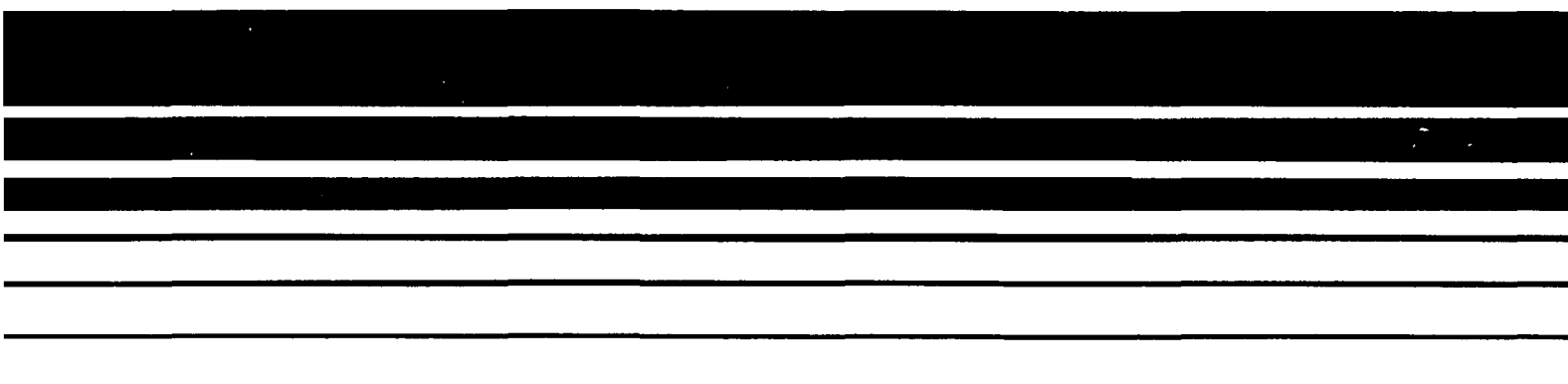




HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES HOLDING LAGOON FIELD STUDY

TEST REPORT FIRST CHEMICAL CORPORATION PASCAGOULA, MISSISSIPPI

SUMMARY REPORT



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FIRST CHEMICAL CORPORATION
WASTEWATER HOLDING
LAGOON FIELD STUDY

Final Report

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency is currently developing emission standards for hazardous waste treatment, storage and disposal facilities (TSDF). To assist with the development of these standards, EPA's Office of Air Quality Planning and Standards (OAQPS) is developing an air emissions data base designed to assess TSDF emission characteristics. Non-point sources such as ponds, land treatment areas and waste water treatment systems are the focus of some of these research activities. To date, many of the air emission estimation techniques in use assume a homogeneous composition in liquid waste impoundments, although this assumption is unverified. The principal purpose of this sampling and analytical program was to evaluate this assumption at an operating site.

1.1 Program Objectives

The primary objective of this field study was to investigate the variability of the organic chemical composition of a liquid surface impoundment at the First Chemical Corporation (FCC) in Pascagoula, Mississippi. Samples were collected from varying horizontal and vertical points within the impoundment to investigate the stratification of material in the lagoon. Below are listed some of the sampling objectives of this program:

- evaluate the three-dimensional variation of organic chemical concentrations in the FCC wastewater holding lagoon;
- collect samples for use in surrogate analytical parameter study to evaluate total organic carbon (TOC) and purgeable organic carbon (POC) as surrogate analyses;
- complete field trials of time-integrated volatile organic compounds (VOC) sampling method using a composite syringe sampler;
- measure lagoon air emissions using emissions isolation flux chambers; and

- characterize the FCC steam stripper treatment process (results are presented in "Field Evaluations of Hazardous Waste Pretreatment as an Air Pollution Technique", Draft, U.S. Environmental Protection Agency, Office of Research and Development, March 31, 1987).

To achieve these objectives a mobile office trailer was set up at FCC and an extended reach boom unit was used to access the desired sampling areas of the lagoon. Technical activities included on and offsite analyses, qualitative and quantitative measurements, visual recordings and meteorological monitoring.

1.2 Site Description

The First Chemical Corporation facility is a chemical manufacturing plant which produces primarily nitrated aromatics and aromatic amines. The raw materials for this process include benzene, toluene, nitric and sulfuric acid. The lagoon which was studied during the testing program was the wastewater holding pond for the wastewater treatment system at the plant. The wastewater treatment system includes two decant tanks, a steam stripper, carbon adsorption system, and final pH adjustment tank prior to the discharge of the wastewater stream into the Mississippi Sound.

1.3 Measurement Program

This Field Study Program was conducted at First Chemical Corporation in Pascagoula, Mississippi during a three day period from November 18 to November 20, 1985.

To investigate the stratification of organic compounds in lagoons, EPA conducted the following sampling and analysis tasks:

- collection of liquid samples from the surface and at various depths at four locations,

- bottom sludge sampling at four locations,
- onsite analysis for pH, turbidity, specific conductance, dissolved oxygen,
- liquid core sampling using a clear PVC core sampler at each sample point,
- meteorological monitoring onsite, and
- a brief study of surface wind effects using a video camera and cassette recorder.

The collection of liquid samples from the surface and at various depths, bottom sludge sampling, and the liquid core sampling were performed to detect any phase separation or stratification within the lagoon. All of the onsite analyses performed are typical indicators of contamination. The meteorological monitoring and the study on surface wind effects were performed in order to quantify evaporation rates and therefore emissions.

Direct measurement of air emission rates were made at four (4) locations concurrently with the liquid stratification sampling program. In addition, two smaller method development tasks were conducted at the FCC lagoon. As a continuing phase of a surrogate analytical parameter study, field samples were collected to further evaluate the ability of TOC and/or POC analyses to serve as surrogates for more expensive compound-specific analyses. In addition, eight (8) hour field trials of a time-integrated VOC sampling method using a composite syringe sampler were performed to further evaluate the utility of this method which may prove useful for the investigation of long-term compositional variations in liquid processes or impoundments.

1.4 Test Parameters

The parameters collected during the technical activities of this field study are itemized below:

- Stratification Study,
 1. Sample locations and depths,
 2. Sample temperatures,
 3. Liquid core pictures and descriptions,
 4. Onsite analyses: pH, turbidity, conductivity, dissolved oxygen,
 5. Laboratory analyses: GC/FID for a limited number of compounds expected to be present; for selected samples by GC/MS for all identifiable compounds which are listed below:
 - Volatiles
 - Benzene
 - Toluene
 - Acetone
 - Semi-Volatiles
 - Phenol
 - 4-Methylphenol
 - 2-Nitrophenol
 - 2,4-Dinitrophenol
 - 2-Methyl-4,6-dinitrophenol
 - Nitrobenzene
 - 2,6-Dinitrotoluene
 - 2,4-Dinitrotoluene
 - Nitroaniline isomers
 6. Meteorological data: ambient wind speed, direction, temperature, and pressure,
 7. Surface wind effects video recording, and
 8. Process data and information monitored by the plant.
- Surrogate Analytical Parameter Study
 1. Collection of additional samples for TOC and POC analyses to compare to GC/MS results from stratification study.
- Syringe Composite VOC Sampler Field Trials
 1. GC/PID analysis of 8 hour composite syringe samples, and
 2. GC/PID analysis of grab samples collected at 2 hour intervals for comparison to composite syringe samples.
- Direct Emissions Measurement
 1. Sample location
 2. Surface liquid concentration
 3. Flux chamber concentrations of specific compounds
 4. Flux chamber purge rate

1.5 Description of Report Sections

The remaining sections of this report present the summary of results and conclusions in Section 2, process description and operation in Section 3, sampling locations in Section 4, sampling and analytical methods in Section 5, detailed results in Section 6, and quality assurance results in Section 7. Also, included as Appendix A is raw data and Appendix B, the report on the flux chamber air emission study.

More detailed description of procedures and methods can be found in the Quality Assurance Project Plan (QAPP) for this program.

2.0 SUMMARY OF RESULTS AND CONCLUSIONS

2.1 Stratification Study

The stratification study results are based upon samples collected at four locations in the wastewater holding lagoon. Samples of liquid and sludge were collected at up to five vertical points at each of these locations. Table 2-1 summarizes the organic analysis results from these samples. The results are presented separately for the liquid and sludge samples. Based on the results of sample analyses, no clear pattern of stratification, either horizontally or vertically, exists in either the liquid or sludge phases in the lagoon. However, the sludge layer is much more concentrated with both volatile and semivolatile organic compounds. Comparison of the calculated relative standard deviations (RSD) included in Table 2-1 with the sampling and analytical method precision estimates reported in the Section 7, Quality Assurance, reveals that the variations in the reported concentrations in both phases are similar in magnitude to the precision estimates reported for the methodology utilized to generate the data.

The data show that approximately 100 times more organic material is present in the bottom sludge than in the liquid phase in the lagoon. This observation is based only on the target compounds analyzed by GC/FID and is, therefore, an underestimate since the GC/MS analyses confirmed the presence of additional compounds in both phases. (Detailed results documenting this conclusion appear in Table 6-6.)

Further review of the onsite analytical results (pH, turbidity, specific conductance and dissolved oxygen) generally supports the nonstratified lagoon conclusion. The two parameters which show variation with depth were pH, which ranged from 4 at the surface to 1 in the bottom sludge, and conductivity, which ranged from 15,000 mhos/cm at the surface to about 60,000 mhos/cm in the bottom sludge.

TABLE 2-1
SUMMARY OF RESULTS¹ STRATIFICATION STUDY

DATE	SAMPLE ³ LOCATION	SAMPLE TYPE	SAMPLE DEPTH	Nitro- benzene	2,4-Dinitro- phenol	4,6-Dinitro- 6-cresol	Benzene	Toluene	2,4-Dinitro- toluene	2-Nitro- phenol
	A-1	LIQUID	0-.3m	440	1,400	32	12	<1	<11	3.5
	B-1	LIQUID	0-.3m	630	160	38	15	<5	<20	<43
	E-1	LIQUID	0-.3m	390	130	25	17	<5	<11	3.5
	F-1	LIQUID	0-.3m	670	470	63	16	<5	<10	<16
	A-2	LIQUID	0.9m	560	250	28	13	<5	<10	<16
	B-2	LIQUID	0.9m	880	320	45	23	<5	<20	<43
	E-2	LIQUID	0.9m	420	<20	15	21	<5	<10	<16
	F-2	LIQUID	0.9m	460	2,000	82	30	<5	<20	<43
	A-3	LIQUID	1.2m	480	210	45	9.4	<5	<10	<16
	E-3	LIQUID	1.2m	380	260	<10	32	<5	<10	<16
	F-3	LIQUID	1.2m	350	110	30	59	<20	<20	<43
	A-4	LIQUID	1.5m	1,100	210	56	23,000 ²	9,900	11	<16
		AVERAGE		563	460	38	22	NA	NA	NA
		SUM(X _i ²)		4,374,800	6,556,200	22,881	7,546.36	NA	NA	NA
		(SUM X _i) ²		45,697,600	30,470,400	210,681	61,206.76	NA	NA	NA
		STD. DEV.		227	604	22	14	NA	NA	NA
		REL.STD.DEV.		40	131	58	63	NA	NA	NA
	A-5	SLUDGE	1.8m	97,000	4,600	2,300	1,000	520	340	260
	B-5	SLUDGE	1.2m	130,000	18,000	7,700	1,000	250	1,400	860
	E-5	SLUDGE	1.5m	14,000	9,300	3,300	372	73	315	1,000
	F-5	SLUDGE	1.5m	120,000	5,200	2,600	2,400	580	380	320
		AVERAGE		87,750	9,275	3,975	1,193	356	609	610
		SUM(X _i ²)		3.91E+10	4.59E+08	8.22E+07	7.90E+05	6.75E+05	2.32E+06	1.91E+06
		(SUM X _i) ²		1.23E+11	1.38E+10	2.53E+08	2.28E+07	2.02E+06	5.93E+06	5.95E+06
		STD. DEV.		52,487	6,180	2,518	857	237	528	375
		REL.STD.DEV.		60	67	63	72	67	87	61

¹ Concentration results are GC/FID analyses, in mg/l for liquids, and mg/kg for sludges.

² Result not included in relative standard deviation calculation due to sludge contamination in sample.

³ See Figure 4-1 for a schematic of the sampling locations in the lagoon.

2.2 Surrogate Analytical Parameter Study

The surrogate parameter study compared the GC/MS organic results to those generated by TOC and POC analyses for both liquid and sludge samples. Correlation factors were calculated based on the surrogate parameter result (POC or TOC) divided by the carbon-weighted cumulative GC/MS analysis results. The correlation factors developed from these comparisons are:

POC, liquid (volatile organics only)	4.26 ± 1.09 , 26% RSD*
TOC liquid (volatile and semivolatile organics)	3.76 ± 1.30 , 35% RSD
TOC sludge (volatile and semivolatile organics)	1.73 ± 1.01 , 58% RSD

* RSD = Relative Standard Deviation

The small size of the data set from which these comparisons were made, is insufficient to determine if the shift from a 1:1 correlation and/or the 26 percent to 58 percent relative standard deviation (RSD) are truly characteristic of the performance of these proposed surrogate parameters. More data are required to further evaluate the performance and adequacy of these analyses.

2.3 Syringe Sampler Field Trial

Two successful field trials were completed during this program. Utilizing the ability of the syringe pump to collect multiple samples, a total of three syringes were collected using the peristaltic pump sample delivery system and two syringes using a capillary tubing delivery system. The analytical results (GC/PID for benzene and toluene) for each composite syringe sample were

compared to the average of five grab samples collected at regular intervals during the sampling run.

In summary, losses of volatile organics were reported for both composite syringe systems. The syringe with the peristaltic pump delivery system was the better of the two syringe systems in terms of the relative amount of VOC loss. On the average the losses, represented by percent differences between the syringe composite sample and the average of five grab samples, were:

Syringe with pump - 19 percent

Syringe with capillary - 42 percent

2.4 Flux Chamber Direct Emission Measurement Program

The results of the flux chamber testing are provided in Appendix B. Calculated air emission rates from the First Chemical Corporation Wastewater Holding Lagoon ranged from 1.36×10^{-3} to 2.76×10^{-2} kg/m²/day of total nonmethane hydrocarbons, and averaged 1.10×10^{-2} kg/m²/day.

3.0 PROCESS DESCRIPTION AND OPERATION

3.1 Process Description

The wastewater treatment system at First Chemical Corporation is comprised primarily of a wastewater holding pond and a steam stripper treatment process. The process described in this section reflects revisions to that presented previously in the QAPP. The revisions are based on the collection of additional data while onsite. The process is outlined in Figure 3-1. There are four wastewater streams handled by this system, two of which pass through the entire treatment process, with two entering the system immediately prior to the discharge of the treated wastewater stream into the Mississippi Sound.

A wastewater stream which enters the process at the beginning is the nitrobenzene production wastewater (K104). This wastewater stream flows into a holding tank, called the "red" tank, due to the color of the wastewater streams. As the tank is filled, the overflow passes through a submerged outlet into the wastewater holding lagoon. The second process stream which enters the lagoon is the plant sump wastewater. This stream is intermittent and occurs primarily during periods of heavy rain. Two sump pumps are activated when needed, both of which pump into the lagoon.

The lagoon is 105m x 36m x 3m (the depth is measured from the plant roadway elevation rather than the top of the berm). It is surrounded by a cement wall and a plant roadway on the east or plant side. The wall extends .3m above the road surface. The berm on the other three sides is 1.7m wide and consists of ground seashells and extends to approximately the same height above the lagoon contents as the cement wall. The liquid level in the lagoon ranged from 4' to 7' in depth, with about 16" of freeboard (measured down from the level of the plant roadway) above the liquid surface. The remaining depth

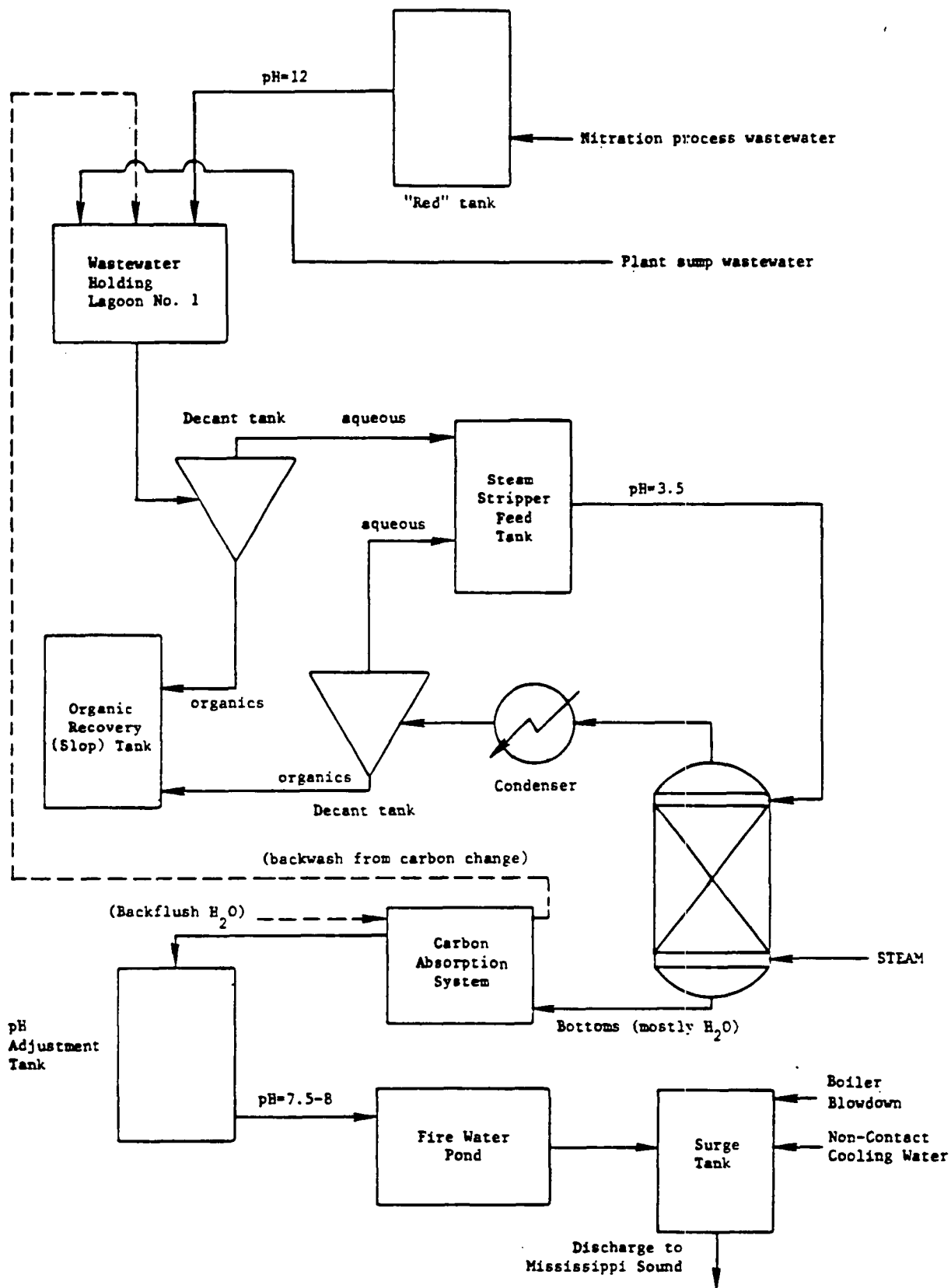


FIGURE 3-1
STEAM STRIPPER PROCESS DIAGRAM

was comprised of a bottom sludge layer the thickness of which was never measured directly. By subtraction this layer varied from about 2' to 5' deep.

From the lagoon the wastewater is pumped to the first of two decant tanks. The bottom organic layer is drawn off and pumped to a holding tank known as the organic recovery or slop tank. At the time of this study, the slop tank was a tanker truck. The tanker truck is changed when it becomes full. The tanker truck and contents are removed from the plant and sold to another chemical plant where this organic waste is used as an alternate fuel source. The aqueous top layer from the initial decant tank flows to the steam stripper feed tank where the pH is adjusted to approximately 3.5.

