	NA	NA	NA	
Method Blank		NA	NA	NA	20 U	0.014	0.2 U	0.005	

STANDARD REFERENCE MATERIAL

MESS-1 SRM
In-house Consensus value #

NA NA
2.12 2.3

NA

MATRIX SPIKE RESULTS

Amount Spiked
361-26/27
361-26/27 + Spike
Amount Recovered
% Recovery

NA NA
17944 9811
NA NA
12005 2194
NA NA
12% x

NA NA
343.0 22.3
NA NA
357.5 9007
NA NA
335.2 4264
NA NA
98%

REPLICATE ANALYSES

361-26/27, Rep 1
361-26/27, Rep 2
361-26/27, Rep 3
RSD%

54.97
NA NA
NA NA
NA NA

7.67
NA NA
NA NA
NA NA

14.73
15.28
15.12
2%

9811
10016
9851
1%

19.25
NA NA
NA NA
NA NA

22.3
NA NA
NA NA
NA NA

2919
NA NA
NA NA
NA NA

NA = Not analyzed

U = Below detection limit

= Value based on past in-house analyses of MESS-1. Not statistically determined.

x = Most likely analyst error and spike not added.

NOTE: Conventional results reported on dry weight basis.

SAIC-GLNPO (CF #361)

ZIMPRO

CONVENTIONALS IN TREATED SEDIMENT

MSL Code MTL	Sponsor ID	% Moisture 0.01%	pH	% Volatile 0.00%	Oil & Grease (mg/kg)	TOC % weight	Total Cyanide (mg/kg)	Total Phosphorus (mg P/kg)
361-29, REP 1	I-TS-ZP	43.3	6.51	7.78	1058	9.28	14.5	4743
361-29, REP 2	I-TS-ZP	NA	6.52	7.19	1093	NA	NA	NA
361-29, REP 3	I-TS-ZP	NA	NA	7.05	702	NA	NA	NA
Method Blank		NA	NA	NA	20 U	0.014	0.2 U	0.005

STANDARD REFERENCE MATERIAL

MESS-1 SRM								
In-house Consensus value #		NA	NA	NA	NA	2.12	NA	NA
						2.3		

MATRIX SPIKE RESULTS

Amount Spiked								
361-26/27		NA	NA	NA	17944	NA	343.0	4177
361-26/27 + Spike		NA	NA	NA	9811	NA	22.3	4743
Amount Recovered		NA	NA	NA	12005	NA	357.5	9007
% Recovery		NA	NA	NA	2194	NA	335.2	4264
					12% x	NA	98%	102%

REPLICATE ANALYSES

361-29, Rep 1	I-TS-ZP, REP 1	43.3	6.51	7.78	1058	9.28	14.5	4743
361-29, Rep 2	I-TS-ZP, REP 2	NA	NA	7.19	1093	NA	NA	NA
361-29, Rep 3	I-TS-ZP, REP 3	NA	NA	7.05	702	NA	NA	NA
	RSD%	NA	NA	5%	23%	NA	NA	NC

NA = Not analyzed

U = Below detection limit

= Value based on past In-house analyses of MESS-1. Not statistically determined.

X = Most likely analyst error and spike not added.

NOTE: Conventional results reported on dry weight basis.

SAIC GLNPO (CF #361)

ZIMPRO

METALS IN UNTREATED SEDIMENT

(Concentrations in ug/g dry weight)

MSL Code	Sponsor ID	Ag		Ba		Cd		Cr		Cu		%Fe		Hg		Mn		Ni		Pb		Sb		Zn	
		AA	AF	AA	AF	AA	AF	AA	AF	AA	AF	AA	AF	CVAA	AA	AF	AA								
361-26/27, Rep 1	I-US-ZP, Rep 1	4.78	21.6	282	7.71	1082	267	17.45	1.385	1920	119	764	5.38	3090											
361-26/27, Rep 2	I-US-ZP, Rep 2	4.90	34.6	281	8.17	1047	250	17.12	1.369	1910	113	707	5.54	2930											
361-26/27, Rep 3	I-US-ZP, Rep 3	4.81	26.6	287	7.35	1096	244	17.22	1.439	1890	112	766	5.41	3070											
Method Blank		0.20	NA	NA	0.006	NA	NA	NA	0.00013	NA	NA	NA	0.22	U											

STANDARD REFERENCE MATERIAL

MSL Code	Sponsor ID	Ag	Ba	Cd	Cr	Cu	%Fe	Hg	Mn	Ni	Pb	Sb	Zn
1646 SRM		0.11	11.26	387	0.40	66	21.4	3.38	0.066	345	30.8	27.5	0.74
NS		NC	11.6	NC	0.36	76	18	3.35	0.063	375	32	28.2	NC
NS		NC	11.3	NC	10.07	13	13	10.1	10.012	120	13	11.8	NC

MATRIX SPIKE RESULTS

Amount Spiked	361-26/27	361-26/27 + Spike	Amount Recovered	Percent Recovery
2	NS	NS	NS	NS
4.83	NS	NS	NS	NS
7.12	NS	NS	NS	NS
2.29	NS	NS	NS	NS
115%	NS	NS	NS	94%

REPLICATE ANALYSES

MSL Code	Sponsor ID	Ag	Ba	Cd	Cr	Cu	%Fe	Hg	Mn	Ni	Pb	Sb	Zn
361-26/27, Rep 1	I-US-ZP, Rep 1	4.78	21.6	282	7.71	1082	267	17.45	1.385	1920	119	764	5.38
361-26/27, Rep 2	I-US-ZP, Rep 2	4.90	34.6	281	8.17	1047	250	17.12	1.369	1910	113	707	5.54
361-26/27, Rep 3	I-US-ZP, Rep 3	4.81	26.6	287	7.35	1096	244	17.22	1.439	1890	112	766	5.41
RSDP%		1%	24%	1%	5%	2%	5%	1%	3%	3%	1%	4%	2%

U - Below detection limits.

NA - Not analyzed

NC - Not certified.

NS - Not spiked.

* - Mean of triplicated sample

x - Sample was inadvertently not spiked

NOTE: All metals results are blank corrected

SAIC-GLNPO (CF #361)

ZIMPRO

METALS IN TREATED SEDIMENT

(Concentrations in ug/g dry weight)

MSL Code	Sponsor ID	Ag		As		Ba		Cd		Cr		Cu		%Fe		Hg		Mn		Ni		Pb		Se		Zn	
		AA	AF	AF	AF	AF	AF	AA	AA	AA	AF	AF	AF	AF	AF	AF	CMA	AF									
MDL		0.007	2.5	43	0.006	33	5.5	0.26	0.0003	5.6	7.5	6.2	0.22	7.8													
361-29, Rep 1	I-TS-ZP, Rep 1	6.97	20.2	351	13.47	1471	299	21.6	2.286	2570	126	938	7.01	3720													
361-29, Rep 2	I-TS-ZP, Rep 2	6.72	35.0	367	12.69	1467	360	22.7	2.253	2700	150	1080	6.41	4260													
361-29, Rep 3	I-TS-ZP, Rep 3	7.04	32.2	387	12.80	1372	392	23.7	2.241	2760	138	1266	6.59	4890													
Method Blank		0.02	NA	NA	0.006 U	NA	NA	NA	0.00013	NA	NA	NA	0.22 U	NA													
1646 SRM	certified value	0.12	12.1	393	0.41	98	21.4	3.39	0.065	323	36.1	26.8	0.87	131.4													
		NC	11.6	NC	0.36	76	18	3.35	0.063	375	32	28.2	NC	138													
		NC	11.3	NC	±0.07	±3	±3	±0.1	±0.012	±20	±3	±1.8	NC	±6													

MATRIX SPIKE RESULTS

Amount Spiked	2	NS	NS	NS	2	NS	NS	NS	1.987	NS	NS	NS	2.73	NS													
361-29*	6.91	NS	NS	NS	13.0	NS	NS	NS	2.260	NS	NS	NS	6.67	NS													
361-29 + Spike	5.63	NS	NS	NS	15.3	NS	NS	NS	4.303	NS	NS	NS	9.47	NS													
Amount Recovered	-1.28	NS	NS	NS	2.3	NS	NS	NS	2.043	NS	NS	NS	2.8	NS													
Percent Recovery	NA x	NS	NS	NS	115%	NS	NS	NS	103%	NS	NS	NS	103%	NS													

REPLICATE ANALYSES

361-29, Rep 1	I-TS-ZP, Rep 1	6.97	20.2	351	13.47	1471	299	21.6	2.286	2570	126	938	7.01	3720														
361-29, Rep 2	I-TS-ZP, Rep 2	6.72	35.0	367	12.69	1467	360	22.7	2.253	2700	150	1080	6.41	4260														
361-29, Rep 3	I-TS-ZP, Rep 3	7.04	32.2	387	12.80	1372	392	23.7	2.241	2760	138	1266	6.59	4890														
	RSD%	2%	27%	5%	3%	4%	13%	5%	1%	4%	8%	15%	5%	14%														

U - Below detection limits.

NA - Not analyzed.

NC - Not certified.

NS - Not spiked.

* - Mean of triplicated sample.

x - Sample was inadvertently not spiked.

NOTE: All metals results are blank corrected.

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN UNTREATED SEDIMENT

Low Molecular Weight PAHs (ng/g dry weight)

MSL Code	Sponsor ID	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene
361-26/27, Rep 1	I-US-ZP, Rep 1	4479 D	3011 D	4404 D	4891 D	16498 D	6282 D
361-26/27, Rep 2	I-US-ZP, Rep 2	4289 D	2975 D	4214 D	4592 D	14979 D	6056 D
361-26/27, Rep 3	I-US-ZP, Rep 3	3749 D	3347 D	4525 D	5120 D	16191 D	6955 D
Method Blank-3		921 DU	987 DU	1389 DU	1163 DU	681 DU	773 DU

STANDARD REFERENCE MATERIAL

SRM-NIST1941	certified value	364 NC	54 U NC	60 U NC	63 U NC	550 577	164 U 202
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MATRIX SPIKE RESULTS

Amount Spiked		4237 D	4237 D				
361-26/27 #		4172 D	3111 D	4381 D	4868 D	15889 D	6431 D
361-26/27 + Spike		7980 D	8037 D	8814 D	9668 D	22250 D	12387 D
Amount Recovered		3808	4926	4433	4800	6361	5956
Percent Recovery		90%	116%	105%	113%	150%	141%

REPLICATE ANALYSES

361-26/27, Rep 1	I-US-ZP, Rep 1	4479 D	3011 D	4404 D	4891 D	16498 D	6282 D
361-26/27, Rep 2	I-US-ZP, Rep 2	4289 D	2975 D	4214 D	4592 D	14979 D	6056 D
361-26/27, Rep 3	I-US-ZP, Rep 3	3749 D	3347 D	4525 D	5120 D	16191 D	6955 D
	RSD%	9%	7%	4%	5%	5%	7%

D - Samples diluted 1:10 and re-run.

U - Below detection limits.

- Mean of triplicated samples.

NC - Not certified.

. - Value outside of internal QC limits (40-120%).

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN UNTREATED SEDIMENT

High Molecular Weight PAHs (ng/g dry weight)

MSL Code	Sponsor ID	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
361-26/27, Rep 1	I-US-ZP, Rep 1	32492 D	32303 D	20862 D	28841 D	24190 D	15552 D	26124 D	18664 D	6622 D	13355 D
361-26/27, Rep 2	I-US-ZP, Rep 2	31816 D	31993 D	21303 D	29430 D	25225 D	15889 D	28986 D	19499 D	7985 D	15571 D
361-26/27, Rep 3	I-US-ZP, Rep 3	35549 D	34572 D	22074 D	29878 D	25514 D	17357 D	27576 D	20438 D	6654 D	14165 D
Method Blank-3		446 DU	465 DU	439 DU	418 DU	335 DU	275 DU	357 DU	367 DU	360 DU	243 D

STANDARD REFERENCE MATERIAL

SRM-NIST1941	certified value	1114	1034	481	703	766	603	500	498	141	421
		1220	1080	550	NC	780	444	670	569	NC	516

MATRIX SPIKE RESULTS

Amount Spiked		4237 D									
361-26/27 #		33286 D	32956 D	21083 D	29136 D	24976 D	16266 D	27562 D	19534 D	10725 D	14364 D
361-26/27 + Spike		43798 D	41981 D	28133 D	36811 D	33607 D	22897 D	35567 D	27151 D	13977 D	18877 D
Amount Recovered		10512	9025	8051	7676	8631	6631	8005	7617	3252	4513
Percent Recovery		248%	213%	190%	181%	204%	157%	189%	180%	77%	107%

REPLICATE ANALYSES

361-26/27, Rep 1	I-US-ZP, Rep 1	32492 D	32303 D	20862 D	28841 D	24190 D	15552 D	26124 D	18664 D	6622 D	13355 D
361-26/27, Rep 2	I-US-ZP, Rep 2	31816 D	31993 D	21303 D	29430 D	25225 D	15889 D	28986 D	19499 D	7985 D	15571 D
361-26/27, Rep 3	I-US-ZP, Rep 3	35549 D	34572 D	22074 D	29878 D	25514 D	17357 D	27576 D	20438 D	6654 D	14165 D
	RSD%	6%	4%	3%	2%	3%	6%	5%	5%	11%	8%

D - Samples diluted 1:10 and re-run.

U - Below detection limits.

- Mean of triplicated samples.

NC - Not certified.

. - Value outside of Internal QC limits (40-120%).