After pH adjustment, the wastewater stream is fed to the steam stripper. The average feed rate is reported to be 90-100 gal/min to the stripper. Steam is fed directly into the bottom of the stripper, stripping the organics from the wastewater as it passes up through the stripper. The overhead from the stripper passes through a condenser to the second decant tank. The bottom organic layer in the decant tank is pumped off to the slop tank, while the top aqueous layer overflows to return to the steam stripper feed tank. The bottoms from the steam stripper which are mainly water, are then pumped through a carbon adsorption system consisting of two columns in parallel. One column is in use at any particular time while the second column is being recharged. A carbon column recharge occurs twice daily (once per day per column) and involves backflushing the column with water and pumping of this backflush water to the wastewater holding lagoon. The carbon recharge water is splash filled into the lagoon through a pipe approximately 2 feet above the lagoon liquid surface. This recharge process removes carbon fines from the columns and possibly contributes to a surface sludge layer in the lagoon which appears as a floating black foam. Fresh carbon is added to the column after the backwash cycle. Calgon Activated Carbon Division has a service contract

with First Chemical to provide fresh carbon and for the removal and disposal of the spent carbon.

After passing through the activated carbon system, the wastewater is pumped to a pH adjustment tank where the pH is adjusted to 7.5 to 8. After pH adjustment the wastewater stream passes to a fire water holding pond. Overflow from the fire water holding pond passes to a surge tank where two additional wastewater streams are added, a boiler blowdown stream and a non-contact cooling water stream. The combined streams are then discharged to the Mississippi Sound.

Table 3-1 presents the liquid sludge and total depth measurements taken during this testing program. The depths were used to calculate total waste volumes and amounts. A summary of the physical characteristics of the Lagoon is provided as Table 3-2. This table includes dimensions, volumes, estimates of retention time and other descriptive information regarding the wastewater holding lagoon.

TABLE 3-1
LAGOON DEPTHS IN METERS

Sample ¹ Location	Liquid	Sludge	Freeboard	Total
A	1.29	1.00	0.76	3.05
B	0.93	1.36	0.76	3.05
E	0.95	1.34	0.76	3.05
F	1.15	1.14	0.76	3.05
Avg.	1.08	1.21	0.76	3.05

¹ See Figure 4-1 for a diagram of the sampling locations.

3.2 Process Operating Conditions

Based on the information obtained in the pretest survey conducted in September 1985, a list of process operational variables was developed for

TABLE 3-2

WASTEWATER HOLDING LAGOON GENERAL CHARACTERISTICS

Variable	Value
Dimension	105m x 36m x 3m
Type of Sides	1:1 slope
Total Capacity	12,000 cubic meters
Berm Type	Crushed Seashells 1m high x 1.5m wide
Liner Type	Packed Clay
Soil Type down to -1m depth -1m depth	Firm to loose fine silty sands Soft clays
Average Depth	
Freeboard	0.8 meters
Liquid	1.1 meters
Sludge	1.1 meters
Estimated Waste Volume	
Liquid	4,400 cubic meters
Sludge	4,100 cubic meters
Retention Time	20.8 days
Influent Wastestreams	K104 - wastewater from production of nitrobenzene
Wastestream Data	
K083	0.1% sulfur 0.1% chloride 10.5% total water pH = 7.4 10,600 Btu/lb Flashpoint = 117 (F) Viscosity = 4.3 (cs)
K104	4.5 ppm phenol 27 ppm 2-nitrophenol 360 ppm 2,4-dinitrophenol 77 ppm 2,6-dinitrophenol 2,000 ppm nitrobenzene pH = 2.6

TABLE 3-3

PROCESS OPERATING PARAMETERS EFFLUENT CONTROL SYSTEM*

Date	Time	Feed Rate to Steam Stripper (gpm)	Inlet to Steam Stripper (pH)	Steam Rate to Stripper (lb/hr)
11/18/85	0500	116	1.93	
	0700	114	2.63	
	0900	114	1.57	4100
	1100	116	4	3700
	1300	120	1.57	3800
	1500	126	1.46	3558
	1700	126	1.67	3558
	1900	120	1.77	3640
	2100	122	1.4	3580
	2300	112	1.58	3765
11/19/85	0100	120	1.5	3547
	0300	110	1.61	2901
	0500			
	0700			
	0900			
	1100		2.01	
	1300			3000
	1500	183	1.85	3572
	1700			
	1900	187	1.85	3740
	2100	195	1.7	3740
	2300	196	1.77	3790
11/20/85	0100	190	1.75	3859
	0300	191	1.81	3944
	0500	194	1.84	3925

* All data included in this table is from the Effluent Control System Data Log provided by First Chemical Corporation.

collection during testing. Data for many variables on this list were unavailable because the plant does not monitor flowrates for many of the selected locations. Copies of the First Chemical Effluent Control System Data Log are included in Appendix A of this report. Selected parameters from this data log are presented in Table 3-3, Process Variables.

Because of an approaching hurricane, an abnormal process condition occurred on 11/20/85, the last or second day of lagoon sampling. The hurricane watch safety practices used by First Chemical included an increase in the process rate for the steam stripper to reduce the liquid level in the lagoon to prevent an overflow in the event of heavy rainfall. The increased rate is noticeable in the stripper feed rate data. During an actual hurricane the production processes are stopped which would further serve to reduce wastewater flow into the lagoon. Weather predictions of the storm track forced evacuation of all testing program personnel from the site by the end of the day on 11/20/85, therefore, the testing program was terminated at this time.

The following flowrates, which were proposed for data collection during the program, were not available:

- decant water return flowrate to the feed tank;
- plant sump wastewater flowrate (this flow was estimated by plant personnel using a flow integrator at about 1,400 gallons for 11/19/85);
- primary plant effluent flowrate;
- boiler blowdown flowrate;
- non-contact cooling water flowrate and
- flowrate through the carbon beds (this flow is reported to be essentially the same as the feedrate to the steam stripper since the only difference is the organic material which is sent to the slop tank).

4.0 SAMPLING LOCATIONS

4.1 Stratification Study

Sampling locations at the FCC wastewater holding lagoon were selected using a systematic approach. The lagoon was divided into fifteen grids of equal area. Figure 4-1 illustrates the lagoon grids and identifies the four grids that were sampled, labeled as A, B, E and F. The grids each represented an area of about 40' x 70' (12m x 21m), or 2800 ft² (252 m²) of the total 117' x 345' (36m x 105m) or 40,365 ft² (3780 m²) for the entire lagoon.

Figure 4-1 has been revised since its inclusion in the QAPP utilizing information obtained from the plant engineering personnel during the field study. The revision entails a correction to the labelling of the influents to the lagoon. Details of these corrections are included in the process description discussion in Section 3 of this report. Originally, it was proposed that eight (8) of the fifteen (15) total grids would be sampled during the field study. These eight grids were labeled A through H in the QAPP. The grids were selected to include in the sampling plan all pertinent areas of the lagoon including active areas near the inflows and outflows, potential stagnant areas in the corners and offshore points near the center line of the lagoon.

During the planning of the sampling program collection of QC samples were determined by assigning method specific QC set collection to specific sampling points: (these designations are detailed in the Table 4-1 of the QAPP and revised in Table 4-1 of this report).

<u>Location</u>	<u>QC Set Designation</u>
A	none
B-1	GC/FID VOC & SVOC
C-3	GC/FID VOC & SVOC
D-4	GC/FID VOC & SVOC
E-5	GC/FID VOC & SVOC
F-1	POC
G-1	TOC
H-5	TOC

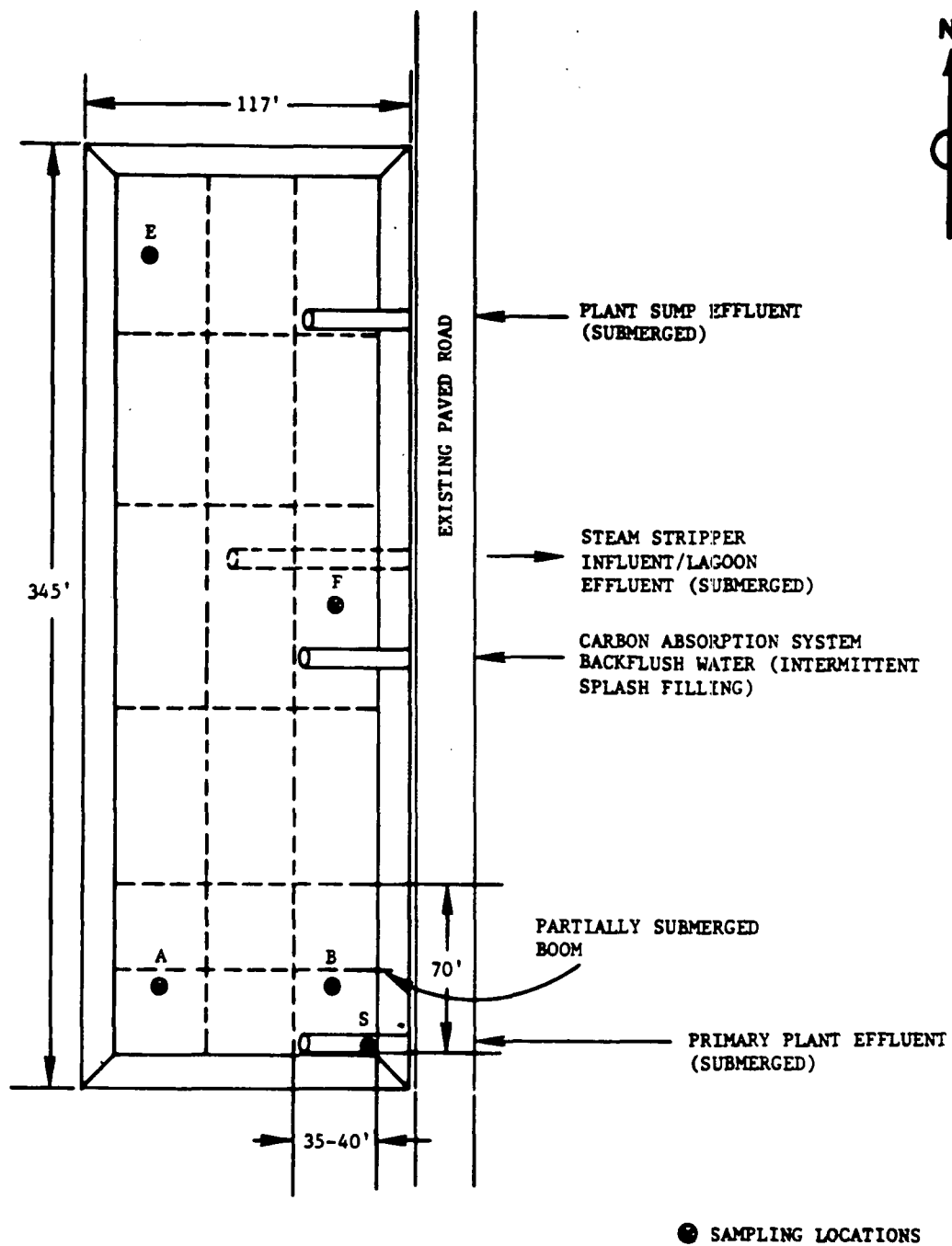


FIGURE 4-1

FCC WASTEWATER HOLDING LAGOON SCHEMATIC AND SAMPLING LOCATIONS

TABLE 4-1
SAMPLING SUMMARY

Location	Depth (meters)	Matrix	Sampling method	GC/FID VOA 40 ml septum vial	GC/MS VOA 40 ml septum vial	GC/FID SVOC 250 or 500 ml Amber glass	GC/MS SVOC 250 or 500 ml Amber glass	Onsite ^a analysis 250 ml Amber glass	TOC 40 ml septum vial	POC 40 ml septum vial
A-1 ^b	0.3	Liquid	Bacon Bomb	X	X	X	X	X	X	X
A-2	0.9	Liquid	Bacon Bomb	X		X		X		
A-3	1.2	Liquid	Bacon Bomb	X		X		X		
A-4	1.5	Liquid	Bacon Bomb	X		X		X		
A-5	1.8	Sediment	Ponar Grab	X	X	X	X	c	X	
B-1 ^b	0.3	Liquid	Bacon Bomb	X*	X	X	X	X	X	X
B-2	0.9	Liquid	Bacon Bomb	X		X		X		
B-5	1.2	Sediment	Ponar Grab	X	X	X	X	c	X	
E-1 ^b	0.3	Liquid	Bacon Bomb	X	X	X	X	d	X	X
E-2	0.9	Liquid	Bacon Bomb	X		X		d		
E-3	1.2	Liquid	Bacon Bomb	X		X		d		
E-5	1.5	Sediment	Ponar Grab	X*	X	X*	X	d	X	
F-1 ^b	0.3	Liquid	Bacon Bomb	X	X	X	X	X	X	X*
F-2	0.9	Liquid	Bacon Bomb	X		X		X		
F-3	1.2	Liquid	Bacon Bomb	X		X		X		
F-5	1.5	Sediment	Ponar Grab	X	X	X		c	X	

^a Onsite analyses included temperature, pH, conductivity, turbidity and dissolved oxygen.

^b Liquid core sample collected for full depth of lagoon at this location.

^c Sediment pH was measured using pH paper, and was the only onsite analytical parameter measured for sediment samples.

^d Onsite laboratory inoperative, therefore, onsite analysis data not available.

* Indicates QC sample set collected at this location for the designated analysis.

The sample locations were not actually assigned to physical points in the lagoon until the field sampling was initiated, since an arbitrary assignment might not provide for optimal returns on the placement of QC set collection within the lagoon.

On November 19 and 20 two grids were sampled each day for a total of four sample locations. Locations A and B were selected for November 19 for several reasons discussed below. The movement of a hurricane weather system into the Pascagoula, MS area on November 20, 1985, made it necessary to select the best two of the remaining six locations for collection on November 20. Locations E and F were selected for the reasons also listed below.

11/19/85 Locations A & B

- These two grids, A and B, were closest to the primary plant effluent along the south side of the lagoon and would possibly provide data most representative of the worst case concentrations in the lagoon.
- Grid location A was designated for no QC sampling and was, therefore, the best choice as the first sampling point for the team to accomplish.
- Grid location B was designated for a GC/FID QC sample set for the surface liquid layer. GC/FID analyses are the primary analyses for the stratification study, therefore, this grid location was selected as the second point.
- On the first day of sampling, it was unclear as to how much time sampling would require, therefore, the two sampled locations were selected side by side to minimize change-over time.

11/20/85 Location E

- Grid E was chosen to collect samples along the north side of the lagoon. The north side location provides a sampling site near the plant sump waste inflow.
- Location E was also selected as a possible "stagnant" area site. The major inflows and outflows are in the south half of the lagoon which might contribute to more static conditions in the north half.

- Originally, site E was chosen to provide one set of samples collected at a site where the surface sludge layer was present. Figure 4-2 illustrates the condition of this layer for the two sampling days. A wind direction change on 11/20/85 prevented this goal from being attained as the sludge layer was blown back to the already sampled south end of the lagoon.

11/20/85 Location F

- Grid location F was selected as the third sampling point due to its proximity to the lagoon effluent. This point was thought to be fairly representative of the steam stripper inlet material.
- Grid F was close to the carbon absorption system backflush water effluent stream which is the major secondary lagoon influent waste water stream.
- The central location selected for F was also intended to obtain samples from the middle of the lagoon.
- Grid F was designated as the point for a QC sample set for POC and as was therefore an important part of the surrogate analytical parameter study.
- Location F was designated for a QC set for the sediment layer by GD/FID.

Table 4-1 summarizes the sampling methods utilized at the various sample locations and lists the designated analyses.

4.2 Surrogate Analytical Parameter Study

Samples collected for analysis by the surrogate techniques, TOC and POC, were collected simultaneously with the stratification study sampling. Table 4-1 outlines the surrogate sampling. In summary, TOC and POC samples were collected from the surface liquid layer at all four locations plus TOC samples from the bottom sludge layer at all four locations.

4.3 Composite VOC Syringe Sample Study

Composite syringe samples and grab samples were collected from the surface liquid layer at the southeast (SE) corner of the lagoon. This corner was

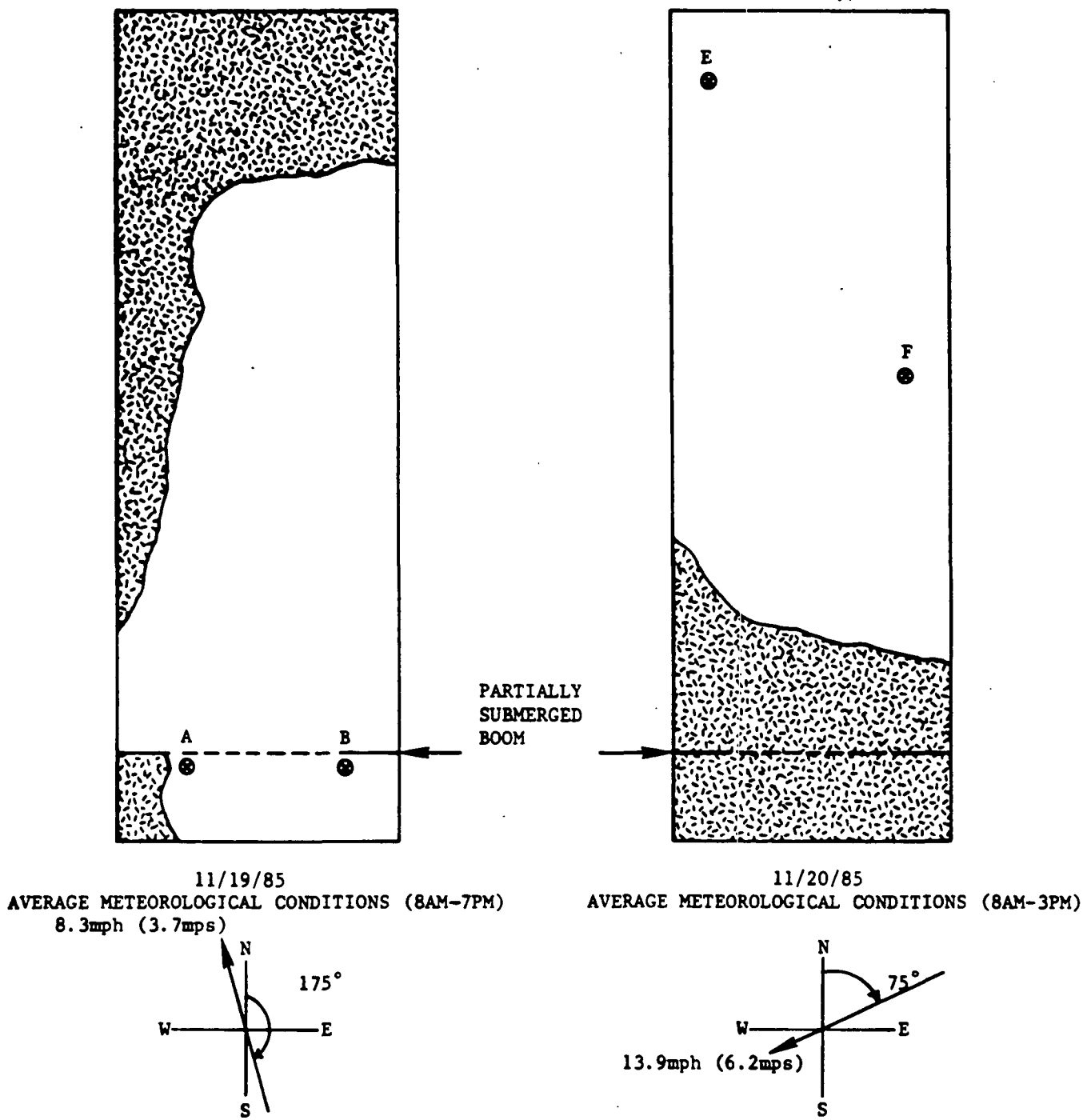


FIGURE 4-2
APPROXIMATE CONDITION OF SURFACE SLUDGE LAYER AT FCC LAGOON

nearest to the main lagoon influent and it was thought that it would yield the highest volatile organics (benzene, toluene) concentrations for this study. The samples were collected through sample lines which extended approximately two feet into the lagoon from the SE corner. The sampling location, designated S, is identified in Figure 4-1.