SAIC GLNPO (CF #361)

ZIMPRO

PAH IN UNTREATED SEDIMENT

MSL Code	Sponsor ID	Surrogate Recovery %		
		D8 Naphthalene	D10 Acenaphthalene	D12 Perylene
361-26/27, Rep 1	I-US-ZP, Rep 1	31% D*	65% D	112% D
361-26/27, Rep 2	I-US-ZP, Rep 2	29% D*	61% D	108% D
361-26/27, Rep 3	I-US-ZP, Rep 3	21% D*	61% D	110% D
Method Blank-3		25% D*	24% D*	90% D

STANDARD REFERENCE MATERIAL

SRM-NIST1941

28%* 47% 74%

MATRIX SPIKE RESULTS

Amount Spiked	NA	NA	NA
361-26/27 #	27% D*	62% D	110% D
361-26/27 + Spike	37% D*	72% D	112% D
Amount Recovered	NA	NA	NA
Percent Recovery	NA	NA	NA

REPLICATE ANALYSES

361-26/27, Rep 1	I-US-ZP, Rep 1	31% D*	65% D	112% D
361-26/27, Rep 2	I-US-ZP, Rep 2	29% D*	61% D	108% D
361-26/27, Rep 3	I-US-ZP, Rep 3	21% D*	61% D	110% D
	RSD%	20%	4%	2%

D - Samples diluted 1:10 and re-run.
 # - Mean of triplicated samples.
 NC - Not certified.
 * - Value outside of Internal QC limits (40-120%).
 NA - Not applicable.

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN TREATED SEDIMENT

Low Molecular Weight PAHs (ng/g dry weight)

MSL Code	Sponsor ID	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene
361-29 R	I-TS-ZP	30	145 U	22 U	18 U	174	39
Method Blank R		11	11 U	16 U	13 U	9	9 U

STANDARD REFERENCE MATERIAL

SRM-NIST1941 certified value

MATRIX SPIKE RESULTS

Amount Spiked	3049	3049	3049	60 U	63 U	550	164 U
361-29 R	30	145 U	22 U	NC	NC	577	202
361-29 + Spike	1931	2139	2376	2376	2628	3074	2322
Amount Recovered	1902	2139	2376	2376	2628	2899	2282
Percent Recovery	62%	70%	78%	78%	86%	95%	75%
Amount Spiked	3623	3623	3623	3623	3623	3623	3623
361-29 R	30	145 U	22 U	18 U	174	39	39
361-29 + Spike DUP	1063	1418	1588	1588	2194	3260	2295
Amount Recovered	1034	1418	1588	1588	2194	3086	2256
Percent Recovery	29%*	39%*	44%	44%	61%	85%	62%

R - Re-extracted sample results.

U - Below detection limits.

NC - Not certified.

* - Value outside of internal QC limits (40-120%).

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN TREATED SEDIMENT

High Molecular Weight PAHs (ng/g dry weight)

MSL Code	Sponsor ID	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
361-29 R	I-TS-ZP	114	181	241	840	286	4 U	273	116	168	189
Method Blank R		9	9	5 U	5	6	5	5	5	4 U	6
STANDARD REFERENCE MATERIAL											
SRM-NIST1941	certified value	1114	1034	481	703	766	603	500	498	141	421
		1220	1080	550	NC	780	444	670	569	NC	516
MATRIX SPIKE RESULTS											
Amount Spiked		3049	3049	3049	3049	3049	3049	3049	3049	3049	3049
361-29 R		114	181	241	840	286	4 U	273	116	168	189
361-29 + Spike		3031	3060	3265	3283	2785	2351	2205	2755	3811	2846
Amount Recovered		2918	2879	3024	2443	2499	2351	1932	2640	3643	2658
Percent Recovery		96%	94%	99%	80%	82%	77%	63%	87%	119%	87%
Amount Spiked		3623	3623	3623	3623	3623	3623	3623	3623	3623	3623
361-29 R		114	181	241	840	286	4 U	273	116	168	189
361-29 + Spike DUP		3436	3459	3541	3499	3220	2853	3092	2931	3944	2942
Amount Recovered		3322	3278	3300	2659	2934	2853	2820	2816	3776	2753
Percent Recovery		92%	90%	91%	73%	81%	79%	78%	78%	104%	76%

R = Re-extracted sample results.

U = Below detection limits.

NC = Not certified.

* = Value outside of internal QC limits (40-120%).

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN TREATED SEDIMENT

MSL Code	Sponsor ID	Surrogate Recovery %		
		D8 Naphthalene	D10 Acenaphthalene	D12 Perylene

361-29 R	I-TS-ZP	23% *	34% *	76%
Method Blank R		51%	62%	72%

STANDARD REFERENCE MATERIAL

SRM: NIST1941		28% *	47%	74%
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MATRIX SPIKE RESULTS

Amount Spiked		NA	NA	NA
361-29 R		23% *	34% *	76%
361-29 + Spike		30% *	66%	64%
Amount Recovered		NA	NA	NA
Percent Recovery		NA	NA	NA
Amount Spiked		NA	NA	NA
361-29 R		23% *	34% *	76%
361-29 + Spike DUP		25% *	41%	73%
Amount Recovered		NA	NA	NA
Percent Recovery		NA	NA	NA

R - Re-extracted sample results.

* - Values outside of Internal QC limits (40-120%).

NA - Not applicable.

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN WATER

Low Molecular Weight PAHs (ng/L)

MSL Code	Sponsor ID	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene
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361-30	I-WR-ZP	956	152 U	218 U	192 U	1037	142 U
Method Blank-7		266 U	275 U	395 U	348 U	230 U	258 U

MATRIX SPIKE RESULTS

Amount Spiked		25000	25000	25000	25000	25000	25000
361-30		956	152 U	218 U	192 U	1037	142 U
361-30+ Spike		5987	8313	7027	12931	20485	14663
Amount Recovered		5031	8313	7027	12931	19448	14663
Percent Recovery		20% .	33% .	28% .	52%	78%	59%
Amount Spiked		25000	25000	25000	25000	25000	25000
Blank-7		266 U	275 U	395 U	348 U	230 U	258 U
Blank-7 + Spike		8947	10024	10259	11685	15262	16941
Amount Recovered		8947	10024	10259	11685	15032	16941
Percent Recovery		36% .	40%	41%	47%	60%	68%

U - Below detection limits.

. - Value outside of internal QC limits (40-120%).

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN WATER

High Molecular Weight PAHs (ng/L)

MSL Code	Sponsor ID	Fluoran- thene	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
361-30	I-WR-ZP	162	137	98 U	95 U	70 U	61 U	79 U	72 U	92 U	70 U
Method Blank-7		175 U	181 U	177 U	171 U	127 U	111 U	143 U	131 U	166 U	142

MATRIX SPIKE RESULTS

Amount Spiked	25000	25000	25000	25000	25000	25000	25000	25000	25000	25000	25000
361-30	162	137	98 U	95 U	70 U	61 U	79 U	72 U	92 U	70 U	70 U
361-30+ Spike	23080	22094	23216	22754	22338	20690	20532	26638	20532	26638	18953
Amount Recovered	22918	21957	23216	22754	22338	20680	15479	15479	20532	26638	18953
Percent Recovery	92%	88%	93%	91%	89%	83%	62%	62%	82%	107%	76%
Amount Spiked	25000	25000	25000	25000	25000	25000	25000	25000	25000	25000	25000
Blank-7	175 U	181 U	177 U	171 U	127 U	111 U	143 U	131 U	166 U	142	142
Blank-7 + Spike	22732	22303	27433	24443	24350	22597	23230	23647	23647	30175	22117
Amount Recovered	22732	22303	27433	24443	24350	22597	23230	23647	23647	30175	21875
Percent Recovery	91%	89%	110%	98%	97%	90%	93%	93%	95%	121%*	88%

U - Below detection limits.

* - Value outside of Internal QC limits (40-120%).

SAIC-GLNPO (CF #361)

ZIMPRO

PAH IN WATER

MSL Code	Sponsor ID	Surrogate Recovery %		
		D8 Naphthalene	D10 Acenaphthalene	D12 Perylene

361-30	I-WR-ZP	35%*	47%	58%
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Method Blank:7		16%*	18%*	80%
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MATRIX SPIKE RESULTS

Amount Spiked	NA	NA	NA	NA
361-30	35%*	47%	58%	58%
361-30+ Spike	20%*	27%*	60%	60%
Amount Recovered	NA	NA	NA	NA
Percent Recovery	NA	NA	NA	NA
Amount Spiked	NA	NA	NA	NA
Blank:7	16%*	18%*	80%	80%
Blank:7 + Spike	22%*	27%*	80%	80%
Amount Recovered	NA	NA	NA	NA
Percent Recovery	NA	NA	NA	NA

* - Value outside of Internal QC limits (40-120%)
 NA - Not applicable

RE-PROCESSED RESULTS (1/92)
PCBs IN UNTREATED SEDIMENT

ZIMPRO
 SAIC-GLNPO (CF #361)

2/12/92

Concentrations in ug/kg dry weight

MSL Code	Sponsor ID	Aroclor			% Surrogate Recovery	
		1242	1248	1254	1260	Tetrachloro- m-Xylene

361-26/27, Rep 1 D	I-US-ZP, Rep 1	2000 U	9470 D	1000 U	1000 U	84.0%	91.6%
361-26/27, Rep 2 D	I-US-ZP, Rep 2	2000 U	9680 D	1000 U	1000 U	81.4%	73.0%
361-26/27, Rep 3 D	I-US-ZP, Rep 3	2000 U	11300 D	3186 D	1000 U	80.9%	89.4%
Blank-0		200 U	200 U	100 U	100 U	53.9%	02.1%

STANDARD REFERENCE MATERIAL

SRM-5 (HS-2)	certified value	100 U	100 U	69	50 U	67.6%	96.2%
		NC	NC	111	NC	NC	NC

MATRIX SPIKE RESULTS

Amount Spiked		NS	NS	4237	NS	NA	NA
361-26/27 #		NS	NS	3108 D	NS	02.1%	04.7%
361-28/27 + Spike		NS	NS	6819	NS	87.3%	91.5%
Amount Recovered		NS	NS	3633	NS	NA	NA
Percent Recovery		NS	NS	86%	NS	NA	NA

REPLICATE ANALYSES

361-26/27, Rep 1 D	I-US-ZP, Rep 1	2000 U	9470 D	1000 U	1000 U	84.0%	91.6%
361-26/27, Rep 2 D	I-US-ZP, Rep 2	2000 U	9680 D	1000 U	1000 U	81.4%	73.0%
361-26/27, Rep 3 D	I-US-ZP, Rep 3	2000 U	11300 D	3186 D	1000 U	80.0%	89.4%
		0%	10%	73%	0%	2%	12%

D = Samples diluted 1:10 and re-run.
 U = Below detection limits.
 * = Value outside of Internal QC limits (40-120%).
 NC = Not certified.
 # = Mean of replicated sample.
 NS = Not spiked. NA = Not applicable.

RE-PROCESSED RESULTS (1/92)

PCBs IN TREATED SEDIMENT

Concentrations in ug/kg dry weight

ZIMPRO
SAIC-GLNPO (CF #361)

2/12/92

MSL Code	Sponsor ID	Aroclor			% Surrogate Recovery		
		1242	1248	1254	Aroclor 1280	Tetrachloro- m-Xylene	Octachloro- naphthalene
361-29	I-TS-ZP	200 U	4908	3555	100 U	67.1%	73.1%
BLANK-6		200 U	200 U	100 U	100 U	53.9%	82.1%
STANDARD REFERENCE MATERIAL							
SRM-5 (HS-2)	certified value	100 U	100 U	60	50 U	67.6%	60.2%
		NC	NC	111	NC	NC	NC
MATRIX SPIKE RESULTS							
Amount Spiked		NS	NS	3876	NS	NA	NA
361-29		NS	NS	3555	NS	67.1%	73.1%
361-29 + Spike		NS	NS	7630	NS	61.6%	93.0%
Amount Recovered		NS	NS	4075	NS	NA	NA
Percent Recovery		NS	NS	105%	NS	NA	NA
Amount Spiked		NS	NS	3049	NS	NA	NA
361-29 DUP		NS	NS	3555	NS	67.1%	73.1%
361-29 + Spike DUP		NS	NS	4052	NS	83.0%	57.7%
Amount Recovered		NS	NS	1297	NS	NA	NA
Percent Recovery		NS	NS	43%	NS	NA	NA

U = Below detection limits.

* = Value outside of Internal QC limits (40-120%).

NC = Not certified.

NS = Not spiked. NA = Not applicable.

RE-PROCESSED RESULTS (1/92)

PCBs IN WATER SAMPLES

Concentrations in ug/L

ZIMPRO
SAIC-GLNPO (CF #361)

2/12/92

MSL Code	Sponsor ID	Aroclor				% Surrogate Recovery	
		1242	1248	1254	1260	Tetrachloro- m-Xylene	Octachloro- naphthalene
381-30	I-WR-ZP	0.2 U	0.2 U	0.1 U	0.1 U	85.8%	90.0%
Blank-7		0.2 U	0.2 U	0.1 U	0.1 U	20.2% *	90.0%

MATRIX SPIKE RESULTS

Amount Spiked								
381-30	NS	NS	NS	25	NS	NA	NA	NA
381-30 + Spike	NS	NS	0.1 U	0.1 U	NS	85.8%	90.0%	90.0%
Amount Recovered	NS	NS	21	21	NS	67.4%	77.8%	77.8%
Percent Recovery	NS	NS	21	84%	NS	NA	NA	NA

U = Below detection limits.

* = Value outside of Internal QC limits (40-120%).

NC = Not certified.

NS = Not spiked. NA = Not applicable.

Appendix E

QUALITY ASSURANCE/QUALITY CONTROL

In order to obtain data of known quality to be used in evaluating the different technologies for the different sediments, a Quality Assurance Project Plan (QAPP) was prepared. The QAPP specified the guidelines to be used to ensure that each measurement system was in control. In order to show the effectiveness of the different technologies, the following measurements were identified in the QAPP as critical - PAHs, PCBs, metals, total solids, oil and grease and volatile solids in the untreated and treated sediments. Other parameters analyzed in the sediments included pH, TOC, total cyanide, and total phosphorus. If water and oil residuals were generated by a technology, then polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined as a check on their fate resulting from in treating the sediments. Each of these measurements and the associated quality control (QC) data will be discussed in this section. It should be noted that the ZIMPRO technology developers do not claim that the process will remove PCBs. Therefore PCB analysis is not critical in demonstrating the effectiveness of this technology.

Also included in this section are a discussion of the QC results, modifications and deviations from the QAPP, and the results of a laboratory audit performed. Any possible effects of deviations or audit findings on data quality are presented.