4.4 Steam Stripper Process Study

The steam stripper process was sampled for one day in conjunction with other work being done by EPA-ORD. The results of this study will be presented in a separate report by EPA-ORD. The sampling performed is outlined in Table 4-2 and Figure 4-3. Table 4-2 summarizes the sampling information and Figure 4-3 illustrates the sampling locations.

4.5 Direct Emissions Measurement Program

Direct emissions measurements were conducted using isolation flux chambers at the four grid points A, B, E, and F. Figure 4-4 presents a diagram of the floating flux chamber sampling system. Sampling involved the collection of teflon air syringes for onsite analysis, and evacuated electropolished stainless steel canister samples for laboratory analysis. Further details can be found in the report included as Appendix B. It should be noted that the lagoon schematic and sampling locations, Figure 3-1 of the report in Appendix B do not reflect the revised influent/effluent designation or the location and extent of the surface sludge layer on the sampling days. Figures 4-1 and 4-2 are more accurate representations of these features.

TABLE 4-2
STEAM STRIPPER SAMPLING

Location	Sample Type/ Analytical Parameter	Number	Sample Volume	Number Duplicates
1. Influent to Stripper	Liquid/VOC	4	40 ml	1
	Liquid/pH ^b	4	50 ml	1
	Liquid/Diss. Solids	1	200 ml	1
2. Stripper Eff./ CA Influent	Liquid/VOC	4	40 ml	1
3. Carbon Absorption (CA) Unit Effluent	Liquid/VOC	4	40 ml	0
4. Aqueous Condensate	Liquid/VOC	4	40 ml	0
5. Organic Condensate	Liquid/VOC	2	40 ml	0
6. Tank Vent	Gas/VOC ^c	4	N/A	1
	Tank Vent Gas Flow ^e Rate	4	800 ml ^e	1

a All liquid samples were grab samples as per Section 4.3.3 of the QAPP except where sampling was conducted from a process line equipped with a valve or tap. In this case, the valve was purged prior to sample collection. The dissolved solids sample was collected in a 200 ml nalgene bottle. Also, one liquid field biased blank (FBB) for VOCs was collected on the day of sampling.

b pH was measured in the field.

c Tank vent was grab sampled at sample location designated on Figure 4-3.

d Gas samples were collected in 800 ml stainless steel sampling canisters. Onsite VOC readings using a portable analyzer were also conducted.

e Gas velocity was measured in the field using a "pitot" type system. The sampling location was an 1" ID vent pipe which was not amenable to velocity monitoring using a conventional EPA Reference Method pitot tube system. Figure 5-6 illustrates the system utilized in an attempt to get an estimate of the gas velocity. Data generated using this system is highly suspect and only useful as an estimate.

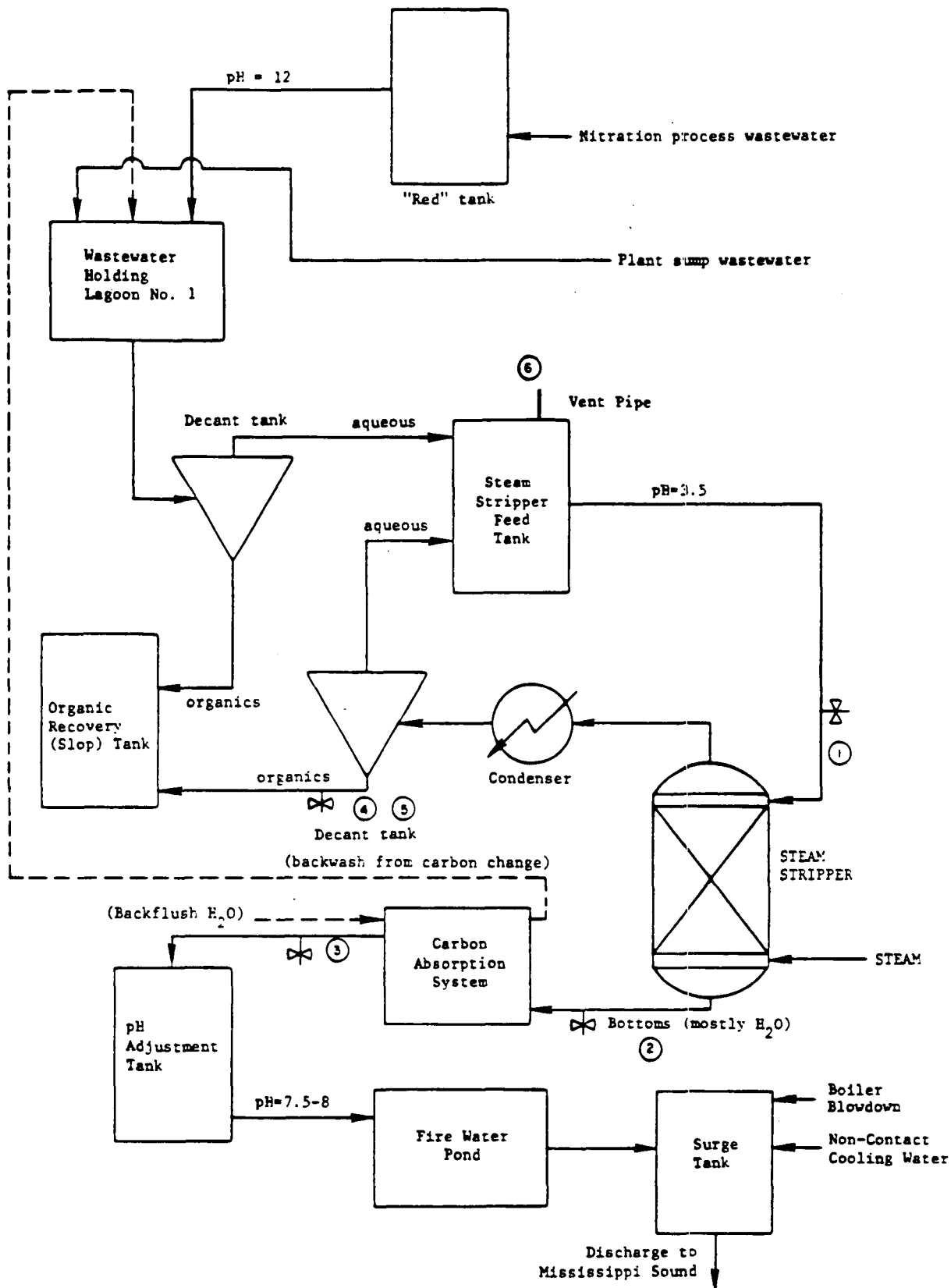
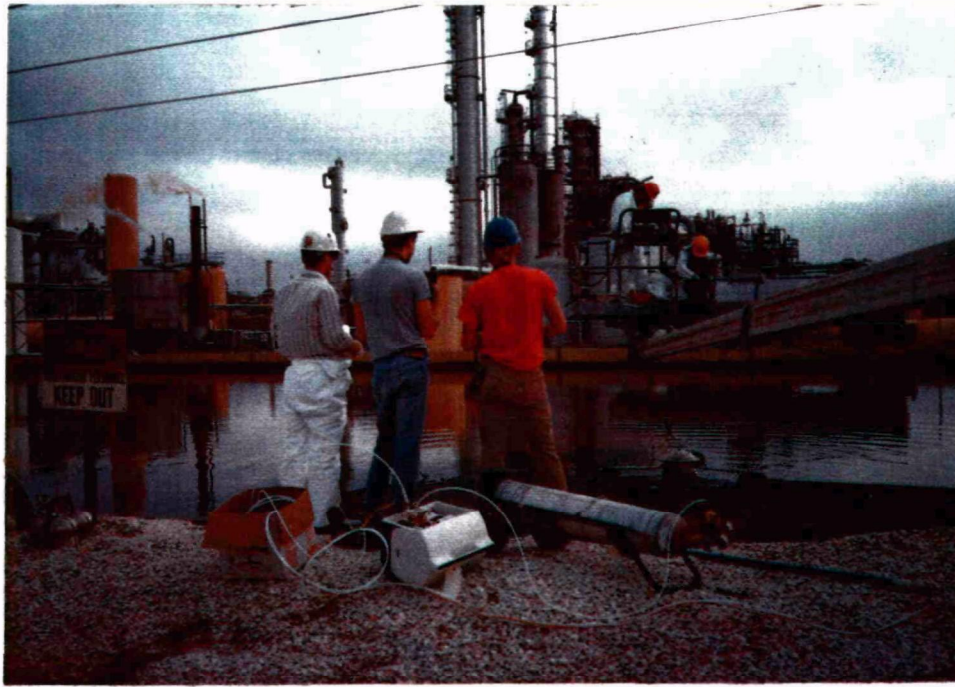


FIGURE 4-3
STEAM STRIPPER PROCESS SAMPLING LOCATIONS

FIGURE 4-4

FLOATING FLUX CHAMBER AND SUPPORT EQUIPMENT



5.0 SAMPLING AND ANALYTICAL METHODS

All sampling and analysis procedures utilized to conduct this field study are fully described in the Quality Assurance Project Plan (QA-064, submitted under EPA Contract 68-02-3892, WA Number 13). Brief overviews and discussions are included in this section of the report along with diagrams illustrating the equipment utilized. All sample containers and sampling equipment were precleaned and prepared as required in the QAPP. Sample coding and preservation procedures for collected samples were also adhered to during this field program. Any deviations or modifications to the procedures and methods described in the QAPP are summarized in Section 7, Quality Assurance.

5.1 Sampling Equipment/Procedures

5.1.1 Liquid and Sediment Sampling

Bacon Bomb Sampler

This sampler was used to obtain liquid grab samples from a specified depth in the lagoon. Made completely of brass, and heavily nickel plated, the bomb is designed to open automatically when the protruding plunger strikes the bottom of a storage tank (see Figure 5-1). The plunger seals automatically when the bomb is raised. For collecting samples at specified depths as intended during this program, a cord was attached to the upper end of the plunger (Figure 5-1, Chain B). A slight pull on the cord opens the bomb; closing is automatic when the tension on the cord is released. Samples were aliquotted from the 500 or 1000 ml sampling capacity of the Bacon Bomb.

The samplers were cleaned with Alconox and water, with a distilled water rinse prior to sampling at each of the four sample locations. Alternatively, if the sampler required additional cleaning between points, an Alconox and water cleaning solution was added. To prevent contamination of samples, no organic solvents were used onsite.

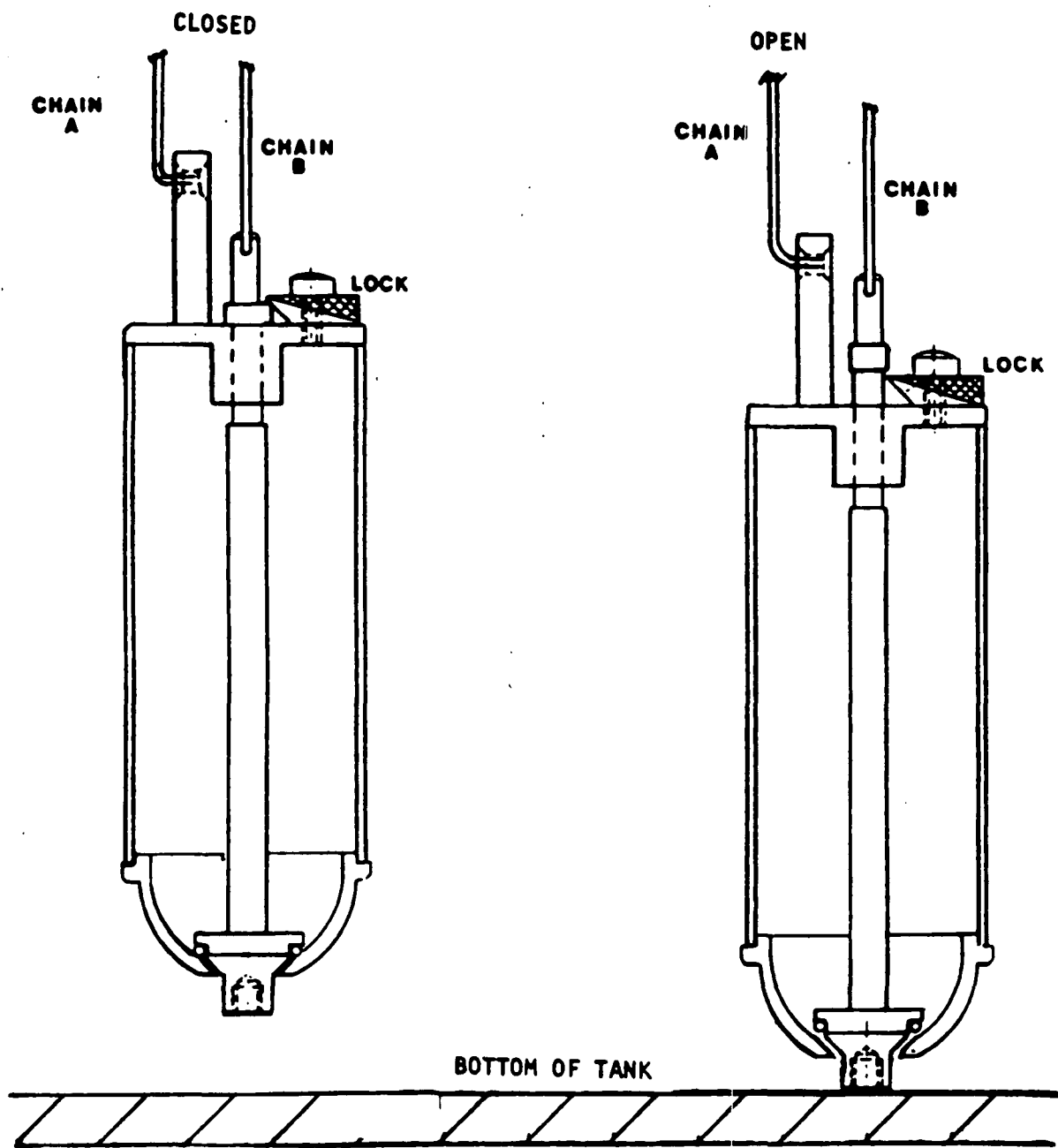


FIGURE 5-1
BACON BOMB SAMPLER

Ponar Grab Sediment Sampler

The Ponar grab sampler is a clamshell type scoop activated by a counter lever system. The shell is opened and latched in place and slowly lowered to the bottom. When tension is released on the lowering cable the latch releases and the lifting action of the cable on the lever system closes the clamshell (see Figure 5-2).

The Ponar sampler was used to sample sediment and sludge from the bottom of the lagoon. The "petite" version was used so it could be operated without a winch or crane.

Penetration depths did not usually exceed several centimeters. Grab samplers are not capable of collecting undisturbed samples. As a result, material in the first centimeter of sludge cannot be separated from that at lower depths. The sampling action of these devices causes agitation currents which may temporarily resuspend some settled solids. This disturbance was minimized by slowly lowering the sampler the last half meter and allowing a soft contact with the bottom. Sediment samples were collected after all overlying water samples were obtained. The sediment sample from the sampler was emptied into a large stainless steel bowl from which the sample bottles were then filled.

Liquid Core Sampler

The liquid core sampler is a modification of the COLIWASA, a much cited sampler designed to permit representative sampling of multiphase wastes. The sampler is fabricated from a variety of materials including PVC and Teflon. In this configuration it consisted of a section of 1 in. ID clear PVC tubing with a Teflon stopper at one end attached by a wire running the length of the tube to a locking mechanism at the other end. Manipulation of the wire locking mechanism opens and closes the sampler by raising and lowering the

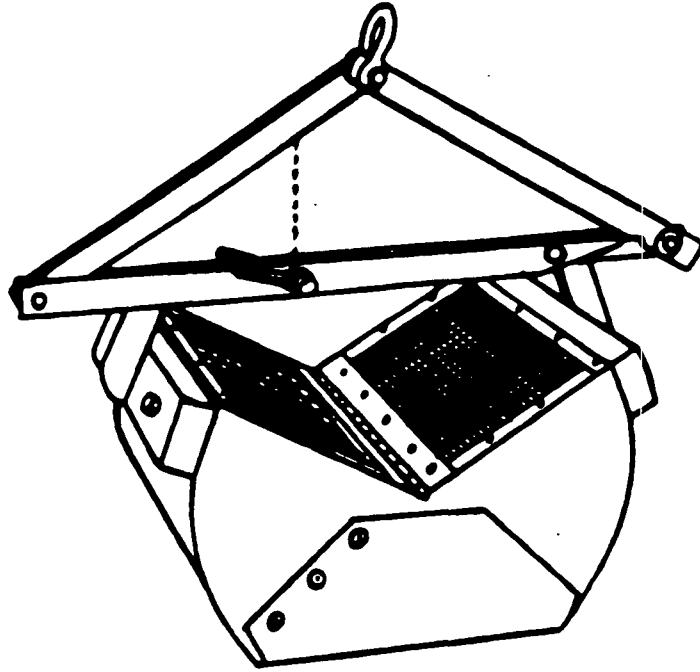


FIGURE 5-2
PONAR GRAB SAMPLER

Teflon stopper. A schematic of the Liquid Core Sampler is shown in Figure 5-3. The Liquid Core Sampler was used at each sample location.

Flanges were cemented to one end of the sampler so that it could be extended for greater depths by adding additional 5 ft lengths of PVC tubing. After photo documentation (see photos, Figures 6-1 through 6-4), the liquid core sample was dumped back into the lagoon.

Liquid Grab Sampling With a Telescoping Pole Sampler

Impoundment grab samples were collected using telescoping aluminum poles modified to hold a sample collection vial, illustrated in Figure 5-4. The collection containers were glass septum vials with a capacity of 40 ml. The screw caps have a center hole and a Teflon-faced silicone septum which is used to seal the vial. Vials and septa were detergent-washed, tap and distilled water rinsed and oven dried at 105°C prior to use.

The general procedure used for the collection of samples is to secure the sample vial to the pole with a screw clamp, extend the pole to the required length and gently submerge and fill the vial. The sample is then carefully retrieved and sealed using the septum cap, such that no air bubbles are entrapped in it (i.e., head space free).