Attached to this appendix is an abridged version of the Data Verification report completed by the ARCS Program QA Officer. Copies of the entire Data Verification report are available from GLNPO.

PROCEDURES USED FOR ASSESSING DATA QUALITY

The indicators used to assess the quality of the data generated for this project are accuracy, precision, completeness, representativeness, and comparability. All indicators will be discussed generally in this section; specific results for accuracy and precision are summarized in later sections.

Accuracy

Accuracy is the degree of agreement of a measured value with the true or expected value. Accuracy for this project will be expressed as a percent recovery (%R).

Accuracy was determined during this project using matrix spikes (MS) and/or standard reference materials (SRMs). Matrix spikes are aliquots of sample spiked with a known concentration of

target analyte(s) used to document the accuracy of a method in a given sample matrix. For matrix spikes, recovery is calculated as follows:

$$\%R = \frac{C_i - C_o}{C_t} \times 100$$

where: C_i = measured concentration in spiked sample aliquot
 C_o = measured concentration in unspiked sample aliquot
 C_t = actual concentration of spike added

An SRM is a known matrix spiked with representative target analytes used to document laboratory performance. For SRMs, recovery is calculated as follows:

$$\%R = \frac{C_m}{C_t} \times 100$$

where: C_m = measured concentration of SRM
 C_t = actual concentration of SRM

In addition, for the organic analyses, surrogates were added to all samples and blanks to monitor extraction efficiencies. Surrogates are compounds which are similar to target analytes in chemical composition and behavior. Surrogate recoveries will be calculated as shown above for SRMs.

Precision

Precision is the agreement among a set of replicate measurements without assumption of knowledge of the true value. When the number of replicates is two, precision is determined using the relative percent difference (RPD):

$$RPD = \frac{(C_1 - C_2) \times 100}{(C_1 + C_2) / 2}$$

where: C_1 = the larger of two observed values
 C_2 = the smaller of two observed values

When the number of replicates is three or greater, precision is determined using the relative standard deviation (RSD):

$$RSD = \frac{S}{X} \times 100$$

where: S = standard deviation of replicates

X = mean of replicates

Precision was determined during this project using triplicate analyses for those samples suspected to be high in target analytes (i.e., untreated sediments). Matrix spike and matrix spike duplicate (MSD) analyses were performed on those samples suspected to be low in target analytes (i.e., treated sediments). A MSD is a second spiked sample aliquot with a known concentration of target analyte used to document accuracy and precision in a given sample matrix.

Completeness

Completeness is a measure of the amount of valid data produced compared to the total amount of data planned for the project. For the ZIMPRO treatability studies, no samples were lost due to field or analytical problems. Though all guidelines for QA objectives were not met, all data generated was deemed useable.

Representativeness

Representativeness refers to the degree with which analytical results accurately and precisely represent actual conditions present at locations chosen for sample collection. Sediment samples were collected prior to this demonstration and were reported to be representative of the areas to be remediated. Samples of untreated and treated sediment and residuals were taken by SAIC personnel during Phase II of these tests. Samples were shipped under chain-of-custody to Battelle Marine Sciences Laboratory in Sequim, Washington. Therefore, the data is representative of material actually treated.

Comparability

Comparability expresses the extent with which one data set can be compared to another. As will be discussed in more detail in the section *Modifications and Deviations From the QAPP*, the data generated are comparable within this project and within other projects conducted for the ARCS

Program. However, because specialized procedures were used in some instances, the data may not be directly comparable to projects outside the ARCS Program.

ANALYTICAL QUALITY CONTROL

The following sections summarize and discuss analytical procedures and the results of the QC indicators of accuracy and precision for each measurement parameter for the ZIMPRO technology evaluation.

PAHs

PAH Procedures

Sediments and waters were extracted and analyzed using modified SW-846 procedures as described in the section *Modifications and Deviations From the QAPP*. Three isotopically-labelled PAH surrogates were added to all samples and blanks prior to extraction. Daily mass tuning was performed using decafluorotriphenylphosphine (DFTPP) to meet the criteria specified in Method 8270. The instrument was calibrated at five levels for the sixteen PAHs. The RSD of the response factors for each PAH was required to be <25 percent. Calibrations were verified every 12 hours for each PAH; criteria for % difference from the initial calibration was <25 percent for each PAH. An internal standard, hexamethyl benzene, was added prior to cleanup and was used to correct PAH concentrations for loss during cleanup and extract matrix effects. Quantification was performed using Selective Ion Monitoring (SIM).

PAH QC Results and Discussion

Surrogate recoveries for all PAH samples for the ZIMPRO demonstration are summarized in Table QA-1. If more than one of the three surrogates fell outside the control limits used, corrective action (reanalysis) was necessary. (This criteria was not applied by Battelle to method blanks.) Surrogate recoveries were generally low for samples and method blanks, indicating a possible analytical problem rather than matrix effects. An investigation indicated possible problems with the evaporator used to concentrate the extracts. In summary, low surrogate recoveries indicate that PAH target concentrations may be biased somewhat low. Since both the untreated and treated sediments were affected similarly, relative removal percentages should be valid.

It should also be noted that surrogate recoveries for both the initial analysis and the re-extracted analysis for the treated solid (I-TS-ZP) did not meet acceptance criteria.

As required by the QAPP, triplicate analyses of the Indiana Harbor untreated sediment (I-US-ZP) were performed to assess precision. These results are summarized in Table QA-2. A matrix spike

TABLE QA-1. PAH SURROGATE RECOVERIES

Sample	d8-Naphthalene (%)	d10-Acenaphthalene (%)	d12-Perylene (%)	Control Limits (%)
I-US-ZP	31*	65	112	40-120
I-US-ZP	29*	61	108	40-120
I-US-ZP	21*	61	110	40-120
Method Blank	25*	24*	90	40-120
I-TS-ZP (Re-extract)	23*	34*	76	40-120
Method Blank	51	62	72	40-120
I-WR-ZP	35*	47	58	40-120
Method Blank	16*	18*	80	40-120

* Outside Control Limits

was performed on this same sample to assess accuracy. These results are included in Table QA-2. All RSDs fell within the control limits specified. Several matrix spike recoveries fell outside control limits due to inappropriate spiking levels. For several compounds, the spiking level was between 10 and 30 percent of the sample concentration. Recoveries for these compounds may not be indicative of actual matrix interferences.

As required by the QAPP, a matrix spike and a matrix spike duplicate (MS/MD) analysis was performed for the treated Indiana Harbor sediment (I-TS-ZP). These results are presented in Table QA-3. Recoveries were generally acceptable. RPDs for the lighter compounds were outside the guidelines specified in the QAPP. As minimal or none of these compounds were present in the sample, project results should not be affected.

A matrix spike analysis was performed on the Indiana Harbor water residual (I-WR-ZP). These results are summarized in Tables QA-4.

One certified National Institute of Science and Technology (NIST) standard reference material (SRM) was extracted and analyzed with the sediment samples. The recoveries for this standard are summarized in Table QA-5.

Method blanks were extracted and analyzed with each set of samples extracted. Minimal quantities of several PAHs were found in all three PAH method blanks; total concentrations are

TABLE QA-2. PAH REPLICATE AND SPIKE RESULTS FOR I-US-ZP

Compound	Replicate 1 dry ppb	Replicate 2 dry ppb	Replicate 3 dry ppb	Mean	RSD (%)	Precision Control Limits (%)	Recovery (%)	Accuracy Control Limits (%)
Naphthalene	4480	4290	3750	4170	9	20	90	40-120
Acenaphthylene	3010	2980	3350	3110	7	20	116	40-120
Acenaphthene	4400	4210	4520	4380	4	20	105	40-120
Fluorene	4890	4590	5120	4870	5	20	113	40-120
Phenanthrene	16500	15000	16200	15900	5	20	150*(1)	40-120
Anthracene	6280	6060	6960	6430	7	20	141*	40-120
Fluoranthene	32500	31800	35500	33300	6	20	248*(1)	40-120
Pyrene	32300	32000	34600	33000	4	20	213*(1)	40-120
Benzo(a)anthracene	20900	21300	22100	21100	3	20	190*(1)	40-120
Chrysene	28800	29400	29900	29100	2	20	181*(1)	40-120
Benzo(b)fluoranthene	24200	25200	25500	25000	3	20	204*(1)	40-120
Benzo(k)fluoranthene	15600	15900	17400	16300	6	20	157*(1)	40-120
Benzo(a)pyrene	26100	29000	27600	27600	5	20	189*(1)	40-120
Indeno(1,2,3,c,d)pyrene	18700	19500	20400	19500	5	20	180*(1)	40-120
Dibenzo(a,h)anthracene	6620	7980	6650	7090	11	20	163*	40-120
Benzo(g,h,i)perylene	13400	15600	14200	14400	8	20	107	40-120

* Outside Control Limits

(1) Spiking level ranged from 10 to 30 percent of sample concentration.

TABLE QA-3. PAH MS/MSD RESULTS FOR I-TS-ZP

Compound	MS Recovery (%)	MSD Recovery (%)	RPD	Accuracy Control Limits (%)	Precision Control Limits (%)
Naphthalene	62	29*	73*	40-120	20
Acenaphthylene	70	39*	57*	40-120	20
Acenaphthene	78	44	56*	40-120	20
Fluorene	86	61	34*	40-120	20
Phenanthrene	95	85	11	40-120	20
Anthracene	75	62	19	40-120	20
Fluoranthene	96	92	4	40-120	20
Pyrene	94	90	4	40-120	20
Benzo(a)anthracene	99	91	8	40-120	20
Chrysene	80	73	9	40-120	20
Benzo(b)fluoranthene	82	81	1	40-120	20
Benzo(k)fluoranthene	77	79	3	40-120	20
Benzo(a)pyrene	63	78	21*	40-120	20
Indeno(1,2,3,c,d)pyrene	87	78	11	40-120	20
Dibenzo(a,h)anthracene	119	104	13	40-120	20
Benzo(g,h,i)perylene	87	76	13	40-120	20

* Outside Control Limits

TABLE QA-4. PAH MS RESULTS FOR I-WR-ZP

Compound	MS Recovery(%)	Control Limits (%)
Naphthalene	20	Not Specified
Acenaphthylene	33	Not Specified
Acenaphthene	28	Not Specified
Fluorene	52	Not Specified
Phenanthrene	78	Not Specified
Anthracene	59	Not Specified
Fluoranthene	92	Not Specified
Pyrene	88	Not Specified
Benzo(a)anthracene	93	Not Specified
Chrysene	91	Not Specified
Benzo(b)fluoranthene	89	Not Specified
Benzo(k)fluoranthene	83	Not Specified
Benzo(a)pyrene	62	Not Specified
Indeno(1,2,3,c,d)pyrene	82	Not Specified
Dibenzo(a,h)anthracene	107	Not Specified
Benzo(g,h,i)perylene	76	Not Specified

TABLE QA-5. PAH SRM RESULTS

Compound	Recovery (%)	Control Limits (%)
Naphthalene	NC	80-120
Acenaphthylene	NC	80-120
Acenaphthene	NC	80-120
Fluorene	NC	80-120
Phenanthrene	95	80-120
Anthracene	NR	80-120
Fluoranthene	91	80-120
Pyrene	96	80-120
Benzo(a)anthracene	87	80-120
Chrysene	NC	80-120
Benzo(b)fluoranthene	98	80-120
Benzo(k)fluoranthene	136*	80-120
Benzo(a)pyrene	75*	80-120
Indeno(1,2,3,c,d)pyrene	88	80-120
Dibenzo(a,h)anthracene	NC	80-120
Benzo(g,h,i)perylene	82	80-120

NC = Not Certified

* = Outside Control Limits

NR = Not Recovered- certified value near detection limit.

unaffected. No corrections were performed for method blanks as no consistent significant contamination problems were observed.

PCBs

PCB Procedures

Sediments and waters were extracted and analyzed using modified SW-846 procedures as described in the section *Modifications and Deviations From The QAPP*. Two surrogates, tetrachloro-m-xylene and octachloronaphthalene, were added to all samples and blanks prior to extraction. The gas chromatograph (GC) employed electron capture detection (ECD) and was calibrated at three levels for each of four Aroclors (1242, 1248, 1254, 1260). The RSD of the response factors for each Aroclor was required to be <25 percent. Calibrations were verified after every ten samples; criteria for percent

difference from the initial calibration was <25 percent. An internal standard, dibromooctafluorobiphenyl, was added prior to cleanup and was used to correct PCB concentrations for loss during cleanup and extract matrix effects.

Quantification of Aroclors was performed on two columns (DB-5, primary and 608, confirmation) as a confirmation of their presence.

PCB QC Results and Discussion

Surrogate recoveries for all PCB samples for the ZIMPRO demonstration are summarized in Table QA-6. If both recoveries fell outside the control limits used, correction action (reanalysis) was necessary. All samples were acceptable with respect to the surrogate criteria used.

TABLE QA-6. PCB SURROGATE RECOVERIES

Sample	Tetrachloro-m-xylene (%)	Octachloronaphthalene (%)	Control Limits (%)
I-US-ZP Rep.1	84	92	40-120
I-US-ZP Rep.2	81	73	40-120
I-US-ZP Rep.3	81	89	40-120
Method Blank	54	82	40-120
I-TS-ZP	67	73	40-120
Method Blank	54	82	40-120
I-WR-ZP	86	90	40-120
Method Blank	20	90	40-120

* = Outside Control Limits

NC = Not Certified

NR = Not recovered - certified value near detection limit.

As required by the QAPP, triplicate analyses of the Indiana Harbor untreated sediment (I-US-ZP) were performed to assess precision. These results are summarized in Table QA-7. A matrix spike using Aroclor 1254 was performed on the same sample to assess accuracy; these results are included in Table QA-7. The RSD and recovery for individual Aroclors are both within control limits. The RSD for total PCBs is 25 percent.

TABLE QA-7. PCB REPLICATE AND SPIKE RESULTS FOR I-US-ZP

Aroclor	Replicate 1 ppb dry	Replicate 2 ppb dry	Replicate 3 ppb dry	Mean	RSD (%)	Precision Guideline Limits (%)	Recovery (%)	Accuracy Control Limits (%)
1242	2000 U	2000 U	2000 U	2000 U	NC	20	NS	40-120
1248	9470	9680	11300	10200	10	20	NS	40-120
1254	1000 U	1000 U	3190	NC	NC	20	86	40-120
1260	1000 U	1000 U	1000 U	1000 U	NC	20	NS	40-120

U = Undetected

* = Outside Control Limits

NC = Not Calculated

NS = Not Spiked

TABLE QA-8. PCB MS/MSD RESULTS FOR I-TS-ZP

PCB	MS Recovery (%)	MSD Recovery (%)	RPD	Accuracy Control Limits (%)	Precision Guideline Limits (%)
Aroclor 1254	105	43	84*	40-120	20

U = Undetected

* = Outside Control Limits

NC = Not Calculated

NS = Not Spiked

As required by the QAPP, a matrix spike and a matrix spike duplicate (MS/MSD) analysis was performed for the treated Indiana Harbor sediment combustor solids (I-TS-ZP). These results are presented in Table QA-8. Matrix spike recoveries were within guidelines but the RPD was not. No explanation was determined. As PCBs were not critical to meeting project objectives, no reanalyses were performed.

A matrix spike analysis was performed on the Indiana Harbor water residual (I-WR-ZP). These results are summarized in Table QA-9.

One standard reference material (SRM) certified by the National Research Council of Canada (NRCC) for Aroclor 1254 was extracted and analyzed with the sediment samples. A recovery of 62% was obtained.

Method blanks were extracted and analyzed with each set of samples extracted. No PCBs were found in any method blanks.

TABLE QA-9. PCB MS RESULT FOR I-WR-ZP

PCB	MS Recovery (%)	Control Limits (%)
Aroclor 1254	84	Not Specified

METALS

Metals Procedure

Sediments were prepared for metals analysis by freeze-drying, blending, and grinding.

Sediments for Ag, Cd, Hg, and Se were digested using nitric and hydrofluoric acids. The digestates were analyzed for Ag, Cd, and Se by graphite furnace atomic absorption (GFAA) by SW-846 Method 7000 series using Zeeman background correction. The digestates were analyzed for mercury by cold vapor AA (CVAA) using SW-846 Method 7470.

Sediments for As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were analyzed by energy-diffusive X-Ray fluorescence (XRF) following the method of Sanders (1987). The XRF analysis was performed on a 0.5 g aliquot of dried, ground sediment pressed into a pellet with a diameter of 2 cm.

Metals QC Results and Discussion

Triplicate analyses of the Indiana Harbor untreated sediment (I-US-ZP) and treated sediment (I-TS-ZP) were performed to assess precision. Matrix spikes were analyzed for the same samples to assess accuracy. Results are summarized in Tables QA-10 and QA-11. It should be noted that the sediments were not spiked for XRF analysis as spiking is not appropriate for that analysis.

Accuracy and precision results for metals were acceptable with only a few minor exceptions, as shown in Tables QA-10 and QA-11. RSD results outside limits are due to concentrations near the analytical detection limits. These exceptions have little, if any, impact on data quality and project results.

One NIST certified standard reference material (SRM) was digested and analyzed twice with the sediment samples for XRF, GFAA, and CVAA analyses. These results are presented in Table QA-12.

Method blanks were digested and analyzed for the metals analyzed by GFAA and CVAA. (Method blanks are not applicable to XRF analysis). If analyte was detected in the method blank, blank correction was performed. Minimal amounts of some metals were detected; data quality is not affected.

OIL AND GREASE

Oil and Grease Procedures

Sediment samples were extracted with freon using Soxhlet extraction according to SW-846 Method 9071. The extract was analyzed for oil and grease by infra-red (IR) as outlined in Method 418.1 (Methods for Chemical Analysis of Water and Wastes, 1983).

Oil and Grease QC Results and Discussion

Both the untreated and treated Indiana Harbor sediment (I-US-ZP and I-TS-ZP) were analyzed for oil and grease in triplicate. In addition, a matrix spike was performed for I-US-ZP. Results are presented in Table QA-13. As indicated, I-US-ZP was probably not spiked due to laboratory error. The RSD for I-TS-ZP was outside control limits; removal efficiencies may be affected minimally.

TABLE QA-10. METALS REPLICATE AND SPIKE RESULTS FOR I-US-ZP

Metal	Method	Replicate 1, ppm dry	Replicate 2, ppm dry	Replicate 3, ppm dry	Mean	RSD (%)	Precision Control Limits (%)	Recovery (%)	Accuracy Control Limits (%)
Ag	GFAA	4.78	4.90	4.81	4.83	1	20	115	85-115
As	XRF	21.6	34.6	26.6	30.9	24*	20	NS	
Ba	XRF	282	281	287	283	1	20	NS	
Cd	GFAA	7.71	8.17	7.35	7.74	5	20	107	85-115
Cr	XRF	1080	1050	1100	1080	2	20	NS	
Cu	XRF	267	250	244	254	5	20	NS	
Fe(1)	XRF	17.4	17.1	17.2	17.3	1	20	NS	
Hg	CVAA	1.38	1.37	1.44	1.40	3	20	103	85-115
Mn	XRF	1920	1910	1890	1910	1	20	NS	
Ni	XRF	119	113	112	115	3	20	NS	
Pb	XRF	764	707	766	746	4	20	NS	
Se	GFAA	5.38	5.54	5.41	5.44	2	20	111	85-115
Zn	XRF	3090	2930	3070	3030	3	20	NS	

NS = Not Spiked

* Outside Control Limits

(1) = Results in Percent for Fe

TABLE QA-11. METALS REPLICATE AND SPIKE RESULTS FOR I-TS-ZP

Metal	Method	Replicate 1, ppm dry	Replicate 2, ppm dry	Replicate 3, ppm dry	Mean	RSD (%)	Precision Control Limits (%)	Recovery (%)	Accuracy Control Limits (%)
Ag	GFAA	6.97	6.72	7.04	6.91	2	20	NS	85-115
As	XRF	20.2	35.0	32.2	29.1	27*	20	NS	
Ba	XRF	351	367	387	368	5	20	NS	
Cd	GFAA	13.5	12.7	12.8	13.0	3	20	115	85-115
Cr	XRF	1470	1470	1370	1440	4	20	NS	
Cu	XRF	299	360	392	350	13	20	NS	
Fe(1)	XRF	21.6	22.7	23.7	22.7	5	20	NS	
Hg	CVAA	2.29	2.25	2.24	2.26	1	20	103	85-115
Mn	XRF	2570	2700	2760	2680	4	20	NS	
Ni	XRF	126	150	138	138	9	20	NS	
Pb	XRF	938	1080	1270	1100	15	20	NS	
Se	GFAA	7.01	6.41	6.59	6.67	5	20	103	85-115
Zn	XRF	3720	4260	4890	4290	14	20	NS	

NS = Not Spiked

* Outside Control Limits

(1) Result in Percent for Fe

TABLE QA-12. METALS SRM RECOVERIES

Metal	SRM-1 (%)	SRM-2 (%)	Control Limits (%)
Ag	NC	NC	80-120
As	97.1	104	80-120
Ba	NC	NC	80-120
Cd	111	114	80-120
Cr	86.8	128*	80-120
Cu	119	119	80-120
Fe	101	101	80-120
Hg	105	103	80-120
Mn	92.0	86.1	80-120
Ni	96.2	113	80-120
Pb	97.5	95.0	80-120
Se	NC	NC	80-120
Zn	88.7	95.0	80-120

* = Outside control limits
 NC = Not Certified

TABLE QA-13. OIL AND GREASE REPLICATES AND SPIKE RESULTS FOR I-US-ZP AND I-TS-ZP

Sample	Replicate 1, ppm dry	Replicate 2, ppm dry	Replicate 3, ppm dry	Mean	RSD (%)	Precision Control Limits (%)	Recovery (%)	Accuracy Control Limits (%)
I-US-ZP	9810	10000	9850	9890	1	20	12*(1)	80-120
I-TS-ZP	1060	1090	702	951	23*	20	NS	80-120

NS = Not Spiked

* = Outside Control Limits

(1) = Laboratory results indicated that the sample probably was not spiked

TOTAL VOLATILE SOLIDS

Total Volatile Solid Procedures

Sediments were analyzed for total volatile solids (TVS) following the procedures in Method 160.4 (Methods for Chemical Analysis of Water and Waste, 1983) modified for sediments. An aliquot of sediment was dried and then ignited at 550°C. The loss of weight on ignition was then determined.

Total Volatile Solid QC Results and Discussion

Both the Indiana Harbor untreated and treated sediment (I-US-ZP and I-TS-ZP) were analyzed for TVS in triplicate. Results are summarized in Table QA-14. Both RSDs fell within specified control limits.

TABLE QA-14. TVS REPLICATES FOR I-US-ZP AND I-TS-ZP

Sample	Replicate 1, % dry	Replicate 2, % dry	Replicate 3, % dry	Mean	RSD (%)	Control Limits (%)
I-US-ZP	14.7	15.3	15.1	15.0	2	20
I-TS-ZP	7.78	7.19	7.05	7.34	5	20

OTHER ANALYSES

pH

Sediment samples were analyzed for pH using SW-846 Method 9045. Sediment and water were combined in a 1:1 ratio and mixed prior to pH determination.

Total Organic Carbon (TOC)

Sediment samples were analyzed for TOC using SW-846 Method 9060. One SRM was analyzed with the sediments, yielding a recovery of 92.2 percent.

Total Cyanide

Sediment samples were analyzed for cyanide by SW-846 Method 9010. Approximately 5 g of sediment was distilled; the distillate was analyzed spectrophotometrically. A matrix spike was analyzed for I-US-ZP; a recovery of 98 percent was obtained.

Total Phosphorus

Sediment samples were analyzed for phosphorus by EPA Method 365.2. Approximately 1 g of sediment was digested; the digestate was analyzed spectrophotometrically. A matrix spike was analyzed for I-TS-ZP; a recovery of 102 percent was obtained.

Total Phosphorus

Sediment samples were analyzed for Phosphorus by EPA Method 365.2. Approximately 1 g of sediment was digested; the digestate was analyzed spectrophotometrically. A matrix spike was analyzed for I-TS-ZP; a recovery of 102 percent was obtained.

AUDIT FINDINGS

An audit of the Battelle-Marine Sciences Laboratory was conducted on September 25 and 26, 1991. Participants included EPA, GLNPO, and SAIC personnel. The path of a sample from receipt to reporting was observed specifically for samples from these bench-scale treatability tests. Two concerns

were identified in the organic laboratory: 1) the preparation, storage, record-keeping, and replacement of standards is not well-documented; and 2) the nonstandard procedures used to extract, clean up and analyze samples needs to be documented with reported data.

During the audit, the use of nonstandard procedures was discussed. It was concluded that data comparability within this project and within the ARCS program should not be an issue, as the Battelle laboratory has performed all analyses to date. However, comparability to data generated outside the ARCS program is not possible.

MODIFICATIONS AND DEVIATIONS FROM THE QAPP

Laboratory activities deviated from the approved QAPP in two areas--analytical procedures and quality assurance (QA) objectives. Specific deviations and their effect on data quality are discussed in this section.

ANALYTICAL PROCEDURES

The Assessment and Remediation of Contaminated Sediments (ARCS) Program was initiated by the Great Lakes National Program Office (GLNPO) to conduct bench-scale and pilot-scale demonstrations for contaminated sediments. To date, all laboratory analyses performed in support of the ARCS Program have been done at the Battelle-Marine Sciences Laboratory (MSL) in Sequim, Washington. Standard procedures used by Battelle-MSL often do not follow those procedures identified in SW-846 and the QAPP. While these nonstandard procedures yield results of acceptable quality, comparability with analyses performed outside the ARCS Program is not possible.

PAH Analysis

- Samples were co-extracted with PCB samples using a modified SW-846 extraction procedure which entailed rolling of the sample in methylene chloride and an additional clean-up step using high pressure liquid chromatography (HPLC). An internal standard, hexamethyl benzene, was added prior to this clean-up step to monitor losses through the HPLC. Final results were corrected for the recovery of this internal standard. A second internal standard, d12-phenanthrene, was added prior to analysis; however, no corrections were made based on its recovery. Neither of these internal standards are specified in Method 8270.
- SW-846 Method 8270 was modified to quantify the samples using Selective Ion Monitoring (SIM) Gas Chromatography/Mass Spectrometry (GC/MS). This modification results in improved detection limits.
- Three isotopically-labelled PAH compounds were used as surrogates rather than those recommended in Method 8270. Recoveries of these compounds should better represent the recoveries of target PAHs.

PCB Analysis

- Samples were extracted using the modified extraction procedures as described for the PAH analysis. An internal standard, dibromooctafluorobiphenyl, was added prior to the HPLC clean-up to monitor losses. Final results were corrected for the recovery of this standard. A second internal standard, 1,2,3-trichlorobenzene (required by QAPP) was added prior to analysis; however, no corrections were made based on its recovery.
- Quantification of PCBs was not done on a total basis as required by SW-846 Method 8080 but by quantifying four peaks for each Aroclor and averaging these results. Peaks were considered valid if the peak shape was good, if there was no tailing, and if there was little or no coelution with other peaks. A definite Aroclor pattern was necessary for quantification of PCBs.
- A three-point calibration for each peak was used instead of the five-point calibration required by Method 8080. This modification should have minimal effect on data quality.
- The surrogate required by the QAPP, tetrachloro-m-xylene, was used. A second surrogate, octochloronaphthalene, was also added to monitor extraction efficiency.

Metals Analysis

- Nine of the 13 metals analyzed for sediment samples were measured by energy-diffusive X-Ray fluorescence (XRF) - As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. This procedure yields a total metals concentration instead of the recoverable metals determined by SW-846 methods.
- Sediments for Ag, Cd, Hg, and Se were subjected to an acid digestion using nitric and hydrofluoric acids. This digestion again yields total rather than recoverable metals.

Oil and Grease

- Oil and grease extracts for sediments were analyzed using infrared (IR) detection rather than the gravimetric procedures specified in the QAPP. This should have no effect on data quality.