Syringe Composite VOC Sampler

A previous EPA task performed involved the research, development, and testing of a composite VOC sampler for collection of liquid wastewaters. This system underwent a field trial as a part of the field program. The field trial involved the collection of duplicate syringe composites and grab samples from a readily accessible surface location at the lagoon. The average concentrations of the four grab samples collected every 2 hours were compared

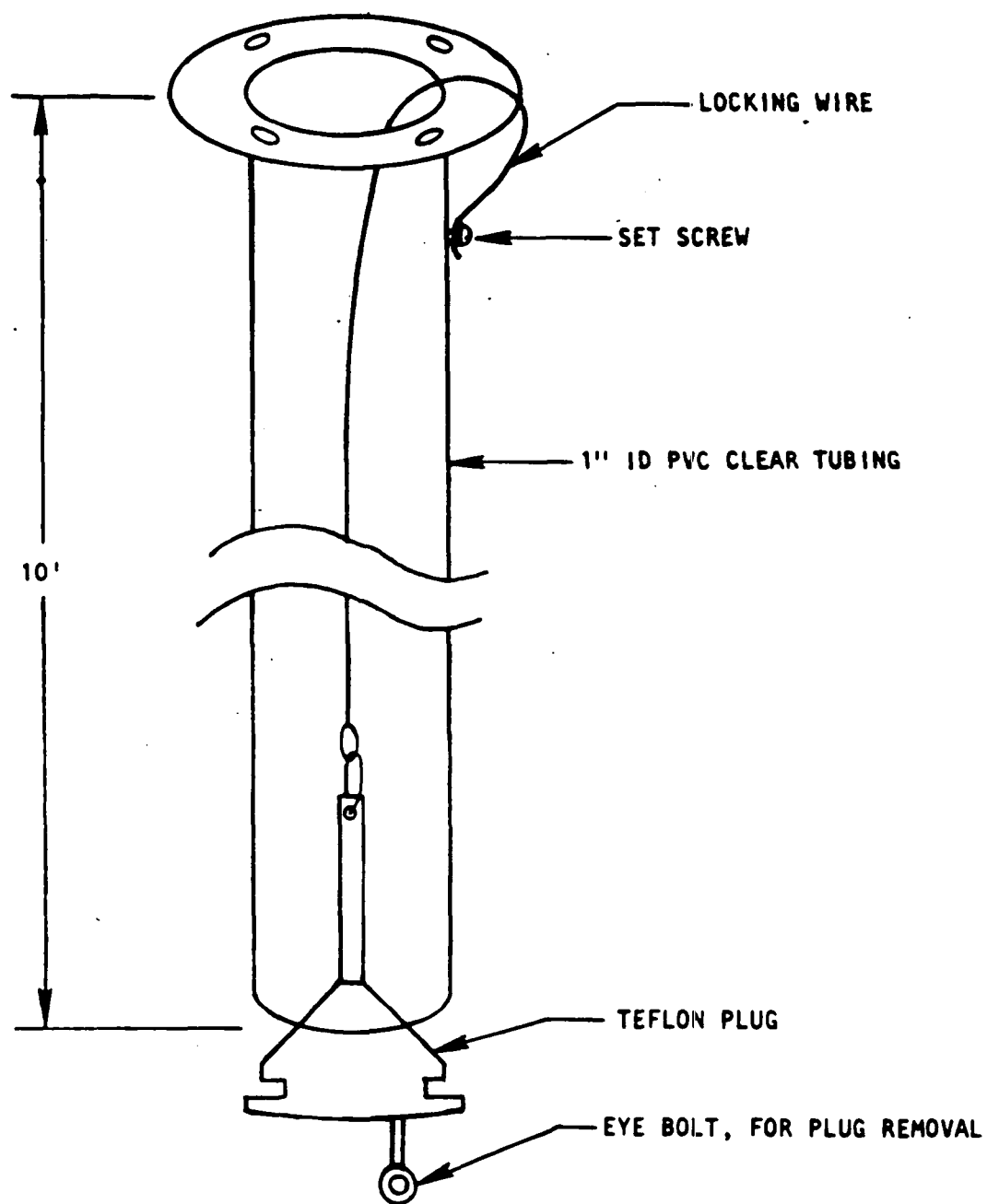


FIGURE 5-3
LIQUID CORE SAMPLER

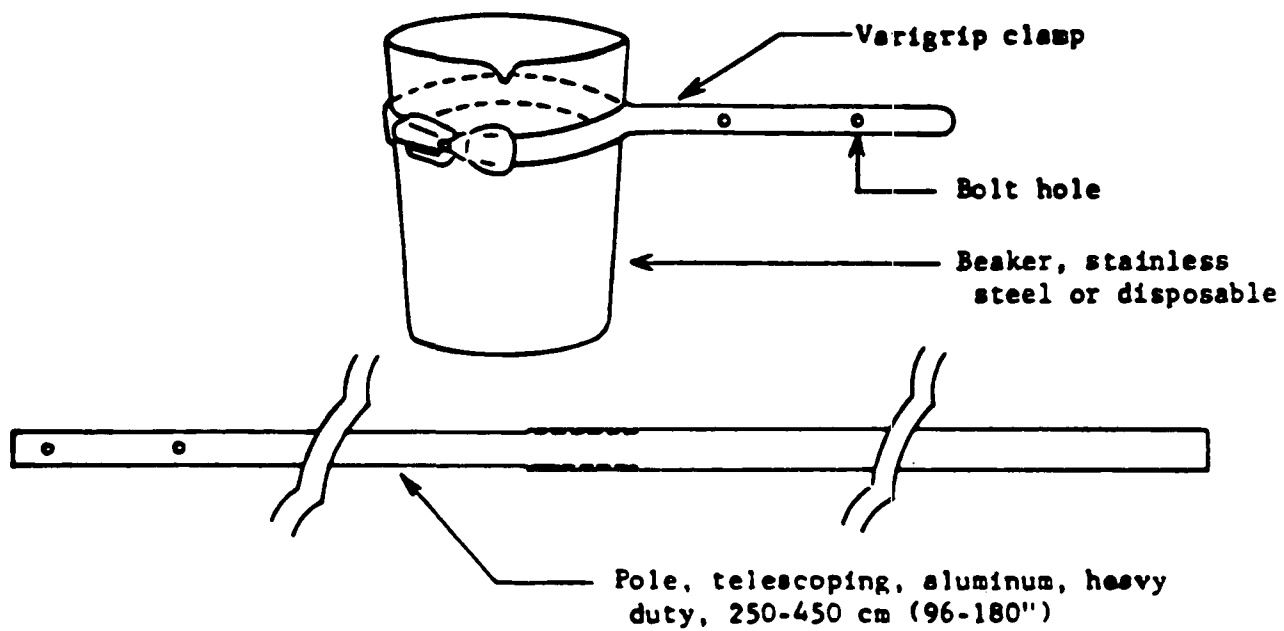


FIGURE 5-4
TELESCOPING POLE SAMPLER

to the result of the syringe composite analysis. One eight (8) hour run was conducted for each sampling day.

The syringe sampler is illustrated in Figure 5-5. The primary sample collection method utilized a peristaltic pump as illustrated in this figure. In the field, three syringes were fitted to the sampler. Two were inserted into separate septum fittings in the sample line as illustrated. The third syringe was connected to a passive collection system consisting of a length of teflon capillary tubing inserted directly onto the syringe needle. The capillary tubing was prefilled with distilled deionized water and extended into the lagoon liquid at the designated sample location. The prefilling was necessary to eliminate any air bubbles from the sample collection system prior to the syringe. At the conclusion of sampling, the inlet end of the capillary tube was inserted into a container of distilled deionized water and the syringe manually withdrawn to flush all sample from the tubing into the syringe. The volume of all diluent water used in this technique was recorded to calculate a dilution correction factor to apply during analytical data reduction.

5.1.2 Air Monitoring

Meteorological Monitoring

A meteorological monitoring station was set up at a down wind location near the lagoon. The station was equipped to measure wind speed and direction. Barometric pressure and temperature was also recorded on days of sampling using data provided through the National Weather Service from Keesler Air Force Base in Pensacola, Florida.

Meteorological equipment for the measurement of wind speed and direction was the Weather Measure Mark III Wind Measuring System. Wind speed is measured by a stainless steel three-cup anemometer, and converted to an

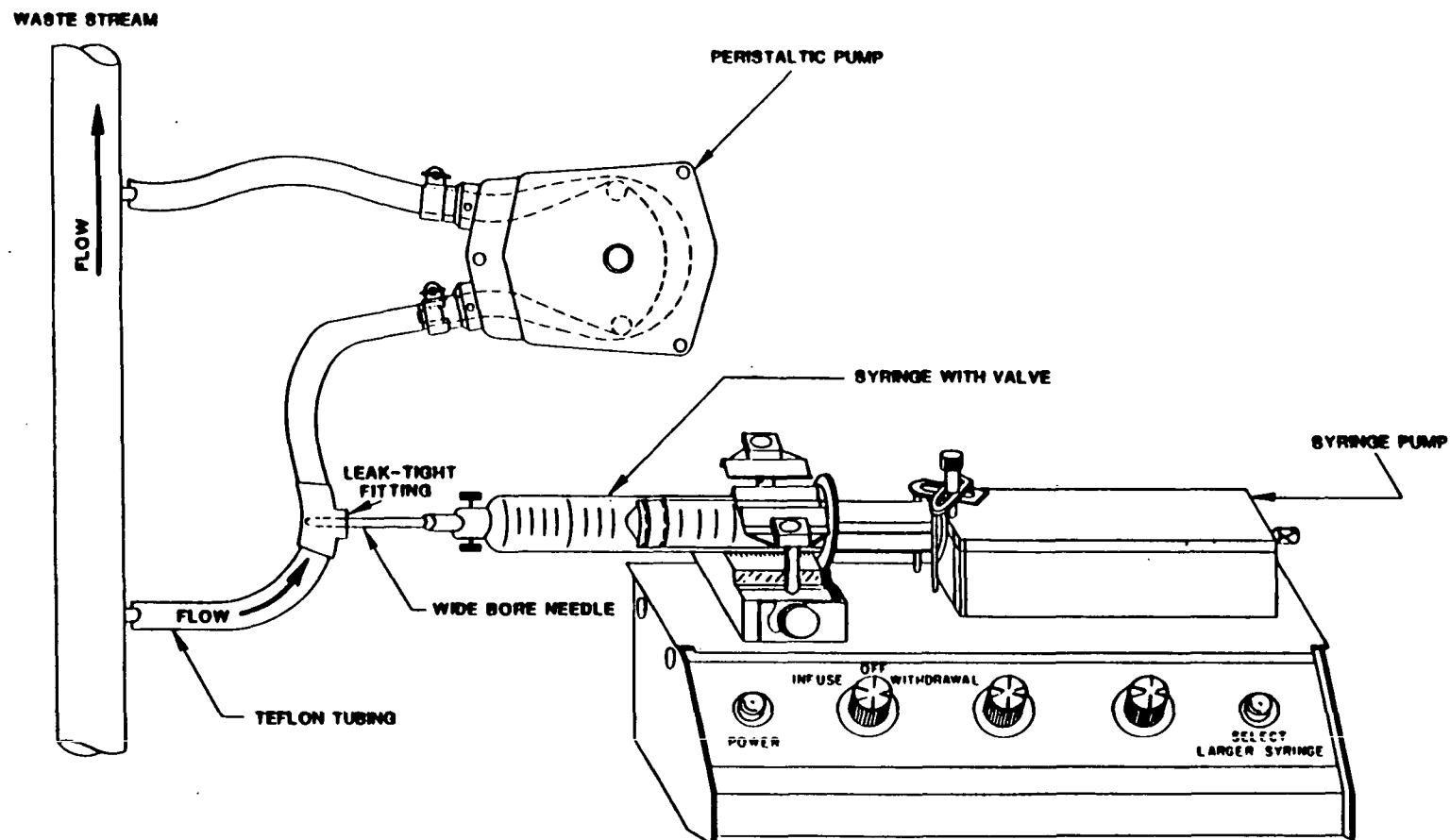


FIGURE 5-5

TIME INTEGRATED LIQUID VOLATILE ORGANIC SAMPLER

electrical signal by a photochopper, which uses a solid state light source for maximum reliability. Wind direction is obtained with a counterbalanced wind vane, coupled to a precision potentiometer. Wind speed and direction was recorded continuously on a dual channel recorder. The meteorological system was calibrated prior to installation on the site using a synchronous motor calibrator for wind speed and a compass for direction (as specified in Section 6.3 of the QAPP). Each instrument and recorder was checked daily to ensure proper operation. The strip chart was labeled for parameter, time and date.

Procedure for Surface Wind Effects Recording

Wind effects on the surface of a liquid impoundment are known to affect the mixing of dissolved and suspended materials within an impoundment. As documentation of surface wind effects, a short test of the micrometeorological conditions was conducted as close as possible to the surface of the Wastewater Holding Lagoon. In general, the test involved the generation of smoke plumes at the upwind edge of the lagoon and videocassette recording of the plumes as they pass over the lagoon surface. The plumes were generated by a carbon dioxide fire extinguisher at the edge of the wastewater lagoon. Plant personnel were consulted prior to conducting this task. The videocassette camera was mounted on a tripod at two different locations during the test, one at 90° to the plume direction and one at 0° to the plume (looking down the plume from upwind).

Flux Chamber Methodology

The stainless steel components of the flux chamber were cleaned with acetone, rinsed with water, and dried before each use. A diagram of the flux chamber is shown in Figure 5-6. The flux chamber was then placed over the

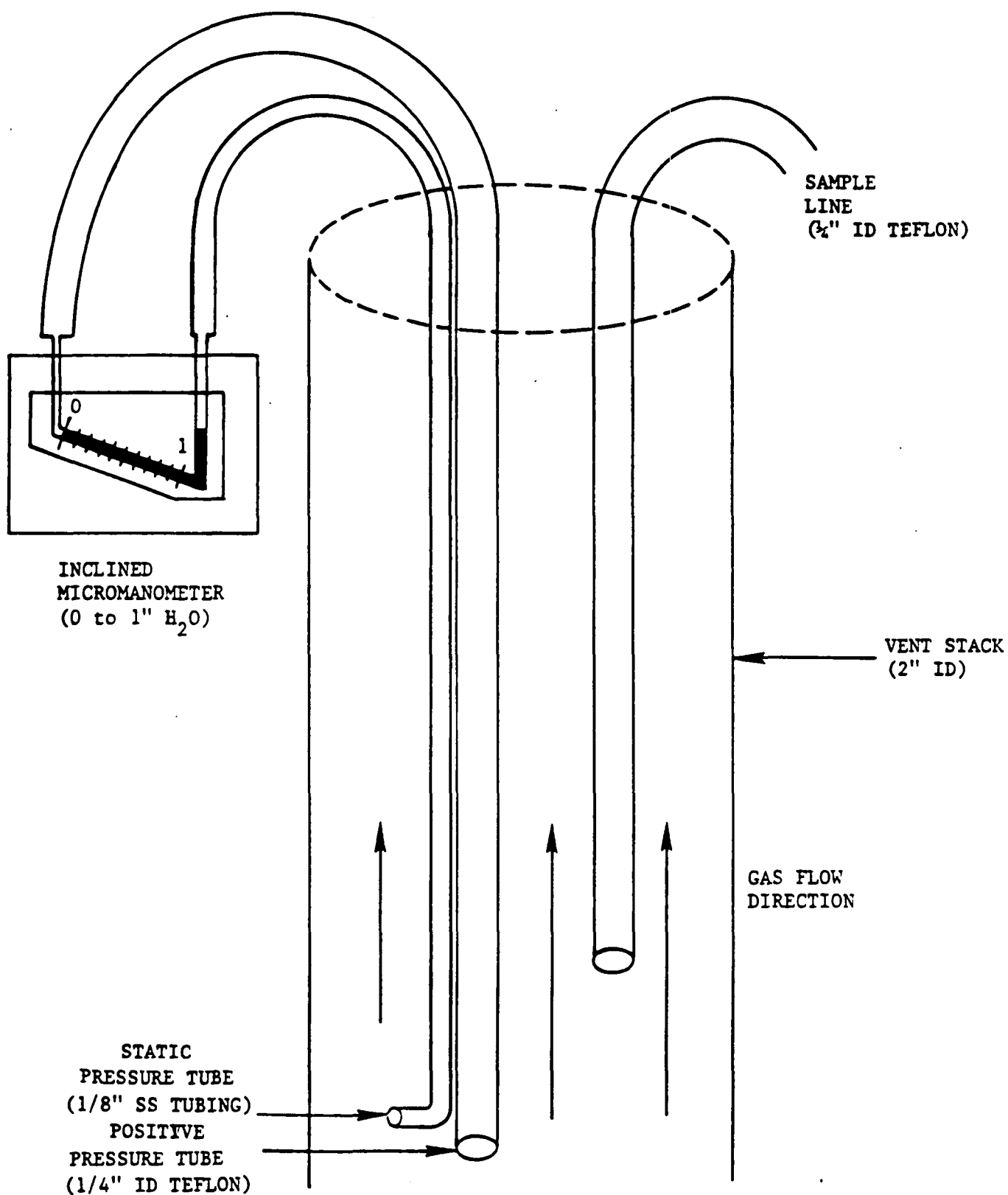


FIGURE 5-6

CUTAWAY DIAGRAM OF FLUX CHAMBER AND SUPPORT EQUIPMENT

surface area to be sampled. The sweep air was turned on, set at 0.005 m³/min (5 l/min) flow rate, and the time noted. The outlet gas concentration was monitored until steady state conditions were reached (typically 3 to 4 residence times). At this time, sample collection was initiated. Samples collected included liquid samples from the outlet of the flux chamber in both electropolished stainless steel canisters and glass syringes. The glass syringe samples were analyzed on site; the remainder of the samples were returned to the laboratory for analysis. A more detailed description is provided in Appendix B and includes a description of the ancillary measurements taken such as flow rates and temperatures.

5.2 Onsite Sample Analysis

Specified parameters were determined onsite with the use of portable analytical instruments. Listed below are the parameters which were measured and the methodology involved. These methods for pH, temperature, turbidity, conductance and dissolved oxygen are all from EPA-600/4-84-017 "Methods for Chemical Analysis of Water and Wastes".

pH

The pH of each sample was determined electrometrically using a glass combination electrode. Samples were analyzed as soon as possible on the same day as sample collection. Calibration and analytical procedures followed EPA Method 150.1.

Water Temperature

The lagoon water temperatures were measured with a thermocouple and digital readout. This thermocouple system measured at-depth liquid temperatures using a 10-foot thermocouple probe graduated at the selected

sampling depths. The general procedure used for this determination is EPA Method 170-1. Calibration prior to sampling was conducted against an NBS traceable mercury in glass thermometer, for 0°C and 100°C. Calibration data sheets are included in Appendix A.

Turbidity

The turbidity of the samples were measured using a HACH DR-EL/2 portable test kit. The turbidimeter consists of a nephelometer with a Tungsten Lamp light source and a photo-electric detector. All samples were analyzed on the same day as collection following procedures specified in EPA Method 180.1.

Specific Conductance

Specific conductance was measured by a Horizon Conductivity meter with a tungsten reference electrode. All samples were analyzed on the same day as collection following procedures specified in EPA Method 120.1.

Dissolved Oxygen

Onsite analysis for dissolved oxygen was accomplished using a YSI Model 54 Dissolved Oxygen meter with a membrane electrode. Samples were analyzed as soon as possible on the same day as sample collection following the procedures of EPA Method 360.1.

During this program no corrections or modifications were employed to eliminate bias from dissolved organic materials or inorganic salts. Calibration against aerated distilled water was the only readily available procedure employed to minimize the expected interferences.

5.3 Laboratory Analytical Procedures

GC/FID Analysis - Volatile Organics

Liquid samples submitted for volatile organics analysis were introduced into the gas chromatograph via direct injection and following the procedures described in Method 8015 (Reference 1). Instrumental operating conditions for this analysis are shown in Table 5-1.

Solid samples were dispersed in methanol as described in Method 8240 (Reference 1). Instrumental analysis was conducted according to Method 8015 (Reference 1) and using the instrumental operating conditions as shown in Table 5-1. Compounds for analysis via this method are shown in Table 5-2.

GC/FID Analysis - Extractable Organics

Liquid samples were prepared for analysis by filtration prior to the methylene chloride extraction as described in Method 625 (Reference 2). Solid samples were soxhlet-extracted in acetone-hexane according to procedures in Method 3540 (Reference 1). Instrumental analysis for phenols determination were conducted according to the procedures in Method 8040 (Reference 1). Quantitation of nitrobenzene and dinitrotoluene followed the protocol in Method 8090 (Reference 1). Instrumental operating conditions are listed in Table 5-3. Compounds for analysis via this method are listed in Table 5-2.

GC/MS Analysis - Volatile Organics

Liquid samples were analyzed by the purge and trap technique described in Method 624 (Reference 2). Instrumental operating conditions are listed in Table 5-1.

Solid samples were dispersed in methanol and analyzed for volatile organics as described in Method 8240 (Reference 1). Instrumental operating conditions are shown in Table 5-1.