QUALITY ASSURANCE OBJECTIVES

Many of the guideline QA objectives and internal QC checks criteria guidelines specified in the QAPP (particularly for organic analyses) are not routinely achievable by standard or nonstandard methods. To avoid excessive reanalyses (both costly and time-consuming), some acceptance criteria established internally by Battelle were used for this project. These internal limits are adequate for use in determining whether or not project results are valid.

PAH Analysis

- Both surrogate and matrix spike objectives for PAHs were specified in the QAPP to be 70 to 130 percent. For surrogates, Battelle actually used internal limits of 40 to 120, with one percent of the three surrogates out of limits being acceptable. If more than

one surrogate did not fall within 40 to 120 percent, reanalysis was required. For matrix spikes, internal limits of 40 to 120 percent were also used; no reanalyses however, were performed based on exceedences of these limits.

- Limits for continuing calibration checks were specified as ± 10 percent in the QAPP; limits of ± 25 percent were used.

PCB Analysis

- Both surrogate and matrix spike objectives for PCBs were specified in the QAPP to be 70 to 130 percent. For surrogates, Battelle actually used internal limits of 40 to 120 percent. If both surrogates exceeded these limits, re-extraction was performed. For matrix spikes, internal limits of 40 to 120 percent were also used; no reanalyses, however, were performed if these limits were exceeded.
- Limits for continuing calibration checks were specified as ± 10 percent in the QAPP; limits of ± 25 percent were used.

Metals Analysis

- Samples analyzed by XRF cannot be spiked. Therefore, no measure of sample accuracy was obtained for those metals previously identified as being analyzed by XRF. An SRM was analyzed, providing a means to measure method accuracy for eight of the nine metals determined by XRF (all but Ba).

SAMPLE HOLDING TIMES

Water Samples

The QAPP specified holding times for water samples only. All water extractions and analyses for the critical parameters were performed within these holding times (from the time of sample receipt).

Sediment Samples

Though holding times for organics in sediment samples were not specified in the QAPP, the referenced SW-846 methods do require that extractions be done within 14 days and that the analysis of the extracts be performed within 40 days after extraction. Any analyses exceeding these criteria for the critical parameters will be discussed below.

PAHs

Initial triplicate analyses of the Indiana Harbor untreated sediments yielded concentrations for several compounds above the calibration range. Dilutions were analyzed approximately two months past the 40 day extract holding time. No significant differences were observed between the original analysis and the diluted analysis; removal efficiencies should not be affected.

The Indiana Harbor treated sediment was re-extracted over two months past the 14 day extraction holding time due to unacceptable surrogate recoveries. (Surrogate recoveries for the re-extracted sample also did not meet acceptance criteria.) The re-extracted values were approximately 60 percent of the initial values. Because of the minimal amounts of PAHs present after treatment relative to the amount in the feed, the accuracy of the results for the treated sediment is less critical. If the concentration of total PAHs were actually two to five times higher than the reported value; removal efficiencies would still be greater than 95 percent.

CONCLUSIONS AND LIMITATIONS OF DATA

Upon review of all sample data and associated QC results, the data generated for the ZIMPRO treatability study has been determined to be of acceptable quality. In general, QC results for accuracy and precision were good and can be used to support technology removal efficiency results.

As discussed previously, the analytical laboratory used several specialized methods when analyzing samples from the ZIMPRO treatability study. These same methods, however, have been used in analyzing all samples generated to date in support of the ARCS Program. Therefore, while the data generated for the ZIMPRO treatability study may not be comparable to data generated by standard EPA methods, it is comparable to data generated within the ARCS Program.

The abridged version of the Data Verification Report prepared by the ARCS Program QA Officer follows.

Data Verification Report For Assessment and Remediation of Contaminated Sediment Program

**Report Number 8
(SAIC, Bench-Scale Tests)**

By

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ABSTRACT

Data submitted by the Science Applications International Corporation (SAIC) of Cincinnati, Ohio, have been verified for compliance of the QA/QC requirements of the Assessment and Remediation of Contaminated Sediment (ARCS) program. This data set includes results from bench-scale technology demonstration tests on wet contaminated sediments using four treatment technologies, namely, B.E.S.T. (extraction process), RETEC (low temperature stripping), ZIMPRO (wet air oxidation), and Soil Tech (low temperature stripping). The primary contaminants in these sediments were polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs). In addition, metal contents and conventionals (% moisture, pH, % total volatile solids, oil and grease, total organic carbon (TOC), total cyanide, and total phosphorus) in these sediments were also considered for this project. The objective of the bench-scale technology demonstration study was to evaluate four different treatment techniques for removing different organic contaminants from sediments. Both treated and untreated sediment samples were analyzed to determine treatment efficiencies.

A total of seven sediment samples from four different areas of concerns (Buffalo River, Ashtabula River, Indiana Harbor, and Saginaw River) were analyzed under the bench-scale technology demonstration project. The samples from these areas of concern (AOCs) were collected by the Great Lakes National Program Office (GLNPO) in Chicago, IL, and sample homogenization was performed by the U. S. EPA in Duluth, MN. SAIC was primarily responsible for the characterization of the sediment samples prior to testing and for the residues created during the test. The solid fraction analyses were performed by SAIC's analytical subcontractor Battelle-Marine Sciences Laboratory of Sequim, Washington, and Analytical Resources Incorporated of Seattle, Washington.

The submitted data sets represent analyses of untreated sediments, as well as solid, water, and oil residues obtained by using different treatments. The verified data set is divided into several parameter groups by sampled media. The data verifications are presented in parameter groups that include: metals, PCBs, conventionals, and PAHs.

The results of the verified data are presented as a combination of an evaluation (or rating) number and any appropriate data flags that may be applicable. The templates used to assess each individual analyte are attached in case the data user needs the verified data of a single parameter instead of a parameter group.

INTRODUCTION

The bench-scale technology demonstration project was undertaken to evaluate the efficiencies of four techniques used for the removal of specific contaminants from wet sediments collected from designated Great Lakes areas of concern. Four different sediment treatment techniques, namely, B.E.S.T (Basic Extraction Sludge Technology), RETEC, ZIMPRO, and Soil Tech were considered for evaluation. B.E.S.T. is a solvent extraction process, RETEC and Soil Tech are low temperature stripping techniques, and ZIMPRO is a wet air oxidation technique. Wet sediments were collected by the Great Lakes National Program Office (GLNPO) from four Great Lakes sites, namely, the Buffalo River in New York, the Saginaw River/Bay (referred to as Saginaw River throughout the following discussions) in Michigan, the Grand Calumet River/Indiana Harbor (referred to as Indiana Harbor throughout the following discussions) in Indiana, and the Ashtabula River in Ohio. The four techniques were used to treat the sediment samples from these four sites. The sediment samples represent the sediment that would be obtained for on-site treatment.

The B.E.S.T. process is a patented solvent extraction technology that uses the inverse miscibility of triethylamine as a solvent. At 65° F, triethylamine is completely soluble in water and above this temperature, triethylamine and water are partially miscible. This property of inverse miscibility is used since cold triethylamine can simultaneously solvate oil and water. RETEC and the Soil Tech (low temperature stripping) are techniques to separate volatile and semivolatile contaminants from soils, sediments, sludges and filter cakes. The low temperature stripping (LTS) technology heats contaminated media to temperatures between 100 -200° F, evaporating off water and volatile organic contaminants. The resultant gas may be burned in an afterburner and condensed to a reduced volume for disposal or can be captured by carbon absorption beds. For these treatability studies, only the processes that capture the driven off contaminants were considered. The ZIMPRO (wet air oxidation) process accomplishes an aqueous phase oxidation of organic and inorganic compounds at elevated temperatures and pressures. The temperature range for this process is between 350 to 600° F (175 to 320° C). System pressure of 300 psi to well over 300 psi may be required. In this process, air or pure oxygen is used as an oxidizing agent.

Samples for the technology demonstration projects were obtained by GLNPO (Chicago, Illinois) and were analyzed by Battelle-Marine Sciences Laboratory (Battelle-MSL, Sequim, WA) and by Analytical Resources Incorporated (Seattle, WA). To evaluate the bench-scale technologies, the sample analyses were divided into four parts: (1) raw untreated sediment samples, (2) treated sediments, (3) water residues, and (4) oil residues. The amount of residues available for the analyses depended upon the corresponding sediment samples and on the individual technology used to treat those sediment samples.

The analyses of sediment and residue parameters for these projects were divided into four different categories: (1) metals, including Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, and Zn; (2) polychlorinated biphenyls (PCBs); (3) polynuclear aromatic hydrocarbons (PAHs);

and (4) conventionals, including percent moisture, pH, percent total volatile, oil and grease, total organic carbon (TOC), total cyanide, and total phosphorus. Analyses of metals and conventionals were performed on treated and untreated sediment samples only for B.E.S.T., ZIMPRO, and Soil Tech, while for the RETEC process, analyses of metals and conventionals were performed on treated and untreated sediment samples as well as water residue samples.

No oil residues were produced by the ZIMPRO technique (wet air oxidation treatment technique), while in the other three techniques, oil residues were analyzed after appropriate sample cleanup steps for PCBs and PAHs.

QUALITY ASSURANCE AND QUALITY CONTROL REQUIREMENTS

The objective behind all quality assurance and quality control (QA/QC) requirements is to ensure that all data satisfy predetermined data quality objectives. These requirements are dependent on the data collection process itself. Under the bench-scale technology demonstration project, QA/QC requirements were established for:

1. Detection limits.
2. Precision.
3. Accuracy,
4. Blank analyses,
5. Surrogate and matrix spike analyses, and
6. Calibration
 - a) initial
 - b) ongoing.

Four parameter groups analyzed in the sediment and water residue phases were of interest in the bench-scale technology demonstration project. These groups included: (a) metals, (b) PCBs, (c) PAHs, and (d) conventionals. The conventionals included: percent moisture, pH, percent total volatile, oil and grease, TOC, total cyanide, and total phosphorus. In addition, total solids, total suspended solids, and conductivity were included in the conventionals group for RETEC conventional analyses. The analyses for metals and conventionals were performed for solids only, except for RETEC, where metals and conventionals were analyzed in solid and water residue phases. Parameter groups analyzed in the oil residue phase are PCBs and PAHs. The objective of these analyses was to characterize samples both before and after each treatment was applied.

The detection limits for metals, PCBs, PAHs, and conventionals (where appropriate) were defined as, three times the standard deviation for 15 replicate analyses of a sample with an analyte concentration within a factor of 10 above the expected or required limit of detection. Individual parameter detection limits are presented in the approved quality assurance project plan for SAIC on file at the Great Lakes National Program Office in Chicago, IL.

Precision requirements were based on analytical triplicate analyses for all parameters of sediment samples and treated residues, at the rate of 1 per 20 samples. The results of the triplicate analyses provided the precision for the analytical laboratory. An acceptable limit was the coefficient of variation less than or equal to 20 percent. The precision requirement was established for all variable types in this project. For treated sediments, the relative percent difference (RPD) between the matrix spike and matrix spike duplicate was used as a measure of precision with an acceptance limit of less than 20% .

Accuracy was defined as the difference between the expected value of the experimental observation and its "true" value. Accuracy in this project was required to be assessed for each variable type using analysis of certified reference materials, where available, at the rate of 1 per 20 samples. Acceptable results must agree within 20 percent of the certified range. Since no PCBs and PAHs were expected to be detected in the treated sediment, matrix spikes and matrix spike duplicate analyses were required during the analyses of treated sediment for the organic parameters. Matrix spike analyses were used as a measure of accuracy for treated sediment analyses, with an acceptance limit of $\pm 30\%$ from the known value.

Matrix spikes were required to be used at a rate of 1 per 20 samples and to be within plus or minus 15 percent of the spiking value for metals and 70 to 130 percent of the spiking value for organics (PCBs and PAHs).

Surrogate spike analyses were only required for each sample in organic analyses. The acceptable limits for the surrogate recovery was between 70 and 130 percent of the known concentration.

The observed values should have been less than the method detection limit for each parameter for method blanks (run at the beginning, middle, and end of each analytical run).

The ongoing calibration checks were required at the beginning, middle, and end of a set of sample analyses for all variable types. The maximum acceptable difference was $\pm 10\%$ of the known concentration value in the mid-calibration range. Initial calibration acceptance limits, for metals, was the ≥ 0.97 coefficient of determination for the calibration curve, while a %RSD of the response factors of less than or equal to 25% was required for organics.

RESULTS AND DISCUSSION

The ARCS QA program was formally adopted for use when SAIC received final approval from the GLNPO on May 31, 1991. An evaluation scale, based upon the QA program developed for the ARCS program, was developed to evaluate the success of the data collection process in meeting the QA/QC requirements of the ARCS program. The following section discusses how to interpret the data verification results.

The Verification Process and Evaluation Scale

For verification purposes, the data set from each technology was divided into 4 different sample media as follows:

1. Untreated sediment,
2. Treated sediment,
3. Water residue, and
4. Oil residue.

The verification process included QA/QC compliance checking for accuracy, precision, matrix spike analysis, surrogate spike analysis, blank analysis, detection limits, initial and ongoing calibration checks, and holding times as well as checks on calculational correctness and validity on a per parameter/analyte basis. Compliance checks were performed to ensure that the QA/QC measurements and samples: (a) met their specified acceptance limits; (b) had reported results that were supported by the raw data; and (c) were analyzed following good laboratory practices, where checking was possible. Upon completion of the verification process, a final rating was assigned for each of the individual categories. The final ratings are presented as a combination of a number value and a flag list.

The numerical value for the rating of a given parameter was assigned based upon the successful completion of each required QA/QC sample or measurement. The QA/QC samples were broken down into four different sample groups, namely, accuracy, precision, blanks, and spike recoveries. A fifth category was included for QA/QC measurements to address the successful completion of instrument calibrations (both initial and ongoing) and the determination of method detection limits. If the laboratory successfully met the acceptance criteria of 50 percent or more of the parameters in a given QA/QC sample group, then the laboratory received the full value for that category. For example, if 50 percent or more of the reagent blanks for the metals in sediment analyses had measured values below the method detection limit, then three points were awarded for that category, assuming reagent blanks were the only blank samples analyzed by the laboratory. The individual point values for each QA/QC sample type or measurement and the minimum acceptance levels for each category are presented in Appendix B. The final numerical rating presented for each parameter category is the summation of the point values from each of the five categories.