TABLE 5-1

INSTRUMENT CONDITIONS FOR VOLATILE ORGANICS ANALYSIS

GC Conditions

Column	1% SP-1000 on Carbopack B, 6 ft. x 2 mm ID column
Temperature program	60°C held for 4 min, then 10/min to 220°C and held
Injector temperature	220°C
Carrier flow	UHP helium, 30 ml/min

GC/FID Instrument Hewlett Packard 5890

GC/MS Instrument Finnegan MAT OWA

Purge and Trap Conditions

Purge gas	UHP helium, 40 ml/min
Desorption temperature	180°C
Desorption time	4 min
Oven temperature	200°C

MS Conditions

Emission	300 a
Electron energy	70 eV
Scan rate	133.3 amu/sec
Mass interval	45-350 amu

TABLE 5-2
VOLATILE AND SEMI-VOLATILE COMPONENTS
FOR GC/FID ANALYSIS

Volatile Organic Species

Benzene

Toluene

Acetone

Semi-Volatile Organic Species

Phenol

4-Methylphenol

2-Nitrophenol

2,4-Dinitrophenol

2-Methyl-4,6-dinitrophenol

Nitrobenzene

2,6-Dinitrotoluene

2,4-Dinitrotoluene

Nitroaniline isomers

TABLE 5-3

GC/MS AND GC/FID OPERATING CONDITIONS FOR EXTRACTABLES ANALYSIS

GC/MS Instrument	Hewlett-Packard 5985, quadrupole mass spectrometer
GC/FID Instrument	Hewlett-Packard 5890
GC Conditions	
Column	DB-5 30M fused silica capillary
Temperature program	50°C held for 4 min then 10°/min to 300 °C and held
Injector temperature	250°C
Injection volume	1 μ l, splitless
Column flow	UHP helium, 0.5 ml/min
MS Conditions	
Emission	300 A
Electron energy	70 eV
Scan time	1.0 s/scan
Mass interval	45 to 450 amu
Source temperature	200°C

GC/MS Analysis - Extractable Organics

Liquid samples were subjected to filtration prior to the methylene chloride extraction described in Method 625 (Reference 2). Instrumental analysis was conducted according to Method 625. Operating conditions are shown in Table 5-3.

Solid samples were soxhlet-extracted in acetone-hexane according to procedures in Method 3540 (Reference 1). Instrumental analysis followed the procedures described in Method 8270 (Reference 1), with instrumental operating conditions listed in Table 5-3.

GC/PID Analysis

Samples submitted from the syringe composite sampler study were analyzed for volatile organics according to the procedures described in Method 8020 (Reference 1), using a GC/PID system.

Total Organic Carbon (TOC)

Total organic carbon analysis was conducted according to the procedures described in EPA Method 415.2 (Reference 2) utilizing a Dohrmann Model DC-80 Total Organic Carbon Analyzer. The injected sample was transferred to a quartz ultraviolet reaction coil where it was subjected to intense ultraviolet illumination in the presence of acidified persulfate reagent. The organic carbon is converted to carbon dioxide which was then measured by a non-dispersive infra-red detector (NDIR).

Solid samples were prepared for analysis by slurrying a weighed aliquot of sediment with a measured volume of deionized water. The resulting extract was then analyzed for TOC as described above.

Purgeable Organic Carbon (POC)

Determination of purgeable organic carbon in the submitted samples was performed utilizing a Dohrmann Model DC-80 Total Organic Carbon Analyzer equipped with a PRG-1 Purgeable Organics accessory (Reference 4). Carbon dioxide from inorganics and the purgeable organics were removed from the sample by the carrier gas. This carrier gas mixture flowed through a lithium hydroxide scrubber that removed the carbon dioxide and allowed the purgeable organics to pass to the hot cupric oxide furnace. The organic matter was then converted to carbon dioxide which was measured by non-dispersive infra-red detector (NDIR).

5.4 References

1. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 2nd Edition, SW 846, U.S. Environmental Protection Agency, Washington, D.C., July 1982.
2. Methods for Chemical Analysis of Water and Wastes, EPA-600/14-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1983.
3. Total Organic Carbon - Systems Manual, Dohrmann Division, Xertex Corporation, Santa Clara, CA, Edition 6, January 1984.

6.0 DETAILED RESULTS

The detailed results for the investigations conducted during this study are presented in this section. Results are included for the lagoon stratification study based on the organic analytical data from samples collected at varying vertical and horizontal locations in the lagoon, a surrogate analytical parameter study based on the comparison of TOC and POC analyses to GC/MS analytical data, the results of field trials of a composite syringe sampler for volatile organic compounds, and the results of flux chamber direct emission measurements conducted by Radian Corporation. Raw data generated from this study, except the flux chamber emissions data, are presented in Appendix A. Flux chamber data are reported separately in Appendix B.

6.1 Stratification Study

The investigation of the stratification of the wastewater holding lagoon at FCC, was the primary goal of this program. The investigation was based on the collection of onsite information as well as the analytical results of samples collected and returned to the laboratory.

Onsite Measurements

The results of the onsite analytical work are included in Table 6-1. The parameters monitored include sample depth, conductivity, temperature, pH, dissolved oxygen, and turbidity. Sampling points ranged from the top liquid layer at the surface of the lagoon to the bottom sludge layer. The liquid depth ranged from 1.4 to 1.7 meters, and the bottom sludge layer varied in depth from 0.8 to 1.4 meters. (Table 3-1 in Section 3 provides more detail on the depths and estimated volumes of materials in the lagoon.) Conductivity readings taken onsite were compromised by the limited range of the field

TABLE 6-1

RESULTS OF ONSITE ANALYSIS

SAMPLE LOCATION	DEPTH (meters)	ONSITE CONDUCTIVITY (μ mhos/cm)	CONDUCTIVITY ^a (μ mhos/cm)	AT-DEPTH SAMPLE TEMPERATURE (Celsius)	pH	DISSOLVED O ₂ (ppm)	TURBIDITY (ntu)
A1	0-0.3	15,500	14,000	21.5	4.2	4.2	971.4
A2	0.9	>20,000	20,000	21.5	2.0	2.8	708.1
A3	1.2	>20,000	58,000	21.5	0.7	5.2	23.5
A4	1.5	>20,000	b	21.5	0.9	6.0	971.4
A5	1.8	b	b	21.5	<1	b	b
B1	0-0.3	16,500	16,000 14,500	23.0	2.6	4.0	971.4
B2	0.9	20,000	15,000	21.0	1.6	4.0	339.5
B5	1.7	b	b	21.0	<1	b	b
E1	0-0.3	c	15,900	c	c	c	c
E2	0.9	c	58,000	c	c	c	c
E3	1.2	c	58,000	c	c	c	c
E5	1.5	c	b	c	c	c	c
F1	0-0.3	>20,000	16,300 15,400 15,700	19.0	2.3	6.0	708.1
F2	0.9	>20,000	56,000	19.0	1.4	3.2	971.4
F3	1.2	>20,000	62,000	18.0	1.2	4.6	971.4
F5	1.5	b	b	19.0	<1	b	b

^a Conductivity analysis performed using a YSI model 31 conductivity bridge which has an extended operating range up to 250,000 μ mhos/cm versus 20,000 for the field unit.

^b Analysis not performed due to potential for damage to analyzer probe.

^c Analysis not performed due to demobilization forced by hurricane evacuation.

analyzer. The 20,000 mhos/cm upper limit was exceeded for most samples necessitating reanalysis following the return of samples to the laboratory. The resulting data indicate an increase in conductivity with depth, with the general trend being from 16,000 mhos/cm at the surface to 60,000 mhos/cm above the bottom sludge layer. No readings were taken of the sludge material itself due to the potential for damage to the analyzer probe.

With the exception of depth and temperature measurements, these laboratory conductivity readings were the only onsite analytical measurements taken for sample location E, due to the hasty evacuation from the site required by an approaching hurricane storm system. In order to complete the evacuation on schedule, the field laboratory was broken down and packed for transport off the site, making it impossible to measure the samples collected from this last sample point.

Temperature readings indicated no significant temperature gradient in the lagoon. The data ranged from 18 to 23 degrees Celsius. Since each horizontal sample location was monitored at a different time over the 2-day sampling period, the temperature fluctuations are more likely due to overall changes in the lagoon temperature from day to day or morning versus afternoon, rather than localized variations within the lagoon.

The sample measurements taken for pH indicated a range of 4.2 to 1. The data clearly indicate that the lagoon becomes more acidic with depth, with pH levels decreasing in a steady progression from the top surface layer to the bottom sludge. The surface layer samples ranged from 2.3 to 4.2, while the bottom sludge samples all measured 1. This data would indicate that waste acids tend to accumulate in the bottom sludge in the lagoon.

No significant variation in the dissolved oxygen content of the lagoon were detected. The collected data ranged from 2.8 to 6.0 ppm, all low values.

The turbidity results present some indication of stratification within the lagoon, however, these results are not conclusive. One reading of 24 ntu at the middle depth of location A indicates a clearer layer at this location, but all the other readings are between 340 and 970 nephelometry turbidity unit (ntu). The sample is compared against a standard which is a suspension of silica of a specified particle size selected such that a 1.0 mg/l suspension is one unit of turbidity. The common method of measurement uses a photoelectric detector that makes use of nephelometry to measure the intensity of the scattered light.

For additional clarification of the appearance of the various liquid layers at the four samples locations, pictures of liquid cores collected at each location are provided in the following Figures 6-1 through 6-4. The low turbidity value for location A-3 coincides with a light yellow layer in the photo. The color ranges from a black bottom sludge and surface sludge layer, to red, orange and yellow zones within the liquid layers.

In addition to these chemical measurements conducted on the samples of the lagoon contents, meteorological monitoring was conducted. The onsite meteorological monitoring station provided ambient wind speed and direction data during the sampling period from sensors mounted on a 10-meter tower at the downwind northwest corner of the lagoon. The results are provided in Tables A-1 and A-2 in Appendix A of this report. Ambient temperature and barometric pressure data were obtained from a National Weather Service monitoring station at nearby Keesler Air Force Base in Pensacola, Florida. These data are also included in Appendix A, Tables A-3 and A-4. Average results for the 2 sampling days (11/19/85 and 11/20/85) are:

Wind speed, 3.7 meters/second (from 0000 11/19/85 to 1500 11/20/85).

Wind direction, 175° (from 0000 11/19/85 to 1900 11/19/85) and 75° (from 1900 11/19/85 to 1500 11/20/85). (Two readings are provided here to indicate the two distinct wind conditions during sampling.)

LIQUID CORE SAMPLE: A

DATE COLLECTED : 11/19/85
TOTAL DEPTH : 1.58 meters
NUMBER OF LAYERS : 4
FILM ROLL NO. : 1
FRAME NO. : 0

Core A shows four distinct zones through the 5 feet of lagoon material collected. The top zone is a very thin layer, 1 cm, of a floating black oily sludge. The second reddish-orange liquid layer is opaque and extends to a depth of 0.6 meters below the surface and blends gradually into the third layer. The third layer is a clearer greenish-yellow liquid with very little visible suspended solids and occupies the depths between 0.6 and 1.29 meters, below the surface. The bottom sludge layer forms a fairly distinct boundary with the bottom liquid layer and occupies the bottom 0.29 meters of the liquid core sample, at a depth from 1.29 to 1.58 meters below the liquid surface. When sampling was conducted no attempt was made to penetrate to the bottom of this sludge layer, therefore, the total depth of sludge is greater than the 0.29 meters observed in the core.

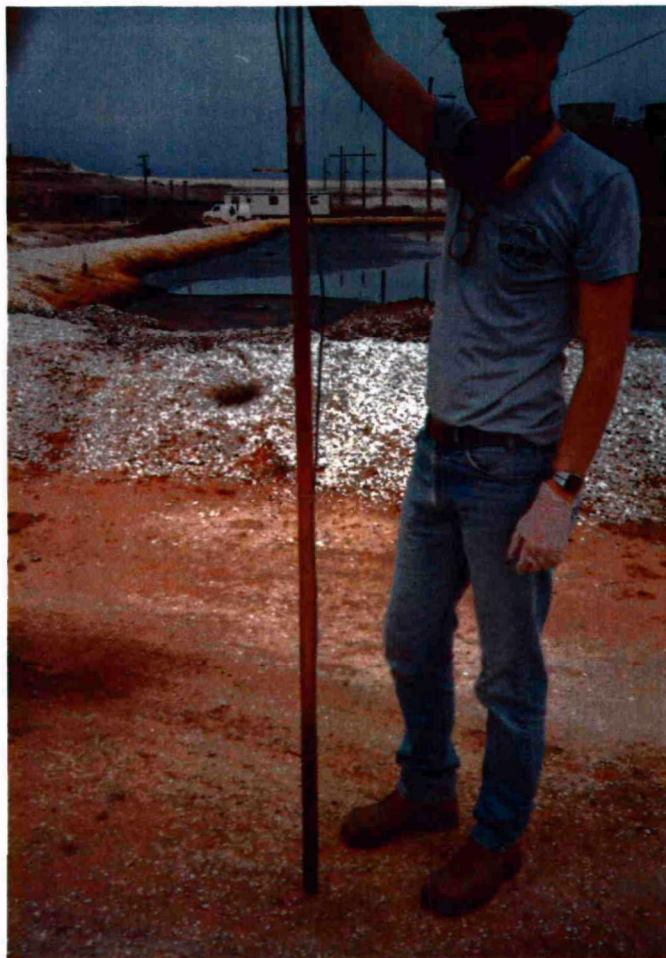


FIGURE 6-1

LIQUID CORE A

LIQUID CORE SAMPLE: B

DATE COLLECTED : 11/19/85
TOTAL DEPTH : 1.21 meters
NUMBER OF LAYERS : 4
FILM ROLL NO. : 1
FRAME NO. : 6

Liquid core sample B, collected from the southeast corner of the lagoon, shows four distinct layers. The top layer is a thin layer of floating black oil or sludge, of 1 cm in depth. The second liquid layer is a dull red ranging from reddish-brown to reddish-orange extending to a depth of 0.5 meters, becoming less opaque with depth. The third layer is a yellowish-green liquid which extends between 0.5 and 0.93 meters. The color changes gradually from yellow-orange at the top of this layer to yellow-green at the bottom. This layer is less opaque than the upper red layer. The bottom layer is a black sludge material comprised of fairly fine grained material which extends between 0.93 and 1.21 meters below the surface. No attempt was made to penetrate to the bottom of this sludge layer when sampling, therefore the total depth of sludge is greater than the 0.28 meters observed in the core.

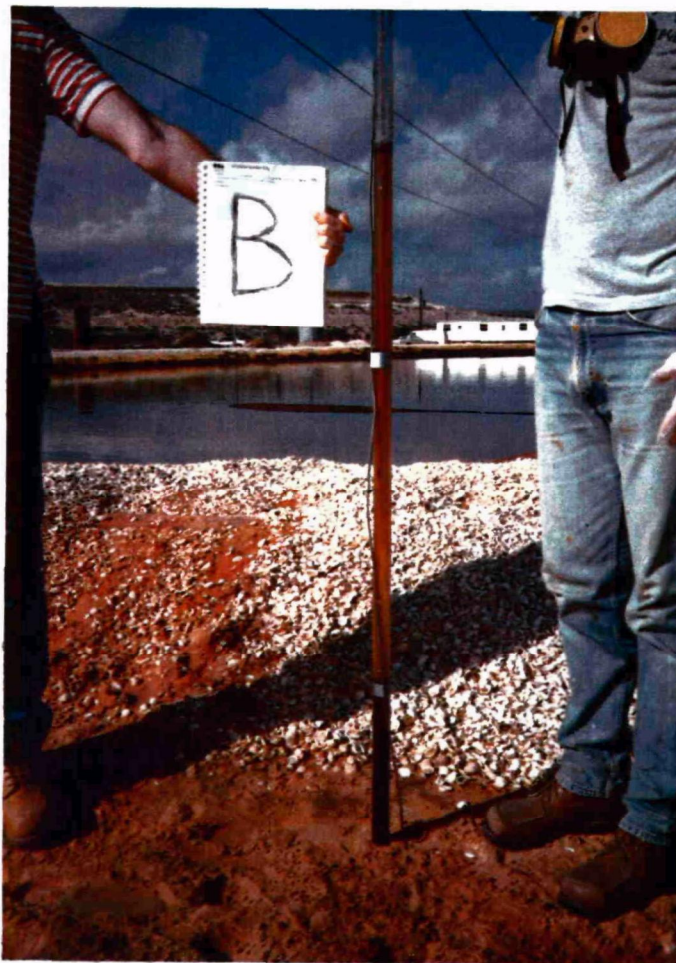


FIGURE 6-2

LIQUID CORE B

LIQUID CORE SAMPLE: E

DATE COLLECTED : 11/20/85
TOTAL DEPTH : 1.22 meters
NUMBER OF LAYERS : 5
FILM ROLL NO. : 1
FRAME NO. : 12

Liquid core E was collected from the northwest corner of the lagoon. This core revealed the presence of five layers in the lagoon. The top-most layer is an oily film of about 2 cm in depth. This layer is black, contains visible solid material and forms a distinct boundary with the liquid layer below it. The second layer is a reddish-orange liquid layer which extends to a depth of 0.52 meters below the surface, becoming less opaque with depth. The third layer is also liquid and occupies the depth between 0.52 and 0.97 meters. This third layer is yellow-green and appears less opaque than the reddish layer above it. Between this lower liquid layer and the bottom sludge or fifth layer is a fourth layer not noticed in the other three cores. This layer is a greyish cloudy mixture which hangs above the bottom sludge. This layer is fairly thin extending only 5 cm in depth. The bottom sludge layer is comprised of a black sludge and was measured to be the bottom 0.2 meters of the core. No attempt was made to penetrate to the bottom of the sludge layer during sampling so the total depth of sludge is greater than that observed in the core sampler.

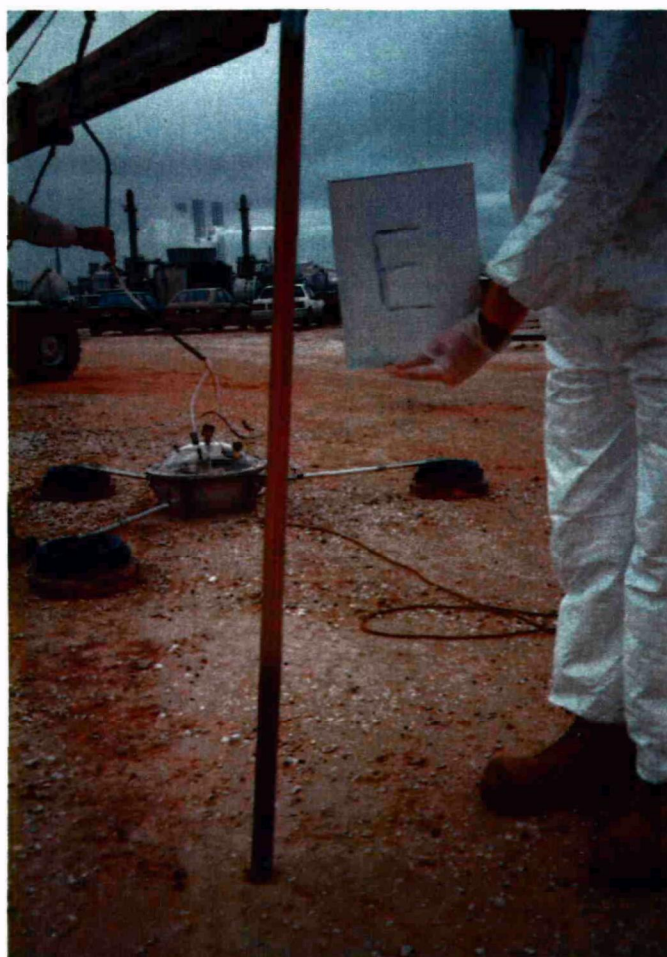


FIGURE 6-3 LIQUID CORE E

LIQUID CORE SAMPLE: F

DATE COLLECTED : 11/20/85
TOTAL DEPTH : 1.76 meters
NUMBER OF LAYERS : 4
FILM ROLL NO. : 1
FRAME NO. : 10

Liquid core sample F was collected from a point near the center of the lagoon. Four layers are present in this core. A thin oily layer is visible as the upper-most layer in the core. This black oily layer is 1 cm in depth. The second layer is the upper liquid layer which is an opaque brownish-yellow color. This brownish-yellow layer extends to a depth of 0.23 meters. The liquid color gradually blends to yellow-orange in the third layer which extends between 0.23 and 1.15 meters. The color in this layer ranges from an opaque yellow-brown at the top to a yellow-green at the bottom. The bottom sludge layer is black in color and extends between 1.15 and 1.76 meters. The bottom sludge layer depth is greater than that observed in the core sampler since no attempt to penetrate this layer was made during sampling.