Along with each numerical rating, a list of appropriate flags has been attached to the final rating value (Appendix C). The flag indicates where discrepancies exist between the laboratory data and the acceptance limits of the required QA program. Different flags are presented for each category of QA sample (accuracy, precision, blanks, and spike recoveries) and for the QA/QC measurements (instrument calibration and detection limit determination). The flags have a letter and subscript configuration, such as A₁. The letter of the flag represents the category of the discrepancy while the subscript designates the form of the discrepancy. For example, the A flags indicate discrepancies in the use of accuracy checking samples, such as reference materials or standards. A flag with a subscript of 1 indicates that the laboratory failed to meet

the acceptance criteria. Using the example of the A₁ flag, this flag would then indicate a failure of the laboratory to meet the QA/QC requirements for the use of reference materials in their appraisal of accuracy. A flag with the subscript 0 indicates that no information was received (or no standards were available in the case of accuracy) from the analytical laboratory, and therefore, no points could be allotted towards the final calculated rating value for that particular category. It should be noted that the 0 flag does not necessarily indicate that the analytical laboratory did not perform the QA/QC analyses, only that no information was received from the laboratory.

The subscript 9 flag indicates that the sample category or QA/QC measurement is not applicable to that particular parameter or parameter group (Appendix C). For example, an S₉ flag indicates that a matrix spike for that given parameter or analyte is not applicable, such as was the case for percent moisture. Where subscript 9 flags occur, an adjustment to the passing and maximum scores (to be discussed) for a parameter group was made and will be reported in the appropriate tables.

A complete presentation of the QA/QC rating factors (point values by sample type) and the various data flags and their subscripts are presented in Appendices B and C, respectively. A more complete discussion of the rating scale can be found in the report submitted to the RA/M workgroup by Schumacher and Conkling entitled, "User's Guide to the Quality Assurance/Quality Control Evaluation Scale of Historical Data Sets."

Individual parameter flags are presented in the templates found in Appendix D. The objective of the presentation of the individual flag templates is to help the data user make a determination regarding the useability of the data set for any given purpose and to provide the data user with a means to assess any individual parameter that may be of specific interest.

The Interpretation and Use of the Final Verified Data Rating Values

The data verification scale was developed to allow for the proper rating of the verified data and the subsequent interpretation and evaluation of the ratings. Two different interpretations can be made using the ratings provided in this report, namely, the actual or "true" rating and the potential rating. The first interpretation is based upon the formal ARCS QA program, while the second interpretation scale is based upon the "full potential" value of the submitted data set. In the following sections, each interpretation of the results will be discussed.

Data Interpretation Based upon the Formal ARCS QA Program

For each of the four parameter categories, the data were initially verified for QA/QC compliance following the requirements specified in the signed QAPP submitted by SAIC and the ARCS QAMP on file at the GLNPO in Chicago, Illinois.

Table 1 provides the verified data ratings for each variable class for the four different technologies studied based on the current ARCS QA program. The ratings of these variable

classes are presented to provide the data user with a means for comparing the ARCS QA program-based verified results with other data sets, using the same or similar parameters, that were generated prior to and after the initiation of the formal ARCS QA program.

Table 2 provides the data user with the full compliance and acceptable scores presented for each parameter group based upon the current ARCS QA program. The full compliance score represents the numerical rating value if all required QA/QC samples and measurements were performed by the analytical laboratory and successfully met all the QA/QC requirements of the ARCS QA program. An acceptable score is lower than the full compliance score and accounts for laboratory error that can be reasonably expected during an analysis of multiple samples. Any final rating value less than the acceptable score indicates that problems were identified in the data that could adversely effect the quality of the data. The acceptable score was set at 60 percent of the full compliance score. To determine the percentage of QA/QC samples and measurements successfully analyzed for a given parameter versus the number analyzed following the complete ARCS QA protocols, divide the numerical rating received by the full compliance score. An acceptable data set, in this case, has a rating of 60 percent or greater.

In some cases, all the QA/QC requirements may not be applicable (e.g., matrix spikes for percent solids are not applicable). If this is the case, a flag with the subscript 9 was used, and the full compliance and acceptable scores were adjusted by lowering the score on appropriate number of points for nonrequired sample type, as identified in Appendix B. An example of this situation is % moisture, as indicated in Table 1, the subscript 9 flag has been applied to accuracy, blank, detection limit, and spike samples. Therefore, the full compliance and acceptable scores (Table 2) are only based upon the possible points for the successful completion of the remaining QA/QC samples that have cumulative points value of 8 (Appendix B).

Data Interpretation Based upon the "Potential" Value of the Data Set

A second interpretation scale has been presented to allow the data user to establish the "full potential" value of the submitted data set. The numerical value and associated flags presented in the first interpretation can be considered as an absolute rating for that data set or parameter. These ratings were based upon all the data submitted to Environmental Monitoring Systems Laboratory - Las Vegas (EMSL-LV) and to Lockheed for review by the analytical laboratory. If one or more parameter or parameter groups qualifying flags had the subscript of 5, 6, 9, or 0 (Appendix C), the required information was not available or not applicable at the time of sample analysis, and consequently was not included during the data verification and review process. The equivalent point value(s) for each individual sample type may be added to the reported point sum to give the data user the full potential value of the data set. This process assumes that if the "missing" QA/QC samples or measurements were performed, the results would fall within the ARCS QA program specified acceptance limits. For example, if the point value (including qualifying flags) for the metals was 6-B₀ C₀ D₀ S₀, then the data user could potentially add 14 points to the score since the blank analyses, spike information, detection limit,

and calibration (initial and ongoing) information was not available for verification. The resulting data would then have a rating of 20.

TABLE 1. Verified Data Ratings Based on the Current ARCS QA Program

Untreated Sediments	B.E.S.T.	ZIMPRO	Soil Tech	RETEC
Metals	12-C ₀ D ₀	12-C ₀ D ₀	12-C ₀ D ₀	12-C ₀ D ₀
%Moisture	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀
pH	0-A, B, C ₀ D, P ₀ S ₀	0-A, B, C ₀ D, P ₀ S ₀	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀
%TVS	6-A, C ₀ D, S ₀	3-A, B, C ₀ D, S ₀	6-A, C ₀ D, S ₀	6-A, C ₀ D, S ₀
Oil and grease	15-A, C ₆	6-A, B ₂ C ₆ D ₁ S ₁	6-A, B ₂ C ₆ D ₁ S ₀	9-A, D ₀ C ₆ S ₀
TOC	12-C ₆ P ₀ S ₀	12-C ₆ P ₀ S ₀	12-C ₆ P ₀ S ₀	9-C ₆ D ₀ P ₀ S ₀
Total cyanide	14-A ₀ P ₀	14-A ₀ P ₀	11-A ₀ P ₀ S ₀	8-A ₀ D ₀ P ₁ S ₀
Total phosphorus	14-A ₀ P ₀	14-A ₀ P ₀	14-A ₀ P ₀	11-A ₀ D ₀ S ₀
PCBs	17-B ₂ D ₀	14-A ₁ B ₂ D ₀	14-A ₁ B ₂ D ₀	11-A ₁ B ₂ D ₀ S ₀
PAHs	17-D ₀ S ₂	11-B ₂ D ₀ S ₁ S ₂	17-D ₀ S ₂	20-D ₀
Treated Sediments				
Metals	12-C ₀ D ₀	12-C ₀ D ₀	12-C ₀ D ₀	12-C ₀ D ₀
%Moisture	0-A, B, C ₀ D, P ₀ S ₀	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀	3-A, B, C ₀ D, S ₀
pH	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀	0-A, B, C ₀ D, P ₀ S ₀	3-A, B, C ₀ D, S ₀
%TVS	6-A, C ₀ D, S ₀	3-A, B, C ₀ D, S ₀	6-A, C ₀ D, S ₀	6-A, C ₀ D, S ₀
Oil and grease	15-A, C ₆	6-A, B ₂ C ₆ D ₁ S ₁	9-A, B ₂ C ₆ D ₁	6-A, C ₆ D ₀ P ₁ S ₀
TOC	12-C ₆ P ₀ S ₀	12-C ₆ P ₀ S ₀	12-C ₆ P ₀ S ₀	12-C ₆ D ₀ S ₀
Total cyanide	14-A ₀ P ₀	14-A ₀ P ₀	14-A ₀ P ₀	11-A ₀ D ₀ P ₀
Total phosphorus	14-A ₀ P ₀	14-A ₀ P ₀	14-A ₀ P ₀	14-A ₀ D ₀
PCBs	14-B ₂ D ₀ P ₁	11-A ₁ B ₂ D ₀ P ₁	14-B ₂ D ₀ P ₁	14-A ₁ B ₂ D ₀
PAHs	14-D ₀ P ₁ S ₂	17-D ₀ S ₂	14-D ₀ P ₁ S ₂	20-D ₀

**TABLE 1. Verified Data Rating Based on the Current ARCS Program
(Continued)**

Water residue				
Metals	**	**	**	20
% Moisture	**	**	**	**
pH	**	**	**	3-A, B, C, D, S,
Total Suspended Solids	**	**	**	6-A, C, D, S,
%TVS	**	**	**	6-A, C, D, S,
Total Solids				6-A, C, D, S,
Oil and grease	**	**	**	12-A, C, D,
TOC	**	**	**	9-A, C, D, S,
Total cyanide	**	**	**	14-A, D,
Total phosphorus	**	**	**	14-A, D,
Conductivity	**	**	**	9-A, C, D, S,
PCBs	14-B ₂ D ₀ P ₀	14-B ₂ D ₀ P ₀	5-A ₁ B ₂ D ₀ P ₀ S ₁ S ₆	5-A ₀ B ₂ D ₀ P ₀ S ₁ S ₆
PAHs	11-A ₀ D ₀ P ₁ S ₂	17-D ₀ S ₂	17-D ₀ P ₀	11-A ₁ D ₀ P ₁ S ₁
Oil residue				
PCBs	11-A ₁ B ₂ D ₀ S ₁	*	17-B ₂ D ₀	11-B ₂ D ₀ P ₀ S ₁
PAHs	11-A ₀ B ₂ D ₀ S ₂	*	14-B ₂ D ₀ S ₂	17-B ₂ D ₀

* No oil residue was produced by this treatment

** Analyses were not conducted for this treatment

TABLE 2. Full Compliance and Acceptable Scores Based on the Current ARCS QA Program

Variable Class	Full Compliance	Acceptable
Metals in Treated Sediment	20	12
Metals in Untreated Sediment	20	12
%Moisture	8	5
pH	8	5
%TVS	9	6
Oil and grease	17	11
TOC	17	11
Total cyanide	20	12
Total phosphorus	20	12
Conductivity	14	9
Suspended Solids	9	6
Total Solids	9	6
PAHs	23	14
PCBs	23	14

Table 3 presents the verified data ratings for each variable class in the four technologies based on their full potential value. All data qualifying flags with the subscripts 5, 6, 9, or 0 have been removed. The appropriate point values for each of the 5, 6, or 0 flags (Appendices B and C) were added to the final rating scores for each parameter or parameter group. In contrast, the removal of the subscript 9 flags resulted in an adjustment to the full compliance and acceptable scores, and not in an addition to the calculated point scores since these analyses were not applicable to the methodologies used by the laboratory (Table 2).

TABLE 3. Verified Data Ratings Based on the Full Potential of the Data set

Untreated Sediments	B.E.S.T.	ZIMPRO	Soil Tech	RETEC
Metals	20	20	20	20
%Moisture	8	8	8	8
pH	8	8	8	8
%TVS	6	6	6	6
Oil and grease	17	8-B ₂ D ₁ S ₁	11-B ₂ D ₁	17
TOC	17	17	17	17
Total cyanide	20	20	20	17-P ₁
Total phosphorus	20	20	20	20
PCBs	20-B ₂	17-A ₁ B ₂	17-A ₁ B ₂	17-A ₁ B ₂
PAHs	20-S ₂	14-B ₂ S ₁ S ₂	20-S ₂	23
Treated Sediments				
Metals	20	20	20	20
%Moisture	8	8	8	8
pH	8	8	8	8
%TVS	6	6	6	6
Oil and grease	17	8-B ₂ D ₁ S ₁	11-B ₂ D ₁	9-P ₁
TOC	17	17	17	17
Total cyanide	20	20	20	20
Total phosphorus	20	20	20	20
PCBs	17-B ₂ P ₁	14-A ₁ B ₂ P ₁	17-B ₂ P ₁	17-A ₁ B ₂
PAHs	17-P ₁ S ₂	20-S ₂	20-S ₂	23

TABLE 3. Verified Data Ratings Based on the Full Potential of the Data set (continued)				
Water residue				
Metals	**	**	**	20
% Moisture	**	**	**	8
pH	**	**	**	8
%TVS	**	**	**	6
Oil and grease	**	**	**	17
TOC	**	**	**	17
Total cyanide	**	**	**	20
Total phosphorus	**	**	**	20
Conductivity	**	**	**	14
Suspended Solids	**	**	**	6
Total Solids	**	**	**	6
PCBs	20-B ₂	20-B ₂	14-A, B ₂ S ₁	20-B ₂
PAHs	17-P ₁ S ₂	20-S ₂	23	14-A, P ₁ S ₁
Oil residue				
PCBs	14-A, B ₂ S ₁	*	20-B ₂	20-B ₂
PAHs	17-B ₂ S ₂	*	17-B ₂ S ₂	20-B ₂

* No oil residue was produced by this treatment

** Analyses were not conducted for this treatment

To evaluate the data using the values presented in Table 3, the final ratings should be compared to the full compliance and acceptable scores presented in Table 2. The data user should bear in mind that these values are only the potential values of the data set and assumes that the "missing" QA/QC data could have been or were performed successfully by the laboratory. Any value falling below the acceptable value presented in Table 2 clearly indicates that major QA/QC violations were identified and the data should be used with a great deal of caution by the data user.

Data Verification Results for Bench-scale Technology Demonstration Project

B.E.S.T.

The B.E.S.T. technology was evaluated by analyzing sediment samples and their treated residues (treated sediments, water residues, and oil residues) for metals, conventionals, PCBs and PAHs. PCB and PAH analyses were performed for sediments, water, and oil residues. The metals and conventional analyses were performed for the sediment samples only.

In the majority of the cases studied, the accuracy objective was satisfactory for the metal analyses in treated and untreated sediments. Of the thirteen metals analyzed, accuracy information was not available for Ba, Se, and Ag. In both treated and untreated sediments, ten of the thirteen metal analyses (As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Pb, and Zn) satisfied ARCS specified QA/QC requirements for accuracy. Four of the thirteen metal analyses (Cd, Hg, Se, and Ag) satisfied QA/QC requirements for blank analyses, while the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, results from blank sample analyses were not applicable. Both initial and ongoing calibration for Cd, Hg, Se, and Ag analyses met the ARCS QA/QC specifications for both treated and untreated sediments, while for the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) calibration information was not available. Detection limits information for metal analyses in treated and untreated sediments were not available for verification except for Cd, Hg, Se, and Ag where detection limits were satisfactory. The precision information for the metal analyses in treated sediment was not available for Se, but was satisfactory for the remaining elements, with the exception of Hg, where precision information did not satisfy QA/QC requirements. The precision information for the metal analyses in untreated sediment was not available for Se, but was satisfactory for the remaining twelve metal (Ag, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) analyses. The matrix spike information for both treated and untreated sediment analyses were satisfactory for Cd, Hg, and Se, were unsatisfactory for Ag, while the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, results from matrix spike analyses were not applicable.

Of the seven conventional analyses, the accuracy information in both treated and untreated sediments was satisfactory for TOC and was not available for total cyanide, and total phosphorus. In the remaining four conventional analyses, accuracy was not applicable. In both sediments, five of the seven conventionals (%TVS, oil and grease, TOC, total cyanide, and total phosphorus) satisfied QA/QC requirements for blank analyses, and the blank information was not applicable for moisture, pH, and TVS. Both initial and ongoing calibration information was satisfactory for all conventional analyses in both treated and untreated sediments except for moisture and pH where calibration information was not available and for TOC and oil and grease where ongoing calibration information was not available. Detection limits were satisfactory for four (oil and grease, TOC, total cyanide, and total phosphorus) of the seven conventional

analyses in treated and untreated sediments, and were not applicable for moisture, pH, and TVS. The precision information was satisfactory for two (%TVS, oil and grease) of the seven conventional analyses in treated and untreated sediments. No precision information was available for the remaining five conventional analyses in treated or untreated sediments. The matrix spike information for both treated and untreated sediment analyses were satisfactory for oil and grease, total cyanide, and total phosphorus, while for the remaining four conventional analyses the matrix spike information was not applicable.

In treated sediments, untreated sediments, and water residues, the accuracy objective for PCBs was satisfactory for Aroclor 1254 analyses only and could be used to represent the whole PCB group. No accuracy information was available for the remaining three Aroclor analyses. In oil residues, accuracy information was not satisfactory for PCB analyses. In both sediments and in both residues, PCB analyses did not satisfy ARCS specified QA/QC requirements for blank analyses indicating potential contamination at the laboratory. Initial and ongoing calibration was satisfactory for all PCB analyses in both treated and untreated sediments as well as in water and oil residues. Detection limit information were not available for PCB analyses in treated and untreated sediments and for water and oil residues. In the untreated sediments, the precision information was satisfactory for Aroclors 1242 and 1254, and no precision information was available for Aroclors 1248 and 1260. In the treated sediments, the precision information was not satisfactory for Aroclor 1254, and no precision information was available for Aroclors 1242, 1248, and 1260. In water residues, no precision information was available for any of the Aroclors. In oil residues, the precision information was satisfactory for Aroclor 1248, and no precision information was available for Aroclors 1242, 1254, and 1260. The matrix spike for Aroclor 1254 was satisfactory for both sediment and water residue analyses and could be used to represent the whole PCB group. The matrix spike for Aroclor 1254 was unsatisfactory for the analyses of oil residue. In both sediment or residue analyses, no matrix spike information was available for Aroclors 1242, 1248, and 1260. The surrogate spike recoveries were satisfactory for PCB analyses in both sediments and residues.

In eight of sixteen PAH analyses of treated and untreated sediments, the accuracy objective was satisfactory. No accuracy information was available for six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, chrysene, and dibenzo(a,h)anthracene) analyses in both treated and untreated sediments. The accuracy objective was not satisfactory for benzo(k)fluoranthene and benzo(a)pyrene in treated or untreated sediments. No accuracy information was available for any of the PAH analyses in water and oil residues. In treated and untreated sediments, and in water residues, PAH analyses satisfied ARCS specified QA/QC requirements for blank analyses. In all cases of oil residues, the blank analyses exceeded the MDL indicating potential contamination at the laboratory. Initial and ongoing calibration limits for PAH analyses met the ARCS QA/QC specifications for both treated and untreated sediments and water and oil residue analyses. Detection limit information was not available for PAH analyses in treated and untreated sediments, nor for water and oil residues. In untreated sediments and oil residues, the precision information was satisfactory for all PAH analyses, except for acenaphthene in untreated sediment, and naphthalene in oil residues where no precision information was available. In treated sediments, the precision information was satisfactory for fluorene, phenanthrene, and

anthracene but was unsatisfactory for the remaining PAH analyses. In water residues, no precision information was available for PAH analyses except for benzo(g,h,i)pyrene where precision was unsatisfactory. The matrix spike information was satisfactory for twelve of sixteen PAH analyses in treated sediment and for eight of the sixteen analyses in untreated sediment and in water and oil residues. Surrogate recoveries were not satisfactory for PAHs in either sediment and residue analyses.

ZIMPRO

The ZIMPRO technology was evaluated by analyzing sediment samples, treated sediments, and water residues for metals, conventionals, PCBs, and PAHs. PCB and PAH analyses were performed for both sediment and water residues. The metals and conventional analyses were performed for the both sediment samples only.

In the majority of the cases studied, the accuracy objective was satisfactory for the metal analyses in treated and untreated sediments. Of the thirteen metals analyzed, accuracy information was not available for Ba, Se, and Ag. In both treated and untreated sediments, ten of the thirteen metal analyses (As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, and Zn) satisfied ARCS specified QA/QC requirements for accuracy. Four of the thirteen metal analyses (Cd, Hg, Se, and Ag) satisfied QA/QC requirements for blank analyses, while the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, blank sample analyses are not applicable. Both initial and ongoing calibration for Cd, Hg, Se, and Ag analyses met the ARCS QA/QC specifications for both treated and untreated sediments while for the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), calibration information was not available. Detection limit information for metal analyses in treated and untreated sediments was not available for verification except for Cd, Hg, Se, and Ag where the detection limits were satisfactory. The precision for the metal analyses in treated sediment was not satisfactory for As, but was satisfactory for the remaining elements. The precision information for the metal analyses in untreated sediment was satisfactory for all elements. The matrix spike information for both treated and untreated sediment analyses were satisfactory for four (Cd, Hg, Se, and Ag) of the thirteen elements while the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, results from matrix spike analyses were not applicable.

Of the seven conventional analyses, the accuracy information in both treated and untreated sediments was satisfactory for TOC and was not available for total cyanide, and total phosphorus. In the remaining four conventional analyses, accuracy was not applicable. In both sediments, three of the seven conventionals (TOC, total cyanide, and total phosphorus) satisfied QA/QC requirements for blank analyses. The blank information was unsatisfactory for oil and grease, was not available for %TVS, and the blank information was not applicable for moisture and pH. Both initial and ongoing calibration information was satisfactory for all conventional analyses in both treated and untreated sediments except for %moisture, pH, and TVS where calibration information was not available, and for TOC and oil and grease, where ongoing

calibration information was not available. Detection limits were satisfactory for three (TOC, total cyanide, and total phosphorus) of the seven conventional analyses in treated and untreated sediments. Detection limits were unsatisfactory for oil and grease analyses in treated and untreated sediments and were not applicable for %moisture, pH, and %TVS. The precision information was satisfactory for pH, %TVS, and oil and grease analyses in treated, and for %moisture, %TVS, and oil and grease analyses in untreated sediment. No precision information was available for %moisture, TOC, total cyanide, and total phosphorus analyses in treated sediment and for pH, TOC, total cyanide, and total phosphorus analyses in untreated sediments. The matrix spike information for both treated and untreated sediment analyses were satisfactory for total cyanide and total phosphorus, were unsatisfactory for oil and grease while for the remaining four conventional analyses the matrix spike information was not applicable.

The accuracy objective was unsatisfactory for the PCB analyses in treated and untreated sediments for Aroclor 1254. No accuracy information was available for the remaining three Aroclor analyses in treated and untreated sediments. In water residue, the accuracy objective for PCBs was satisfactory for Aroclor 1254 analyses only and could be used to represent the whole PCB group. No accuracy information was available for the remaining three Aroclor analyses in water residues. In water residues and in both treated and untreated sediments, the blank analyses exceeded the detection limits specified in the QAPP indicating potential contamination at the laboratory. Initial and ongoing calibration was satisfactory for all PCB analyses in both treated and untreated sediments as well as in water residues. Detection limits information were not available for PCB analyses in treated and untreated sediments, nor in the water residues. In untreated sediment analyses, most PCB observations were below the instrument detection limits, therefore it was not possible to calculate meaningful precision information for PCB Aroclors, with the exception of Aroclor 1248 analyses, where precision information satisfied QA/QC requirements. No precision information was available for PCB analyses in treated sediments, except for Aroclor 1254 in treated sediment where it did not satisfy QA/QC requirements. In the water residue, no PCB precision information was available. The matrix spike for Aroclor 1254 was satisfactory for both sediments, and the water residue analyses and could be used to represent the whole PCB group. The matrix spike information for sediments and water residue analyses for Aroclor 1242, 1248, and 1260 were not available for verification. The surrogate recoveries were satisfactory for PCB analyses in sediment and residue analyses.

In ten of the sixteen PAH analyses in treated sediment and nine of the sixteen PAH analyses in untreated sediments, the accuracy objective was satisfactory. No accuracy information was available for six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, chrysene, and dibenzo(a,h)anthracene) analyses in treated and untreated sediment. The accuracy objective was not satisfactory for benzo(k)fluoranthene in untreated sediment. Accuracy information in water residue was unsatisfactory for naphthalene, acenaphthylene, acenaphthene, phenanthrene, and benzo(a)pyrene. Accuracy was satisfactory for the rest of the PAH analyses in water residues. In treated sediments and water residues, PAH analyses satisfied ARCS specified QA/QC requirements for blank analyses. In all cases of untreated sediment analyses, the blank analyses exceeded the detection limit specified in the QAPP. Calibration limits for

PAH analyses met the ARCS QA/QC specifications for both treated and untreated sediments, and also for water residue analyses. Detection limits information were not available for PAH analyses in treated and untreated sediments, nor for the water residues. The precision information was satisfactory for PAH analyses in both sediments except for naphthalene, acenaphthylene, acenaphthene, fluorene, and benzo(a)pyrene analyses in treated sediment and for naphthalene, acenaphthene, phenanthrene, and benzo(a)pyrene in water residue, where precision was unsatisfactory. The matrix spike information was satisfactory for fifteen of the sixteen PAH analyses in treated sediment, for five of the sixteen analyses in untreated sediment and for eleven of the sixteen analyses in water residues. Surrogate recoveries were not satisfactory for PAHs in the sediment and residue analyses.

SOIL TECH

The Soil Tech technology was evaluated by analyzing sediment samples and their treated residues (treated sediments, water residues, and oil residues) for metals, conventionals, PCBs, and PAHs. PCB and PAH analyses were performed for sediment and residues. The metals and conventional analyses were performed for the sediment samples only.

In the majority of the cases studied, the accuracy objective was satisfactory for the metal analyses in treated and untreated sediments. Of the thirteen metals analyzed, accuracy information was not available for Ba, Se, and Ag. Four of the thirteen metal analyses (Cd, Hg, Se, and Ag) satisfied QA/QC requirements for blank analyses, while the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, blank sample analyses are not applicable. Both initial and ongoing calibration for Cd, Hg, Se, and Ag analyses met the ARCS QA/QC specifications for both treated and untreated sediments while for the remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), calibration information was not available. Detection limits information for metal analyses in treated and untreated sediments were not available for verification except for Cd, Hg, Se, and Ag where detection limits were satisfactory. The precision information for the metal analyses in treated sediment was not available for Se and Hg but was satisfactory for the remaining elements with the exception of Cr, where precision information did not satisfy the QA/QC requirements. The precision information for the metal analyses in untreated sediment was satisfactory for all metal analyses. The matrix spike information were satisfactory for four (Cd, Hg, Se, and Ag) of the thirteen elements for treated sediments and two (Cd, Hg) of the thirteen elements for untreated sediments. The matrix spike information were unsatisfactory for Se and Ag analyses in untreated sediments. The remaining nine metals (As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, results from matrix spike analyses were not applicable.

Of the seven conventional analyses, the accuracy information in both treated and untreated sediments was satisfactory for TOC and was not available for total cyanide, and total phosphorus. In the remaining four conventional analyses, accuracy was not applicable. In both sediments, four of the seven conventionals (%TVS, TOC, total cyanide, and total phosphorus)

satisfied QA/QC requirements for blank analyses, and the blank information was not applicable for moisture and pH, while blank analyses was not satisfactory for oil and grease. Both initial and ongoing calibration information was satisfactory for all conventional analyses in both treated and untreated sediments, except for %moisture, pH, and %TVS where calibration information was not available. Ongoing calibration information was not available for TOC and oil and grease. Detection limits were satisfactory for three (TOC, total cyanide, and total phosphorus) of the seven conventional analyses in treated and untreated sediments. Detection limits were unsatisfactory for oil and grease and were not applicable for %moisture, pH, and %TVS. The precision information was satisfactory for %moisture, %TVS, and oil and grease in treated sediments. The precision information was satisfactory for %TVS, and oil and grease in treated sediments. No precision information was available for the remaining conventional analyses in treated or untreated sediments. The matrix spike information were satisfactory for oil and grease, total phosphorus, and total cyanide in treated sediment analyses and for total phosphorus in untreated sediment analyses. The matrix spike information were not available for oil and grease and total cyanide in untreated sediment analyses. While for the remaining four conventional analyses, the matrix spike information was not applicable.