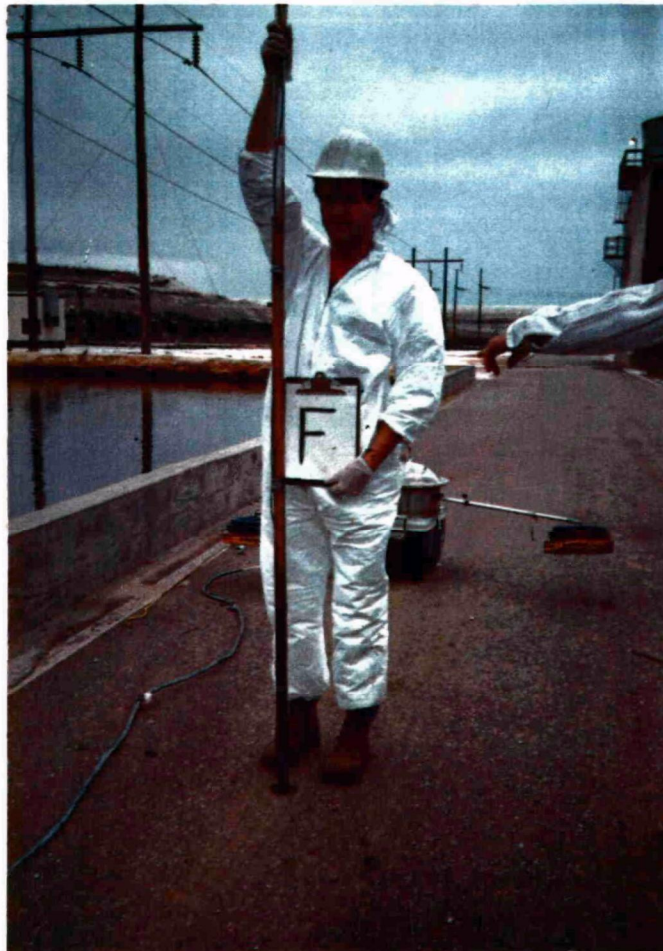


FIGURE 6-4

LIQUID CORE F

Ambient air temperature, 22°C (from 0000 11/19/85 to 2400 11/20/85).

Barometric pressure, 30.1 inches of Hg (from 0000 11/19/85 to 2400 11/20/85).

GC/FID Organic Analyses

Samples collected at all liquid depths and from the bottom sludge were subjected to GC/FID analysis for volatile organics and extractable (or semi-volatile) organics. The results for these analyses are presented in the following Tables 6-2 through 6-5, for grid points A, B, E, and F. Summary tables are provided in Appendix A which summarize the results of all GC/FID analyses for volatile organics, Table A-5 and for extractable organics, Table A-6. Review of these results for each grid point provides fairly conclusive evidence of stratification between the liquid and sludge layers in the lagoon but not in the liquid layer itself, with the sludge layer ranging up to several hundred-fold more concentrated than the liquid layer.

With a few exceptions the seven volatile and extractable organics identified in the liquid layer samples indicate a close agreement in concentrations for the various layers sampled at each location as well as between locations. The major components of the liquid samples as measured by the GC/FID method in order of decreasing concentration are: nitrobenzene, 2,4-dinitrophenol, 4,6-dinitro-o-cresol and benzene.

The major components of the sludge layer are the same as measured in the liquid samples: nitrobenzene, 2,4-dinitrophenol, 4,6-dinitro-o-cresol and benzene. The concentration of organic materials in the sludge is much higher for every compound reported, ranging up to several hundred times more concentrated for some locations. If it is assumed that the sludge results are representative of the entire depth of the sludge layer, it is clear that the organic material found in the liquid layer is only a small fraction of the

TABLE 6-2

LAGOON CONCENTRATIONS AS MEASURED BY GC/FID ANALYSES^{a,b}

Grid Point: A
Date Sampled: 11/19/1985

Compound	depth =	A-1 Liquid (0-0.3m) (mg/l)	A-2 Liquid (0.9 m) (mg/l)	A-3 Liquid (1.2 m) (mg/l)	A-4 ^c Liquid (1.5 m) (mg/l)	A-5 Bottom Sludge (1.8 m) (mg/kg)
Benzene		12	13	9.4	23,000 (12,000)	(1,000)
Toluene		<1	<5	<5	9,900 (4,700)	(520)
Nitrobenzene		440	560	580	1,100	(87,000)
2,4 Dinitrotoluene		<11	<10	<10	11	(340)
2-Nitrophenol		3.5	<16	<16	<16	(260)
2,4-Dinitrophenol		1,400	250	210	210	(4,600)
4,6-Dinitro-o-cresol		32	28	45	56	(2,300)

a Concentrations in parentheses are for sludges; all others represent liquid concentrations.

b Results are averages where multiple analyses were conducted.

c The volatile fraction of A-4 contained a large amount of sludge material, such that the liquid and the sludge fractions were analyzed separately.

TABLE 6-3

LAGOON CONCENTRATIONS AS MEASURED BY GC/FID ANALYSES^{a,b}

Grid Point: B
Date Sampled: 11/19/1985

Compound	depth =	B-1 Liquid (0-0.3m) (mg/l)	B-2 Liquid (0.9 m) (mg/l)	B-3 Bottom Sludge (1.2 m) (mg/l)
Benzene		15	23	(1,000)
Toluene		<5	<5	(250)
Nitrobenzene		630	880	(130,000)
2,4 Dinitrotoluene		<20	<20	(1,400)
2-Nitrophenol		<43	<43	(860)
2,4-Dinitrophenol		160	320	(18,000)
4,6-Dinitro-o-cresol		38	45	(7,700)

a Concentrations in parentheses are for sludges; all others represent liquid concentrations.

b Results are averages where multiple analyses were conducted.

TABLE 6-4

LAGOON CONCENTRATIONS AS MEASURED BY GC/FID ANALYSES^{a,b}

Grid Point: E
Date Sampled: 11/20/1985

Compound	depth =	E-1 Liquid (0-0.3m) (mg/l)	E-2 Liquid (0.9 m) (mg/l)	E-3 Liquid (1.2 m) (mg/l)	E-5 Bottom Sludge (1.5 m) (mg/kg)
Benzene		17	21	32	(372)
Toluene		<5	<5	<5	(73)
Nitrobenzene		390	420	380	(14,000)
2,4 Dinitrotoluene		<11	<10	<10	(315)
2-Nitrophenol		3.5	<16	<16	(1,000)
2,4-Dinitrophenol		130	<20	260	(9,300)
4,6-Dinitro-o-cresol		25	15	<10	(3,300)

a Concentrations in parentheses are for sludges; all others represent liquid concentrations.

b Results are averages where multiple analyses were conducted.

TABLE 6-5

LAGOON CONCENTRATIONS AS MEASURED BY GC/FID ANALYSES^{a,b}

Grid Point: F
Date Sampled: 11/20/1985

Compound	depth =	F-1 Liquid (0-0.3m) (mg/l)	F-2 Liquid (0.9 m) (mg/l)	F-3 Liquid (1.2 m) (mg/l)	F-5 Bottom Sludge (1.5 m) (mg/kg)
Benzene		16	30	59	(2,400)
Toluene		<5	<5	<20	(580)
Nitrobenzene		670	460	350	(120,000)
2,4 Dinitrotoluene		<10	<20	<20	(380)
2-Nitrophenol		<16	<43	<43	(320)
2,4-Dinitrophenol		470	2,000	110	(5,200)
4,6-Dinitro-o-cresol		63	82	30	(2,600)

^a Concentrations in parentheses are for sludges; all others represent liquid concentrations.

^b Results are averages where multiple analyses were conducted.

total organics in the lagoon. When these concentration results are combined with the liquid and sludge volume estimates (provided in the preceding Table 3-1) a rough idea of the ratio between the weight of organics present in the liquid and sludge layers can be determined. Table 6-6 provides the results of such a comparison using an average concentration for each of the four primary lagoon organic components reported in the liquid and sludge layers.

The results indicate clearly that the majority of the organic material in the lagoon is in the sludge layer. The ratio of organic weight between the sludge and liquid layer in this comparison ranged from 19 to 144, with an average of 77.

GC/MS Organic Analyses

The analytical procedure followed for the previously reported GC/FID analyses called only for the reporting of the targeted compounds listed in the project QAPP. In order to document these results and to determine if any other organic compounds were present at detectable levels, GC/MS confirmational analyses were conducted on the surface liquid layer samples, A-1, B-1, E-1, F-1, and on the bottom sludge samples, A-5, B-5, E-5, F-5. These samples were analyzed for any compound present above the method detection limit, identifiably using the mass-spectral computer-matching library of the GC/MS instrument. Using the integration capabilities of the instruments data reduction software, an integrated total organic estimate was also calculated. Tables 6-7 and 6-8 provide the results for the liquid and sludge samples, respectively.

6.2 Surrogate Analytical Parameter Study

The stratification study results provide compound-specific analytical data required for the investigation of surrogate analytical parameters on samples

TABLE 6-6

LIQUID:SLUDGE ORGANIC CONTENT COMPARISON

	LIQUID DATA	SLUDGE DATA	WEIGHT RATIO SLUDGE:LIQUID
ESTIMATED WASTE VOLUME:	4400 cubic meters	4100 cubic meters	
AVERAGE WASTE CONCENTRATIONS: ¹			
Nitrobenzene	560 mg/l	88,000 mg/kg	
2,4 Dinitrophenol	460 mg/l	9,300 mg/kg	
4,6-Dinitro-o-cresol	38 mg/l	4,000 mg/kg	
Benzene	22 mg/l	1,200 mg/kg	
ESTIMATED WEIGHT OF WASTE COMPOUND: ²			
Nitrobenzene	2,500 kg	360,000 kg	144
2,4 Dinitrophenol	2,000 kg	38,000 kg	19
4,6-Dinitro-o-cresol	170 kg	16,000 kg	94
Benzene	100 kg	4,900 kg	49
			AVERAGE = 77

1 Average concentrations calculated using all liquid values greater than detection limits from Tables 6-2 through 6-5.

2 Weights for liquid calculated as per the following equation:

$$\text{weight} = (\text{mg/l})(\text{m}^3 \text{ of liquid})(1.0\text{E}+03 \text{ l/m}^3)/(1.0\text{E}+06 \text{ mg/kg})$$

Weights for sludge calculated as per the following equation:

$$\text{weight} = (\text{mg/kg})(\text{m}^3 \text{ of sludge})(\text{g sludge/ml})(1.0\text{E}+06 \text{ ml/m}^3)/$$

$$(1.0\text{E}+03 \text{ g/kg})(1.0\text{E}+06 \text{ mg/kg})$$

(density of 1 g/ml used for sludge for calculation purposes, the higher actual density will increase for these waste estimates)

TABLE 6-7

LAGOON CONCENTRATIONS AS MEASURED BY GC/MS ANALYSES
SURFACE LIQUID LOCATION

Date Sampled: 11/20/1985

Compound	depth	A-1	B-1	E-1	F-1
		(0-0.3 m) (mg/l)	(0-0.3 m) (mg/l)	(0-0.3 m) (mg/l)	(0-0.3 m) (mg/l)
Benzene		17	17	14	14
Toluene		2.0	2.3	2.3	2.1
Nitrobenzene*		23/320	36/270	39/240	52/340
Unknown VOC (1)		<10	<10	<10	<10
Unknown VOC (2)		<10	<10	<10	<10
2-Nitrophenol		9.7	7.0	6.7	7.9
2,4 Dinitrophenol		1,100	190	180	300
4,6-Dinitro-o-cresol		83	34	33	47
4-Nitrophenol		<3.0	3.5	3.4	6.1
Benzoic acid			3.0	2.6	
SUM of reported VOCs		42	55	55	68
Calculated SUM ^b -all VOCs		32	30	27	32
SUM of reported SVOCs		1,510	508	466	736
Calculated SUM ^b -all SVOCs		101,730	199,840	37,445	208,600
TOTAL of reported HCs		1552	563	521	804
Calculated TOTAL-all HCs		101,762	199,870	37,472	208,632

^a calculated relative to internal standard^b calculated SUMs determined by integrating entire chromatograph and quantifying against the nearest internal standard

TABLE 6-8

LAGOON CONCENTRATIONS AS MEASURED BY GC/MS ANALYSES
 BOTTOM SLUDGE LOCATIONS
 Date Sampled: 11/20/1985

Compound	depth	A-5	B-5	E-5	F-5
		(1.8 m) (mg/kg)	(1.2 m) (mg/kg)	(1.5 m) (mg/kg)	(1.5 m) (mg/kg)
Benzene		1,100	1,100	1,500	2,100
Toluene		620	300	430	590
Nitrobenzene*		450/61,000	740/135,000	1,000/8,100	1,500/121,000
Unknown VOC (1)		<100	<100	<100	800
Unknown VOC (2)		500	300	450	440
2-Nitrophenol		<2,000	760	120	125
2,4 Dinitrophenol		6,400	11,700	5,500	16,800
4,6-Dinitro-o-cresol		4,300	5,100	3,300	12,600
4-Nitrophenol		<2,000	<550	200	<500
Benzoic Acid		<1,000	<550	<1,000	<500
Isomer of Nitrobenzene		4,800	6,800	1,380	41,150
Isomer of Nitrobenzene			2,300	175	14,650
Isomer of Nitrobenzene			14,200	960	27,000
Isomer of Nitrobenzene			2,100	670	2,350
SUM of reported VOCs		2,700	2,400	340	5,400
Calculated SUM ^b -all VOCs		2,100	1,700	2,800	3,400
SUM of reported SVOCs		76,500	177,200	20,405	235,675
Calculated SUM ^b -all SVOCs		101,730	199,840	37,445	208,600
TOTAL of reported HCs		79,200	179,600	20,745	241,075
Calculated TOTAL-all HCs		103,830	201,540	40,245	212,000

^a calculated relative to internal standard

^b calculated SUMs determined by integrating entire chromatograph and quantifying against the nearest internal standard

collected at the First Chemical wastewater holding lagoon. The selected surrogate parameters to which these compound-specific results are compared are purgeable organic carbon (POC) and total organic carbon (TOC). The goal of this investigation is to compare the sum of carbon-weighted compound specific results to POC and TOC analyses of the same samples. POC analyses are compared to the results of GC/MS volatile organic results and TOC analyses are compared to the results of GC/MS volatile organic and semi-volatile organic results.

Samples were collected from the surface liquid layer and the bottom sludge layer to evaluate the correlation factors for the two sample matrices. The liquid samples were evaluated for both the POC and TOC surrogates and the sludge samples were evaluated only for TOC. The correlation factors were calculated by dividing the surrogate result by the sum of the carbon-weighted compound-specific results provided by the GC/MS analysis. The data generated by this comparison are presented in the following Tables 6-9, 6-10 and 6-11. (QC results for the TOC and POC analyses including EMSL spikes, matrix spikes, duplicates, and blanks are included in Section 7). Table 6-9 presents the data generated for the POC comparison of the liquid samples, Table 6-10 the results of the TOC comparison for the liquid samples, and Table 6-11 the results of the TOC comparison for the sludge samples. The populations for these three comparisons are very small, with four (4) data pairs for each category. The abbreviated sampling program was a critical factor in this outcome, as the original goal was to have eight (8) data pairs for each comparison.

The following results were obtained for correlation factors:

POC Liquid	4.26 +/- 1.09
TOC Liquid	3.76 +/- 1.30
TOC Sludge	1.73 +/- 1.01

TABLE 6-9

SURROGATE STUDY RESULTS, POC VS. GC/MS VOC

SAMPLE LOCATION	Cs POC (ppm)	Ct GC/MS VDA**	Ri Cs/Ct	GC/MS PARAMETER	MW MOLECULAR WEIGHT	NUMBER OF CARBONS	Wcx WEIGHT of CARBONS	Cx SAMPLE CONCENTRATION (ppm)	Cti WEIGHTED CONCENTRATION
A-1	178	30.97	5.75	Benzene	78.12	6	72.06	17.0	15.68
				Toluene	92.15	7	84.07	2.0	1.82
				Nitrobenzene	123.11	6	72.06	23.0	13.46
B-1	166	38.85	4.26	Benzene	78.12	6	72.06	17.0	15.68
				Toluene	92.15	7	84.07	2.3	2.10
				Nitrobenzene	123.11	6	72.06	36.0	21.07
E-1	144	37.84	3.82	Benzene	78.12	6	72.06	14.0	12.91
				Toluene	92.15	7	84.07	2.3	2.10
				Nitrobenzene	123.11	6	72.06	39.0	22.83
F-1	145	45.27	3.20	Benzene	78.12	6	72.06	14.0	12.91
				Toluene	92.15	7	84.07	2.1	1.92
				Nitrobenzene	123.11	6	72.06	52.0	30.44
AVG of Ri =				4.26					
SUM of (Ri) ² =				76.05					
(SUM of Ri) ² =				290.05					
S =				1.09					

TABLE 6-10

SURROGATE STUDY RESULTS, TOC VS. GC/MS VOC AND SVOC LIQUID SAMPLES

SAMPLE LOCATION	Cs TOC (ppm)	Ct GC/MS (ppm)	Ri Cs/Ct	GC/MS PARAMETER	MW MOLECULAR WEIGHT	NUMBER OF CARBONS	Wcx WEIGHT of CARBONS	Cx SAMPLE CONCENTRATION (ppm)	Cti WEIGHTED CONCENTRATION
A-1	1454	675.59	2.15	Benzene	78.12	6	72.06	17.0	15.68
				Toluene	92.15	7	84.07	2.0	1.82
				Nitrobenzene	123.11	6	72.06	320.0	187.31
				2-Nitrophenol	139.11	6	72.06	9.7	5.02
				2,4-Dinitrophenol	184.11	6	72.06	1,100.0	430.54
				4,6-Dinitro-o-cresol	198.14	7	84.07	83.0	35.22
				4-Nitrophenol	139.11	6	72.06	<3	0.00
				Benzoic Acid	122.13	7	84.07	ND	0.00
B-1	1250	272.11	4.59	Benzene	78.12	6	72.06	17.0	15.68
				Toluene	92.15	7	84.07	2.3	2.10
				Nitrobenzene	123.11	6	72.06	270.0	158.04
				2-Nitrophenol	139.11	6	72.06	7.0	3.63
				2,4-Dinitrophenol	184.11	6	72.06	190.0	74.37
				4,6-Dinitro-o-cresol	198.14	7	84.07	34.0	14.43
				4-Nitrophenol	139.11	6	72.06	3.5	1.81
				Benzoic Acid	122.13	7	84.07	3.0	2.07
E-1	1240	246.97	5.02	Benzene	78.12	6	72.06	14.0	12.91
				Toluene	92.15	7	84.07	2.3	2.10
				Nitrobenzene	123.11	6	72.06	240.0	140.48
				2-Nitrophenol	139.11	6	72.06	6.7	3.47
				2,4-Dinitrophenol	184.11	6	72.06	180.0	70.45
				4,6-Dinitro-o-cresol	198.14	7	84.07	33.0	14.00
				4-Nitrophenol	139.11	6	72.06	3.4	1.76
				Benzoic Acid	122.13	7	84.07	2.6	1.79
F-1	1183	359.49	3.29	Benzene	78.12	6	72.06	14.0	12.91
				Toluene	92.15	7	84.07	2.1	1.92
				Nitrobenzene	123.11	6	72.06	340.0	199.01
				2-Nitrophenol	139.11	6	72.06	7.9	4.09
				2,4-Dinitrophenol	184.11	6	72.06	300.0	117.42
				4,6-Dinitro-o-cresol	198.14	7	84.07	47.0	19.94
				4-Nitrophenol	139.11	6	72.06	8.1	4.20
				Benzoic Acid	122.13	7	84.07	ND	0.00
AVG of Ri				=	3.76				
SUM of (Ri) ²				=	61.77				
(SUM of Ri) ²				=	226.73				
S				=	1.30				