The accuracy objective was satisfactory for the PCB analyses in treated sediments and in oil residue analyses for Aroclor 1254 only and could be used to represent the whole PCB group. The accuracy objective was unsatisfactory for the PCB analyses in untreated sediments and in water residue analyses for Aroclor 1254. No accuracy information was available for the remaining three Aroclor analyses in sediment or residue analyses. In both residues and in both treated and untreated sediments, the blank analyses exceeded the detection limits specified in the QAPP, except for Aroclor 1260 in oil residue. Initial and ongoing calibration was satisfactory for all PCB analyses in both treated and untreated sediments, as well as in both water and oil residues. Detection limit information was not available for PCB analyses in both sediments and residues. In untreated sediment analyses, most PCB observations were below the instrument detection limits, therefore, it was not possible to calculate meaningful precision information for PCB Aroclors, with the exception of Aroclor 1248 analyses, where precision information satisfied QA/QC requirements. No precision information was available for PCB analyses in treated sediment, except for Aroclor 1254, where it did not satisfy QA/QC requirements. No precision information was available for PCB analyses in oil and water residues, except for Aroclor 1248 in oil residue, where precision was satisfactory. The matrix spike for Aroclor 1254 was satisfactory for both sediments and the oil residue analyses and could be used to represent the whole PCB group. The matrix spike for Aroclor 1254 was unsatisfactory for the water residue analyses, and the matrix spike information for both sediment and residue analyses for Aroclor 1242, 1248, and 1260 were not available for verification. The surrogate recoveries were satisfactory for PCB analyses in sediment and residue analyses, except for water residue where surrogate information was not available.

In eight of sixteen PAH analyses in treated and untreated sediments, the accuracy objective was satisfactory. No accuracy information was available for six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, chrysene, and dibenzo(a,h)anthracene) analyses in both treated and untreated sediments. The accuracy objective was not satisfactory for benzo(k)

fluoranthene in treated or untreated sediments nor for benzo(g,h,i)perylene in untreated sediment. Accuracy information was satisfactory for the PAH analyses in water and oil residues. In treated and untreated sediments and water residues, PAH analyses satisfied ARCS specified QA/QC requirements for blank analyses. In all cases of oil residues, the blank analyses exceeded the MDL. Calibration limits for PAH analyses met the ARCS QA/QC specifications for both treated and untreated sediments as well as water and oil residue analyses. Detection limit information was not available for PAH analyses in treated and untreated sediments nor for water and oil residues. In untreated sediment and oil residues, the precision information was satisfactory for all PAH analyses, except for acenaphthene and acenaphthene in untreated sediment, and naphthalene in oil residues, where no precision information was available. In treated sediments, the precision information was satisfactory for naphthalene, acenaphthylene acenaphthene, fluorene, phenanthrene, and anthracene, and was unsatisfactory for the remaining PAH analyses. In water residues, no precision information was available for any of the PAH analyses. The matrix spike information was satisfactory for twelve of sixteen PAH analyses in treated sediment, and for thirteen of the sixteen analyses in untreated sediment and ten of the sixteen analyses in water and all analyses in oil residues. Surrogate recoveries were unsatisfactory for PAHs in either sediment and oil residue analyses but were satisfactory in water residue.

RETEC

The RETEC technology was evaluated by analyzing sediment samples and their treated residues (water residues and oil residues) for metals, conventionals, PCBs and PAHs. PCB and PAH analyses were performed for sediment and residues. The metals and conventional analyses were performed for both sediment samples and water residues.

In a majority of the cases studied, the accuracy objective was satisfactory for the metal analyses in treated and untreated sediments. Of thirteen metals analyzed, accuracy information was not available for Ba, Se, and Ag. In both treated and untreated sediments, ten of the thirteen metal analyses (As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Hg, and Zn) satisfied ARCS specified QA/QC requirements for accuracy. The accuracy objective was satisfactory for all metal analyses in water, except for Se, where accuracy did not satisfy QA/QC requirements. Four of the thirteen metal analyses (Cd, Hg, Se, and Ag) satisfied QA/QC requirements for blank analyses. The remaining nine metal analyses (As, Ba, Cr, Cu, Fe, Pb, Mn, Ni, and Zn) were analyzed by XRF techniques. In all of the XRF analyses, blank sample analyses are not applicable. In water residue, blank analyses were satisfactory for all metals except for Fe, Mn, and Se, where blank analyses exceeded the detection limits specified in the QAPP, and for Ba, where no information regarding blank analyses was available. Both initial and ongoing calibration met the ARCS QA/QC specifications for Cd, Hg, Se, and Ag for both treated and untreated sediments, and for all metals in water residue analyses. While in both treated and untreated sediments the remaining nine metals (As, Ba, Cr, Cu, Fe, Pb, Mn, Ni, and Zn), calibration information were not available. Detection limits information for metal analyses in treated and untreated sediments were not available for verification, except for Cd, Hg, Se, and

Ag, where detection limits were satisfactory. Detection limits for metal analyses in water residue were satisfactory, except for Mn, Se, and Zn, where detection limits exceeded the QA/QC requirements. The precision information for the metal analyses in treated and untreated sediments, and in water residue was satisfactory for all elements, except for Hg in treated sediment, and Se and Hg in water residue analyses, where precision information did not satisfy QA/QC requirements. The matrix spike information for treated sediment analyses were satisfactory for Cd, Hg, and Ag, and was not satisfactory for Se. The matrix spike information for untreated sediment analyses were satisfactory for Cd and Hg, and was not satisfactory for Se and Ag. The remaining nine metals (As, Ba, Cr, Cu, Fe, Pb, Mn, Ni, and Zn) were analyzed by XRF techniques for treated and untreated sediment. In all of the XRF analyses, matrix spike analyses are not applicable. The matrix spike information for water residue analyses was satisfactory for all metals except for Ag where matrix spike information did not satisfy QA/QC requirement.

Of the seven conventional analyses in both treated and untreated sediments, accuracy information was satisfactory for TOC, and was not available for total cyanide, or total phosphorus. In the remaining four conventional analyses accuracy was not applicable. Of ten conventional analyses in water residue, accuracy information was not available for TOC, total cyanide, total phosphorus, and conductivity. In the remaining seven conventional analyses accuracy was not applicable. In both treated and untreated sediments and in water residue analyses, %TVS, oil and grease, TOC, total cyanide, and total phosphorus satisfied QA/QC requirements for blanks. Also, the blank information was satisfactory for total solids and total suspended solids in water residue analyses. The blank information was not applicable for the remaining conventional analyses in sediment and water residue analyses. Both initial and ongoing calibration information was satisfactory for all conventional analyses in both sediment and water residue, except for %moisture (in sediment), pH, and TVS, TSS, TS where calibration information was not available, and for TOC and oil and grease, where ongoing calibration information was not available. Detection limit information was not available in both treated and untreated sediments and in water residue for oil and grease, TOC, total cyanide, and total phosphorus, and was not applicable for the remaining conventional analyses. In treated sediment, the precision information was not satisfactory for oil and grease and no precision information was available for total cyanide. In untreated sediment, the precision information was not satisfactory for total cyanide, and no precision information was available for TOC. The precision information was satisfactory for the remaining five conventional analyses in treated and untreated sediments. In water residue, the precision information was satisfactory for all the conventionals, except for moisture, where no precision information was available. The matrix spike information was not available for oil and grease, and was satisfactory for total cyanide and total phosphorus in treated sediment analyses. The matrix spike information was not available for oil and grease, total cyanide, and total phosphorus in untreated sediment analyses. The matrix spike information was satisfactory for oil and grease, total cyanide, and total phosphorus in water residue analyses. The matrix spike information for the remaining conventional analyses was not applicable for sediment and water residue analyses.

The accuracy objective was unsatisfactory for the PCB analyses in treated sediments, untreated sediments, and oil residue for Aroclor 1254 and could be used to represent the whole PCB group. No accuracy information was available for the remaining three Aroclor analyses in treated and untreated sediments. No accuracy information was available for PCB analyses in water residues. In both sediments and residues, the blank analyses exceeded the detection limits specified in the QAPP. Both initial and ongoing calibration for PCB analyses met the ARCS QA/QC specifications for both treated and untreated sediments, as well as for water and oil residues. Detection limit information was not available for PCB in either sediments or residue analyses. The precision information for the PCB analyses in treated and untreated sediment was satisfactory for Aroclor 1254. In all remaining analyses, precision information was not available. The matrix spike was satisfactory for Aroclor 1254 in treated sediment and in oil residue analyses, and could be used to represent the whole PCB group. The matrix spike information was not available for the remaining Aroclors in treated sediment and oil residues. The matrix spike information was not available for PCB analyses in untreated sediment and in water residues. The surrogate recoveries were satisfactory for PCB analyses in sediment and residue analyses.

In ten of the sixteen PAH analyses in treated sediments and in seven of the sixteen PAH analyses in untreated sediments, the accuracy objective was satisfactory. No accuracy information was available for six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, chrysene, dibenzo(a,h)anthracene) analyses in treated and untreated sediment. The accuracy objective was not satisfactory for benzo(k)fluoranthene, benzo(a)pyrene, and benzo(g,h,i)perylene in untreated sediment. Accuracy information was satisfactory for fourteen of the sixteen PAH analytes in oil residue. Accuracy information was unsatisfactory for PAH analyses in water residue, except for benzo(k)fluoranthene, indeno(1,2,3,c,d)pyrene, dibenzo(a,h)anthracene. The blank analyses for the PAHs in treated and untreated sediment was satisfactory in all cases except for acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. In water residues, all PAH analyses satisfied ARCS specified QA/QC requirements for blank analyses. In all oil residues, the blank analyses exceeded the detection limit specified in the QAPP. Both initial and ongoing calibration information for PAH analyses met the ARCS QA/QC specifications for both treated and untreated sediments, and also for water and oil residue analyses. Detection limit information was not available for PAH analyses in either sediments or residues. The precision information was satisfactory for PAH analyses in treated sediments, except for benzo(k)fluoranthene, where precision did not satisfy QA/QC requirements. The precision information was satisfactory for PAH analyses in untreated sediments except for acenaphthylene and acenaphthene, where precision information was not available, and for benzo(k)fluoranthene, where precision did not satisfy QA/QC requirements. The precision information was satisfactory for PAH analyses in oil residue, except for benzo(k)fluoranthene, where precision information did not satisfy QA/QC requirements. In water residue, precision was unsatisfactory for PAH analyses except for benzo(k)fluoranthene, indeno(1,2,3,c,d)pyrene, and dibenzo(a,h)anthracene, where precision was satisfactory. The matrix spike information was satisfactory for ten of the sixteen PAH analytes in treated sediment, for fourteen of the analytes in untreated sediment, for thirteen of the analytes in oil residues, and for three of the analytes in water residues. Surrogate recoveries were satisfactory

for PAHs in both treated and untreated sediments as well as for oil and water residue analyses.

Summary

Based on the compliance with the ARCS QA/QC requirements, SAIC was capable of supplying acceptable results for metals, conventionals, PCBs, and PAHs. The results received for all four technologies satisfied ARCS QA/QC requirements.

An examination of results of the bench scale technology demonstration data set indicates, that SAIC could have successfully provided acceptable data for all parameters. The data user should be aware that some QA/QC discrepancies were identified, as indicated by subscript 1 and 2 flags in Table 3.

NOTE

Appendix A - Laboratory Submitted Data Summary Sheets

and

Appendix D - ARCS Data Verification Templates by Parameter

are not included with this report.

Copies are available from GLNPO upon request.

APPENDIX B

QA/QC Sample Rating Factors

<u>CATEGORY</u>	<u>RATING FACTORS</u>	<u>SCORE</u>	<u>CATEGORY ACCEPTABILITY LEVEL</u>
<u>Accuracy</u>	Certified Reference Material	= 3	Acceptable = 3
<u>Precision</u>	Analytical Replicate	= 3	Acceptable = 3
<u>Spike Recovery</u>	Matrix Spike	= 3	Acceptable = 3
	Surrogate Spike (organics)	= 3	(organics) = 6
<u>Blanks</u>	Blanks	= 3	Acceptable = 3
<u>Miscellaneous</u>	Instrument Calibration (initial)	= 3	
	Instrument Calibration (on going)	= 2	
	Instrument Detection Limit	= 3	Acceptable = 3

APPENDIX C

Data Verification Flags

A = Accuracy Problem

- A₀ = no standard available/no information available**
- A₁ = accuracy limit for the reference materials exceeded**
- A₉ = accuracy is not applicable**

B = Blank Problem

- B₀ = no information available**
- B₂ = reagent blank value exceeded MDL**
- B₉ = blanks are not applicable**

C = Calibration Problem

- C₀ = no information available**
- C₁ = initial calibration problem**
- C₂ = on-going calibration problem**
- C₅ = no information on initial calibration**
- C₆ = no information on on-going calibration**
- C₉ = on-going calibration is not applicable**

D = Detection Limit Problem

- D₀ = no information available**
- D₁ = detection limit exceeded**
- D₉ = detection limit is not applicable**

H = Holding Times Exceeded

P = Precision Problem

P₀ = no information available

P₁ = precision limit for analytical replicate exceeded the QA/QC requirements

P₃ = MSD exceeded the QA/QC requirement

P₉ = precision is not applicable

S = Spike Recovery Problem

S₀ = no information available on spike

S₁ = limit of matrix spike recovery exceeded

S₂ = limit of surrogate spike recovery exceeded

S₃ = no information available on matrix spike recovery

S₅ = no information available on surrogate spike recovery

S₉ = spike recovery not applicable