TABLE 6-11

SURROGATE STUDY RESULTS, TOC VS. GC/MS VOC AND SVOC SLUDGE SAMPLES

	Cs	Ct	Ri		MW		Wcx	Cx	Cti
SAMPLE LOCATION	TOC (ppm)	GC/MS (ppm)	Cs/Ct	GC/MS PARAMETER	MOLECULAR WEIGHT	NUMBER OF CARBONS	WEIGHT of CARBONS	SAMPLE CONCENTRATION (ppm)	WEIGHTED CONCENTRATION
A-5	86,946	4,4424.44	1.96	Benzene	78.12	6	72.06	1,100.0	1,014.67
				Toluene	92.15	7	84.07	620.0	565.64
				Nitrobenzene	123.11	6	72.06	61,000.0	35,705.14
				2-Nitrophenol	139.11	6	72.06	<2,000	0.00
				2,4-Dinitrophenol	184.11	6	72.06	6,400.0	2,504.94
				4,6-Dinitro-o-cresol	198.14	7	84.07	4,300.0	1,824.47
				4-Bitrophenol	139.11	6	72.06	<2,000	0.00
				Benzoic Acid	122.13	7	84.07	<1,000	0.00
				Isomer of Nitrobenzene	123.11	6	72.06	4,800.00	2,809.58
B-5	120,862	102,312.26	1.18	Benzene	78.12	6	72.06	1,100.0	1,014.67
				Toluene	92.15	7	84.07	300.00	273.70
				Nitrobenzene	123.11	6	72.06	135,000.0	79,019.58
				2-Nitrophenol	139.11	6	72.06	760.0	393.69
				2,4-Dinitrophenol	184.11	6	72.06	11,700.0	4,579.34
				4,6-Dinitro-o-cresol	198.14	7	84.07	5,100.0	2,163.91
				4-Nitrophenol	139.11	6	72.06	<550	0.00
				Benzoic Acid	122.13	7	84.07	<550	0.00
				Isomer of Nitrobenzene	123.11	6	72.06	25,400.00	14,867.39
E-5	36,854	12,100.01	3.05	Benzene	78.12	6	72.06	1,500.0	1,383.64
				Toluene	92.15	7	84.07	430.0	392.30
				Nitrobenzene	123.11	6	72.06	8,100.0	4,741.17
				2-Nitrophenol	139.11	6	72.06	120.0	62.16
				2,4-Dinitrophenol	184.11	6	72.06	5,500.0	2,152.68
				4,6-Dinitro-o-cresol	198.14	7	84.07	3,300.0	1,400.18
				4-Nitrophenol	139.11	6	72.06	200.0	103.60
				Benzoic Acid	122.13	7	84.07	<1,000	0.00
				Isomer of Nitrobenzene	123.11	6	72.06	3,185.00	1,864.28
F-5	99,620	135,127.52	0.74	Benzene	78.12	6	72.06	2,100.0	1,937.10
				Toluene	92.15	7	84.07	590.0	538.27
				Nitrobenzene	123.11	6	72.06	121,000.0	70,824.95
				2-Nitrophenol	139.11	6	72.06	125.0	64.75
				2,4-Dinitrophenol	184.11	6	72.06	16,800.0	6,575.46
				4,6-Dinitro-o-cresol	198.14	7	84.07	12,600.0	5,346.13
				4-Nitrophenol	139.11	6	72.06	<500	0.00
				Benzoic Acid	122.13	7	84.07	<500	0.00
				Isomer of Nitrobenzene	123.11	6	72.06	85,150.00	49,841
AVG of Ri				=	1.73				
SUM of (Ri) ²				=	15.05				
(SUM of Ri) ²				=	47.91				
S				=	1.01				

Theoretically, one would expect that the correlation factors would range much closer to one, however, with the complex sample matrix found at this lagoon, the shift away from a one to one correlation is not unexpected. Also, one variable involved in the POC comparison is the difference in the purge time utilized by the two different methods. The GC/MS method has a characteristically different purge cycle than the less flexible POC analyzer. A definitive conclusion as to the adequacy of the surrogate nature of the POC and TOC analyses is not possible based on the small data set presented in this report, however, the statistical distribution of the four results within each category are fairly close as evidenced by the standard deviation for the correlation factors being between 26 percent and 35 percent of the average for both liquid surrogates. The correlation factor for sludges is much closer to 1 at 1.73, but demonstrated a higher standard deviation of about 60 percent of this average. More extensive application of this surrogate analysis program is necessary before any further conclusions can be drawn. Ideally, a larger numbers of samples and a greater variety of waste types should be evaluated.

6.3 Syringe Composite VOC Sampler

During this testing program field trials of a time-integrating volatile organic compounds sampler were conducted. The sampler is illustrated in the sampling methods discussion of Section 5. Again due to the abbreviated duration of the field testing program, only a small data set was obtained. In order to maximize the results obtained from this study triplicate analyses were performed on all syringe samples collected. The results of the syringe to grab sample comparisons are presented in Table 6-12. In all cases the syringe composite sample analysis was compared to the average of the results of five (5) grab samples collected at two (2) hour intervals during the runs.

TABLE 6-12

SYRINGE SAMPLER FIELD TRIAL RESULTS

CONTROL NUMBER	SAMPLE TYPE	GC/PID RESULTS	GC/PID RESULTS	AVERAGE BENZENE CONCENTRATION (mg/l)	PERCENT DIFFERENCE	TOLUENE CONCENTRATION (mg/l)	PERCENT DIFFERENCE
		BENZENE (mg/l)	TOLUENE (mg/l)				
46477	GRAB #1	27	2.7				
46479	GRAB #2	28	3.2				
46481	GRAB #3	28	2.8				
46483	GRAB #4	26	2.8				
46485	GRAB #5	31	2.7	26.0		2.84	
46488	SYRINGE PUMP	23	2.9				
	SYRINGE PUMP	23	2.8				
	SYRINGE PUMP	22	2.8	22.7	-19.05	2.83	-0.23
46490	SYRINGE CAPILLARY	17	1.3				
	SYRINGE CAPILLARY	17	1.2				
	SYRINGE CAPILLARY (dilution factor = 1.32)	17	1.3	17.1	-38.91	1.25	-55.99
46478	GRAB #1	34	5.1				
46480	GRAB #2	36	4.3				
46482	GRAB #3	33	3.8				
46484	GRAB #4	34	5.0				
46486	GRAB #5	27	4.4	32.8		4.52	
46489A	SYRINGE PUMP	26	3.8				
	SYRINGE PUMP	27	3.7				
	SYRINGE PUMP	27	3.8	26.7	-18.70	3.77	-16.67
46489A	SYRINGE PUMP - DUP	24	3.2				
	SYRINGE PUMP - DUP	25	3.1				
	SYRINGE PUMP - DUP	24	3.0	24.3	-25.81	3.10	-31.42
46490	SYRINGE CAPILLARY	25	2.6				
	SYRINGE CAPILLARY	24	2.5				
	SYRINGE CAPILLARY (dilution factor = 1.39)	24	2.5	24.1	-26.60	2.55	-43.67

All analyses were done via GC/PID for two principle volatile organic components of the lagoon wastewater, benzene and toluene.

A total of three runs were conducted, one each on 11/18/85, 11/19/85 and 11/20/85. Run 1 collected on 11/18/85 was discarded in the field due to a jam in the syringe withdrawal mechanism, therefore no analyses were performed for this run. The jam was discovered too late to prevent a significant loss of sample in the syringe. Run 2, collected on 11/19/85, was uneventful and involved the collection of duplicate syringe samples. One syringe was used to sample from the peristaltic sample delivery system for the full run. The second syringe sampled the lagoon through a passive capillary tubing delivery system which used no pumping device but drew sample simply from the withdrawal of the syringe barrel. (The particulars of the two methods themselves are described in Section 5). Run 3 involved the collection of three syringe samples. Two syringes were used to collect duplicate samples using the peristaltic pump sampling system. The third syringe was used with the capillary tubing sampling system.

This study resulted in the collection of three (3) syringe composite samples with the peristaltic pump system and two (2) syringe composite samples using a capillary tubing sampling system. Review of the results provided in Table 6-12 indicates that both syringe sampling methods resulted in significant volatile organic losses. The limited amount of data precludes the application of more elaborate statistical evaluations of this data, however, the percent differences are indicative of the composite sampler performance.

The following percent differences were reported:

Syringe with Pump--	
benzene	-19, -19 and -26 %
toluene	-0.2, -17 and -31 %
Syringe with Capillary Tubing--	
benzene	-39, and -27 %
toluene	-56, and -44 %

Earlier bench studies conducted using this sampler indicated that the syringe was capable of accurately sampling a test tank under varying dilute concentrations of volatile organics. The major differences in the field application of this methodology versus the bench study are likely to contribute to the observed sample loss. These differences are listed below:

1. Both of the sampling systems employed to deliver lagoon wastewater to the syringe used five (5) foot lengths of 1/8 inch diameter teflon tubing extending from the lagoon surface to the syringe sampler. It is possible sample losses occurred through adsorption or absorption of sample components to the tubing walls. The bench study involved collection of samples through a much shorter length of tubing, about one (1) foot.
2. The concentrations of the volatile organic components of the wastewater were much higher than the test stream generated during the bench study. The lagoon had concentrations of 1 to 36 mg/l levels versus the 100 g/l levels used during the bench study. These higher concentrations could have contributed to the poorer performance of the syringe sampler.
3. Beyond the elevated volatile organics concentrations cited previously, the complex sample matrix of the lagoon wastewater could also have impacted syringe sampler performance. The bench study utilized a dilute water stream which is enormously different from the concentrated mixture of volatile and semivolatile components of the lagoon wastewater.

6.4 Flux Chamber Direct Emission Measurement Program

The specific objective for this program was to conduct volatile organic compound emission rate measurements using an isolation flux chamber and associated sampling techniques and analyses. In support of this objective, gas and liquid samples were collected at each of the four grid locations at the wastewater holding lagoon for analysis.

The emission rate data obtained from this program are tabulated in the following tables:

6-13 - Emission Rates as Measured by On-Site Syringe Sample Analyses

6-14 - Average Surface Liquid Concentrations

TABLE 6-13

EMISSION RATES MEASURED USING THE
FLUX CHAMBER - SYRINGE SAMPLE

	Emission Rate (mg/m ² -hr) ^a				Mean
	Grid A	Grid B	Grid E	Grid F	
Total NMHC	167	316	237	195	226

a Average emission rate based upon analysis of duplicate samples, TNMHC.

TABLE 6-14
Average Surface Liquid Concentrations

Compound	Henry's Constant (atmm ³ /mol)	Grid A (ppm)	Grid B ^a (ppm)	Grid E ^a (ppm)	Grid F ^a (ppm)	SW Corner ^a (ppm)	Mean Conc. (ppm)
N-Butane	2.15E+01 ^b	0.00E+00	4.87E-02	0.00E+00	0.00E+00	0.00E+00	1.35E-02
1-Nonene	1.57E+00 ^b	0.00E+00	0.00E+00	0.00E+00	6.94E-02	0.00E+00	1.39E-02
Chloromethane	1.01E+00 ^b	0.00E+00	0.00E+00	6.14E-03	0.00E+00	0.00E+00	1.23E-03
Cyclohexane	9.57E-01 ^b	0.00E+00	6.41E-02	0.00E+00	5.58E-02	6.97E-02	3.79E-02
Chloroethane	3.08E-01 ^b	0.00E+00	0.00E+00	1.28E-01	0.00E+00	1.91E-02	2.94E-02
Tetrachloroethylene	2.80E-02	0.00E+00	2.89E-02	0.00E+00	0.00E+00	2.63E-01	5.84E-02
Toluene	6.64E-03	2.45E+00	1.88E+00	2.29E+00	2.05E+00	4.49E+00	2.63E+00
Benzene	5.50E-03	2.02E+01	1.42E+01	1.41E+01	1.33E+01	2.54E+01	1.74E+01
N-Undecane	4.59E-03 ^b	1.80E-01	1.20E-01	1.46E-01	1.11E-01	1.67E-01	1.45E-01
Methylchloride	3.19E-03	<.007	2.68E-02	3.82E-02	7.27E-02	7.15E-03	2.89E-02
Methylcyclopentene	8.67E-04 ^b	4.42E-01	1.64E-01	2.92E-01	1.77E-01	1.73E-01	2.50E-01
2,3-Dimethylpentane + Isoheptane		6.23E-02	0.00E+00	4.99E-02	4.72E-02	5.18E-02	4.22E-02
C9 Alkane		0.00E+00	1.15E-01	0.00E+00	0.00E+00	0.00E+00	2.30E-02
C10 + Alkane		2.09E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.18E-03
Isobutene + 1-Butene		3.79E-02	3.18E-02	2.52E-02	9.27E-02	0.00E+00	3.75E-02
2-Methyl-2-Butene		0.00E+00	0.00E+00	0.00E+00	3.50E-03	0.00E+00	7.00E-04
C-2-Butene		0.00E+00	5.50E-02	0.00E+00	0.00E+00	0.00E+00	1.10E-02
A-Pinene		1.36E-01	8.86E-02	1.12E-01	7.12E-02	1.20E-01	1.05E-01
Styrene		0.00E+00	8.94E-02	0.00E+00	0.00E+00	0.00E+00	1.79E-02
C8 Alkene		2.38E-02	2.27E-02	0.00E+00	1.89E-02	0.00E+00	1.31E-02
C10 + Aromatic		5.55E-02	6.39E-01	4.72E-02	6.22E-02	0.00E+00	1.61E-01
Trichlorofluoromethane		8.85E-02	4.39E-01	8.92E-01	5.20E-01	6.89E-01	5.26E-01
1,1-Dichloroethylene		0.00E+00	1.43E-02	0.00E+00	0.00E+00	5.46E-02	1.38E-02
Paraffins		2.82E-01	2.57E-01	1.96E-01	1.31E-01	2.62E-01	2.25E-01
Olefins		6.39E-01	2.42E-01	4.16E-01	3.87E-01	2.93E-01	3.95E-01
Total Aromatics		2.27E+01	1.65E+01	1.64E+01	1.54E+01	2.99E+01	2.01E+01
Total Halogenated HC		6.33E-01	3.17E-01	1.15E+00	5.35E-01	1.25E+00	7.76E-01
Unidentified VOC		7.64E+01	4.46E+01	5.34E+01	3.62E+01	5.85E+01	5.38E+01
Total NMHC		1.01E+02	6.18E+01	7.16E+01	5.26E+01	8.99E+01	7.54E+01

^aAverage concentration based upon duplicate gas canister samples.

^bEstimated value, (Equation A-6).

- 6-15 - Emission Rates as Measured by Canister Sample Analysis
- 6-16 - Summary of Mass Transfer Rates
- 6-17 - Summary of Concentration Data for Grid Point A
- 6-18 - Summary of Concentration Data for Grid Point B
- 6-19 - Summary of Concentration Data for Grid Point E
- 6-20 - Summary of Concentration Data for Grid Point F
- 6-21 - Summary of Concentration Data for Southwest Corner
- 6-22 - Summary of Flux Chamber Sampling and Analyses

The emission factors isolation flux chamber (or flux chamber) is an enclosure device used to make direct emission rate measurements. The flux chamber isolates a defined surface area and encloses gaseous emissions. Clean, dry sweep air is added to the chamber at a fixed, controlled rate. The sweep air flow rate through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The emission rate is calculated as:

$$ER_i = \frac{(Y_i)(Q)}{A}$$

Where:

ER_i = emission rate of species, i, ($\mu\text{g}/\text{m}^2 \cdot \text{min}$)
 Y_i = measured concentration of species i, ($\mu\text{g}/\text{l}$)
 Q = sweep air flow rate (l/min)
 A = exposed surface area, m^2

Normally three to five residence times (volume divided by flow rate) is needed to establish steady-state conditions in the chamber for sampling. The analytical results of a sample of the floating foam material on the lagoon surface are presented in Appendix B, along with the full report of the flux chamber monitoring activities.

TABLE 6-15

Emission Rates Measured Using the Flux Chamber - Canister Samples

Compound	Henry's Constant (atm m ³ /mol)	Emission Rates (kg/m ² -day) ^a					
		Grid A (ppm)	Grid B (ppm)	Grid E (ppm)	Grid F (ppm)	SW Corner (ppm)	Mean (ppm)
N-Pentane	6.05E+00b	0.00E+00	0.00E+00	2.78E-04	0.00E+00	0.00E+00	5.56E-05
N-Hexane	1.78E+00b	0.00E+00	0.00E+00	3.60E-04	0.00E+00	0.00E+00	7.20E-05
Cyclohexane	9.57E-01b	6.41E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.28E-06
N-Heptane	5.40E-01b	0.00E+00	0.00E+00	1.09E-04	0.00E+00	0.00E+00	2.18E-05
Tetrachloroethylene	2.80E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.61E-06	5.22E-07
N-Decane	1.52E-02b	0.00E+00	2.76E-05	0.00E+00	0.00E+00	0.00E+00	5.52E-06
Toluene	6.64E-03	5.14E-03	2.87E-03	8.51E-04	1.12E-03	2.69E-04	2.05E-03
Ethylbenzene	5.88E-03b	0.00E+00	0.00E+00	0.00E+00	3.75E-05	0.00E+00	7.50E-06
Benzene	5.50E-03	9.42E-03	6.69E-03	3.86E-03	6.92E-03	7.58E-04	5.53E-03
1,1,1-Trichloroethane	4.92E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.13E-05	8.26E-06
N-Undecane	4.59E-03b	1.33E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.66E-06
Chloroform	3.93E-03	3.53E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.06E-07
Methylchloride	3.19E-03	3.38E-04	4.80E-06	2.71E-05	2.90E-05	3.69E-05	8.72E-05
Trichloroethylene + Bromodichloromethane		0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.14E-06	4.28E-07
C3 VOC		3.43E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.86E-06
Paraffins		4.14E-05	2.76E-05	7.48E-04	0.00E+00	0.00E+00	1.63E-04
Olefins		4.53E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.06E-04
Total Aromatics		1.45E-02	6.52E-03	4.71E-03	8.07E-03	1.03E-03	6.97E-03
Total Halogenated HC		3.40E-04	4.80E-06	2.71E-05	2.90E-05	4.15E-05	8.85E-05
Unidentified VOC		8.12E-03	5.01E-03	2.29E-04	1.14E-03	2.99E-04	2.96E-03
Total NMHC		2.76E-02	1.16E-02	5.35E-03	9.25E-03	1.36E-03	1.10E-02

^aAverage emission rate based upon duplicate gas canister samples.^bEstimated value, (Equation A-6).

TABLE 6-16

Summary of Mass Transfer Rates
Calculated from Measured Emission Rates

Compound	Henry's Constant (atm m ³ /mol)	Liquid Conc. ^a (mg/m ³)	Emission Rate ^b (mg/sec m ²)	Mass Transfer Rate (m/s)
N-Butane	2.15E+01 ^c	1.35E+01		
N-Pentane	6.05E+00 ^c		6.43E-04	
N-Hexane	1.78E+00 ^c		8.33E-04	
1-Nonene	1.57E+00 ^c	1.39E+1		
Chloromethane	1.01E+00 ^c	1.23		
Cyclohexane	9.57E-01 ^c	3.79E+1	1.48E-05	3.91E-07
N-Heptane	5.40E-01 ^c		2.52E-04	
Chloroethane	3.08E-01 ^c	2.94E+1		
Tetrachloroethylene	2.80E-02 ^d	5.84E+1	6.04E-06	1.03E-07
N-Decane	1.52E-02 ^c		6.39E-05	
Toluene	6.64E-03 ^d	2.63E+3	2.37E-02	9.02E-06
Ethylbenzene	5.88E-03 ^c		8.68E-05	
Benzene	5.50E-03 ^d	1.74E+4	6.40E-02	3.68E-06
1,1,1-Trichloroethane	4.92E-03 ^d		9.56E-05	
N-Undecane	4.59E-03 ^c	1.45E+2	3.08E-05	2.13E-07
Chloroform	3.93E-03 ^d		8.17E-06	
Methylchloride	3.19E-03 ^d	2.89E+1	1.01E-03	3.49E-05
Methylcyclopentene	8.67E-04 ^c	2.50E+2		
Trichloroethylene + Bromodichloromethane			4.95E-06	
C3 VOC			7.94E-05	
2,3-Dimethylpentane + Isoheptane		4.22E+1		
C9 Alkane		2.30E+1		
C10 + Alkane		4.18		
Isobutene + 1-Butene		3.75E+1		
2-Methyl-2-Butene		7.00E-1		
C-2-Butene		1.10E+1		
A-Pinene		1.05E+2		
Styrene		1.79E+1		
C8 Alkene		1.31E+1		
C10 + Aromatic		1.61E+2		
Trichlorofluoromethane		5.26E+2		
1,1-Dichloroethylene		1.38E+1		
Paraffins		2.25E+2	1.89E-03	8.37E-06
Olefins		3.95E+2	1.05E-02	2.65E-05
Total Aromatics		2.01E+4	8.06E-02	4.00E-06
Total Halogenated HC		7.76E+2	1.02E-03	1.32E-06
Unidentified VOC		5.38E+4	3.42E-02	6.37E-07
Total NMHC		7.54E+4	1.27E-01	1.69E-06

^aAverage of concentrations measured at Grid Points A,B,E,F and the SW Corner, VOA vials

^bAverage of concentrations measured at Grid Points A,B,E,F and the SW Corner, gas canister.

^cEstimated value (Equation A-6).

TABLE 6-17

Syringe, Canister, and Liquid Concentration Data
for Grid Point A

Compound	Henry's Constant (atm m ³ /mol)	Syringe Sample ^a (g/m ³)	Canister Conc. ^b (g/m ³)	Liquid Conc. (ppm)
N-Butane	2.15E+01			0.0189
Cyclohexane	9.57E-01c		1.14E-04	
Toluene	6.64E-03		9.14E-02	2.45
Benzene	5.50E-03		1.68E-01	20.2
N-Undecane	4.59E-03c		2.39E-04	0.18
Chloroform	3.93E-03		6.28E-05	
Methylchloride	3.19E-03		6.02E-03	<.007
Methylcyclopentene	8.67E-04c			0.442
2,3-Dimethylpentane + Isoheptane				0.0623
C-3 VOC			6.10E-04	
C8 Alkane			9.88E-05	
C9 Alkane			1.81E-04	
C10 + Alkane				0.0209
C8 Alkene			1.05E-04	0.0238
Isobutene + 1-Butene				0.0379
A-Pinene				0.136
C10 + Aromatic				0.0555
Trichlorofloromethane				0.0885
Paraffins			7.39E-04	0.282
Olefins			8.06E-02	0.639
Total Aromatics			2.59E-01	22.7
Total Halogenated HC			6.05E-03	0.633
Unidentified VOC			1.45E-01	76.4
Total NMHC		8.59E-02	4.90E-01	101

^aCalculated as toluene.

^bAverage concentrations based upon duplicate samples.

^cEstimated value (Equation A-6).

TABLE 6-18

Syringe, Canister, and Liquid Concentration Data
for Grid Point B

Compound	Henry's Constant (atm m ³ /mol)	Syringe Sample ^{a,b} (g/m ³)	Canister Conc. ^b (g/m ³)	Liquid Conc. ^b (ppm)
N-Butane	2.15E+01c			0.0487
Cyclohexane	9.57E-01c			0.0641
Tetrachloroethylene	2.80E-02			0.0289
N-Decane	1.52E-02c		4.91E-04	
Toluene	6.64E-03		1.36E-02	1.875
Benzene	5.50E-03		1.02E-01	14.2
N-Undecane	4.59E-03c			0.1195
Methylchloride	3.19E-03		8.54E-05	0.02675
Methylcyclopentene	8.67E-04c			0.164
C9 Alkane				0.115
C8 Alkene				0.0227
Isobutene + 1-Butene				0.0318
C-2-Butene				0.055
A-Pinene				0.08855
Styrene				0.0894
C10 + Aromatic				0.639
Trichlorofloromethane				0.439
1,1-Dichloroethylene				0.0143
Paraffins			4.91E-04	0.2565
Olefins				0.2415
Total Aromatics			1.16E-01	16.45
Total Halogenated HC			8.54E-05	0.317
Unidentified VOC			8.91E-02	44.55
Total NMHC		1.62E-01	2.05E-01	61.8

^aCalculated as toluene.

^bAverage concentrations based upon duplicate samples.

^cEstimated value (Equation A-6).

TABLE 6-19

Syringe, Canister, and Liquid Concentration Data
for Grid Point E

Compound	Henry's Constant (atm m ³ /mol)	Syringe Sample ^a (g/m ³)	Canister Conc. ^b (g/m ³)	Liquid Conc. ^b (ppm)
N-Pentane	6.05E+00c		4.95E-03	
N-Hexane	1.78E+00c		6.41E-03	
1-Nonene	1.57E+00c			
Chloromethane	1.01E+00c			0.00614
Cyclohexane	9.57E-01c			
N-Heptane	5.40E-01c		1.94E-03	
Chloroethane	3.08E-01c			0.128
Toluene	6.64E-03		1.51E-02	2.29
Benzene	5.50E-03		6.87E-02	14.05
N-Undecane	4.59E-03c			0.1455
Methylchloride	3.19E-03		4.82E-04	0.03815
Methylcyclopentene	8.67E-04c			0.2915
2,3-Dimethylpentane + Isoheptane				0.0499
Isobutene + 1-Butene				0.0252
A-Pinene				0.112
C10 + Aromatic				0.0472
Trichlorofloormethane				0.8915
Paraffins			1.33E-02	0.1955
Olefins				0.416
Total Aromatics			8.38E-02	16.35
Total Halogenated HC			4.82E-04	1.1515
Unidentified VOC			4.08E-03	53.35
Total NMHC		1.22E-01	9.51E-02	71.55

^aCalculated as toluene.

^bAverage concentrations based on duplicate samples.

^cEstimated value (Equation A-6).

TABLE 6-20

Syringe, Canister, and Liquid Concentration Data
for Grid Point F

Compound	Henry's Constant (atm m ³ /mol)	Syringe Sample ^a (g/m ³)	Canister Conc. ^b (g/m ³)	Liquid Conc. ^b (ppm)
1-Nonene	1.57E+00c			0.0694
Cyclohexane	9.57E-01c			0.0558
Toluene	6.64E-03		1.99E-02	2.045
Ethylbenzene	5.88E-03c		6.67E-04	
Benzene	5.50E-03		1.23E-01	13.25
N-Undecane	4.59E-03c			0.111
Methylchloride	3.19E-03		5.15E-04	0.07265
Methylcyclopentene	8.67E-04c			0.177
2,3-Dimethylpentane + Isoheptane				0.0472
C8 Alkene				0.0189
Isobutene + 1-Butene				0.09265
2-Methyl-2-Butene				0.0035
A-Pinene				0.0712
C10 + Aromatic				0.0622
Trichlorofloromethane				0.52
Paraffins				0.13085
Olefins				0.3865
Total Aromatics			1.44E-01	15.35
Total Halogenated HC			5.15E-04	0.5345
Unidentified VOC			2.04E-02	36.15
Total NMHC		1.00E-01	1.65E-01	52.55

^aCalculated as toluene.

^bAverage concentrations are based on duplicate samples.

^cEstimated value (Equation A-6).

TABLE 6-21

Canister and Liquid Concentration Data
for Southwest Corner

Compound	Henry's Constant (atm m ³ /mol)	Syringe Sample (g/m ³)	Canister Conc. ^a (g/m ³)	Liquid Conc. ^a (ppm)
Cyclohexane	9.57E-01b			0.0697
Chloroethane	3.08E-01b			0.019145
Tetrachloroethylene	2.80E-02		4.65E-05	0.263
Toluene	6.64E-03		4.78E-03	4.49
Benzene	5.50E-03		1.35E-02	23.35
1,1,1-Trichloroethane	4.92E-03		7.35E-04	
N-Undecane	4.59E-03b			0.1665
Methylchloride	3.19E-03		6.57E-04	0.00715
Methylcyclopentene	8.67E-04b			0.173
2,3-Dimethylpentane + Isoheptane				0.0518
A-Pinene				0.1195
Trichlorofloromethane				0.6885
1,1-Dichloroethylene				0.0546
Trichloroethylene + Bromodichloromethane			3.81E-05	
Paraffins				0.2615
Olefins				0.2925
Total Aromatics			1.83E-02	29.85
Total Halogenated HC			7.39E-04	1.245
Unidentified VOC			5.31E-03	58.45
Total NMHC		N/A	2.43E-02	89.9

^aAverage concentrations are based on duplicate samples.

^bEstimated value (Equation A-6).

TABLE 6-22

Summary of Flux Chamber Sampling and Analyses

Sample Number	Sampling Point	Sample Type	Analysis Type
1	A	Syringe	HNU GC
2	A	Canister	Varian 401 GC
3	A	Canister	Varian 401 GC
4	A	Liquid	Varian 401 GC
7	B	Syringe	HNU GC
8	B	Canister	Varian 401 GC
9	B	Canister	Varian 401 GC
10	B	Liquid	Varian 401 GC
11	B	Liquid	Varian 401 GC
12	B	Syringe	HNU GC
13	F	Syringe	HNU GC
14	F	Canister	Varian 401 GC
15	F	Canister	Varian 401 GC
16	F	Liquid	Varian 401 GC
17	F	Liquid	Varian 401 GC
20	E	Syringe	HNU GC
21	E	Canister	Varian 401 GC
22	E	Canister	Varian 401 GC
23	E	Liquid	Varian 401 GC
24	E	Liquid	Varian 401 GC
25	SW Corner	Canister	Varian 401 GC
26	SW Corner	Canister	Varian 401 GC
27	SW Corner	Sludge	Varian 401 GC
28	SW Corner	Liquid	Varian 401 GC
29	SW Corner	Liquid	Varian 401 GC

^aHNU GC analyses performed on site. Varian 3700 GC analyses performed at Radian's Gas Chromatography Lab in Austin, Texas

7.0 QUALITY ASSURANCE/QUALITY CONTROL

7.1 Method Precision, Accuracy, and Completeness

As part of a rigorous Quality Assurance Program, quality control procedures were routinely implemented during the performance of this field monitoring program. The QAPP submitted to EPA for this project describes in detail the technical approach for the three major tasks conducted; the stratification study, the surrogate analytical parameter study, and the composite VOC syringe sampler field trial. Quality control results are presented in this section for the assessment of method precision, accuracy, and completeness. Goals for each of the methods utilized are provided in Table 7-1 and discussed in the method specific discussions which follow. Assessment of sampling and analytical methods for precision and accuracy was accomplished in the following manner.

It must be emphasized that the precision and accuracy estimates reported for each of the methods utilized in this program are just that; estimates. The data set sizes upon which these estimates are made are often very small, ranging from a single data point to larger data sets. Thus, true method precision and accuracy determinations are not possible. These estimations are made, however, for all methods, due to the importance of understanding the influence of measurement errors on the reported lagoon characteristics and air emission estimates. Also, these estimations will hopefully assist in the ultimate selection of sampling and analytical methodology for use in monitoring compliance with future regulations.

Precision

Sampling and analytical precision is assessed through replicate sampling and analysis. To maximize the amount of precision information available for review, a detailed QC Sample Set was designed. This QC sample set was

TABLE 7-1

SAMPLE QA OBJECTIVES FOR PRECISION, ACCURACY, AND COMPLETENESS
- OFFSITE LABORATORY ANALYSIS

Matrix	Parameter	Method ^a	Precision (Relative Standard Deviation)	Accuracy (% Recovery)	Completeness (%)
Liquid	Volatiles	GC/FID	_50	60-145	95
		GC/MS	_50	60-145	95
	Extractables	GC/FID	_50	10-130	95
		GC/MS	_50	10-130	95
	TOC	EPA 415.2	_15	85-115	95
	POC	b	c	c	95
Sediment	Volatiles	GC/FID	_75	50-160	95
		GC/MS	_75	50-160	95
	Extractables	GC/FID	_75	10-150	95
		GC/MS	_75	10-150	95
	TOC	EPA 415.2	_25	75-125	95

a Complete descriptions of these methods and their references are available in Section 7.0 Analytical Procedures.

b Refer to TOC instrument manual.

c Precision and accuracy goals were not available at the time of QA Plan preparation.

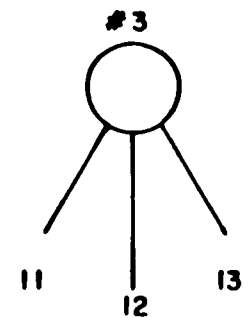
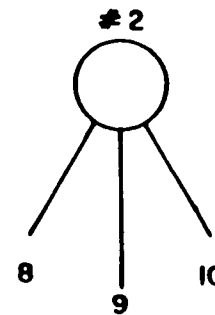
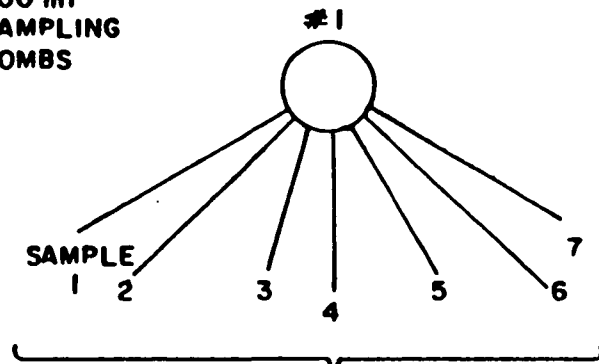
collected for those lagoon samples requiring POC, TOC, and volatile and extractable organics analysis by GC/FID at locations shown in Table 4-1. Each QC sample set included three Bacon bomb samples which were collected from the same sampling point (see Figure 7-1). The first sampling bomb was aliquoted into seven replicate samples; the standard deviation of the analytical results of these seven samples indicating the homogeneity of the bomb sample. The remaining two bombs were each aliquoted into triplicate samples resulting in a total number of 13 samples from one sampling point.

Overall measurement precision is estimated by the standard deviation of the analytical results for all 13 samples. Analytical precision is estimated by the standard deviation of a triplicate analyses performed on one sample from each one of the QC sampling sets described above (usually aliquot number 4). Since no QC sample sets were collected for GC/MS and GC/PID analysis, the laboratory performed a triplicate analysis on a randomly selected sample for each parameter to assess analytical precision. Ideally sampling precision could be determined by subtracting the analytical precision achieved from the overall measurement precision. Realistically, however, this is not the case and sampling precision is estimated as the standard deviation of the analytical results of samples 1 through 7 of the QA samples set.

Accuracy

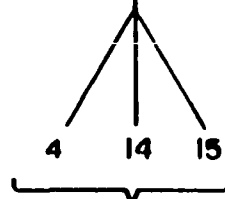
Measurement accuracy cannot readily be estimated since the true content of the wastewater holding lagoon samples is not known. The accuracy of the analytical procedures alone is assessed through the use of spiked field samples (matrix spike and matrix spike duplicates) and laboratory control samples whose true values are known to the Laboratory QC Coordinator. Analytical accuracy is estimated as the percent recovery of the known value.

500 ml
SAMPLING
BOMBS



STANDARD DEVIATIONS OF THE
ANALYTICAL RESULTS WILL
ASSESS BOMB HOMOGENITY
(SAMPLE COLLECTION)

STANDARD DEVIATIONS OF THE ANALYTICAL
RESULTS WILL ASSESS SAMPLING AND
ANALYTICAL PRECISION (MEASUREMENT)



STANDARD DEVIATIONS OF TRIPPLICATE
ANALYSIS OF ONE ALIQUOT WILL ASSESS
ANALYTICAL PRECISION ALONE (ANALYTICAL)

FIGURE 7-1

QUALITY CONTROL SAMPLING SET

Completeness

Completeness is defined as the percentage of measurements made judged to be valid measurements. Every attempt was made to have all data generated be valid data. The objective was to have 95 percent of the data valid. Results are presented with each method.

7.2 Laboratory Analyses

GC/FID Volatile Organic Analyses - Liquids

Quality control analyses conducted for the GC/FID volatile organic liquid sample analytical activities included analysis of field-biased blanks (FBB) and method blanks (MB), replicate sample analyses, matrix spikes (MS), and matrix spike duplicates (MSD). The results of these analyses are summarized in this section. Table 7-2 provides the results of blank sample analyses, Table 7-3 presents the results of replicate analyses, and Table 7-4 presents the results of matrix spike and matrix spike duplicates.

Overall, the GC/FID volatile organic analysis of liquid samples generated the following precision, accuracy, and completeness results; based on the benzene results only, since no toluene was found above the method detection limits,

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Overall measurement	34	50
Sample collection	33	
Analytical	NA	
<u>Accuracy (% REC)</u>	118	60 - 145
<u>Completeness (%)</u>	100	95

TABLE 7-2

GC/FID VOLATILE ORGANIC ANALYSES, LIQUID SAMPLES
BLANK RESULTS

SAMPLE LOCATION	Benzene (mg/l)	Toluene (mg/l)
FBB-19	<5	<5
FBB-20	<5	<5
BLANK	<5	<5

TABLE 7-3

GC/FID VOLATILE ORGANICS, LIQUID SAMPLES
REPLICATE ANALYSES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	QC SET ALIQUOT NUMBER	Benzene (mg/l)	Toluene (mg/l)
B-1	Liquid	46380	1	9	<1
B-1	Liquid	46381	2	12	<1
B-1	Liquid	46382	3	12	<1
B-1	Liquid	46383	4	12	<1
B-1	Liquid	46384	5	22	<5
B-1	Liquid	46385	6	20	<5
B-1	Liquid	46386	7	19	<5
B-1	Liquid	46387	8	19	<5
B-1	Liquid	46388	9	18	<5
B-1	Liquid	46375	10	11	<1
B-1	Liquid	46376	11	6	<1
B-1	Liquid	46377	12	17	<1
B-1	Liquid	46378	13	11	<1
<hr/>					
MEASUREMENT		AVERAGE		14	--
(1-13)		SUM (x_i^2)		3,010	--
		(SUM x_i) ²		35,344	--
		STD.DEV.		5	--
		REL.STD.DEV.		34%	--
<hr/>					
SAMPLE COLLECTION		AVERAGE		15	--
(1-7)		SUM (x_i^2)		1,758	--
		(SUM x_i) ²		11,236	--
		STD.DEV.		5	--
		REL.STD.DEV.		33%	--
<hr/>					
ANALYTICAL ^a		AVERAGE		NA	--
(4,14,15)		SUM (x_i^2)		NA	--
		(SUM x_i) ²		NA	--
		STD.DEV.		NA	--
		REL.STD.DEV.		NA	--

^a Aliquot 14 and 15 were not analyzed.

TABLE 7-4

GC/FID VOLATILE ORGANIC ANALYSES, LIQUID SAMPLES
MATRIX SPIKE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED ^a (mg/l)	TRUE VALUE (mg/l)	PERCENT RECOVERY		
B-1	46375	Liquid-MS	Benzene	310	250	124%		
		Liquid-MSD		300	250	120%		
		Liquid-MS	Toluene	540	250	216% ^b		
		Liquid-MSD		470	250	186% ^b		
		A-1	46368	Liquid-MS	Benzene	193	250	77%
				Liquid-MSD		178	250	71%
Liquid-MS	Toluene			188	250	75%		
Liquid-MSD				173	250	69%		
AVERAGE					118%			

^a Value corrected for native concentration.

^b Response increased by occurrence of chromatographic interference.

All blank results in Table 7-2 were below the method detection limit of 5 mg/L for both target compounds, benzene and toluene. These results indicate that no contamination of samples occurred between the field and the laboratory based on the results of the two field-biased blanks. The three method blank analyses indicate the lack of sample contamination due to analytical reagents of glassware. In this case, all blanks were samples of distilled deionized water which were carried through the same sample preparation and analytical procedures as the samples.

Precision data is provided in Table 7-3. Table 7-3 presents the replicate analyses for a surface liquid sample collected at Location B-1 in the lagoon. This sample was designated for a full QC set analysis. Due to an oversight, the triplicate split proposed in the QC set outline for assessment of the analytical precision was not performed. The available analytical data indicate a sampling precision for benzene of 33 percent relative standard deviation (RSD), and an overall measurement precision of 34 percent RSD. The close agreement between the sampling and overall measurement values would indicate good analytical precision (in the absence of the proposed triplicate analysis).

In addition to the results of these replicate analyses, matrix spike (MS) and matrix spike duplicate (MSD) analyses were conducted, the results of which are reported in Table 7-4. The 118 percent average recovery is an indication of acceptable method accuracy.

GC/FID Volatile Organic Analyses - Sludges

Precision, accuracy and completeness estimates were also made for the GC/FID volatile organic analysis of sludge samples. The QC samples used to make this assessment included blanks, replicates, and spikes. Overall, the results were:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Overall measurement	67	75
Sample collection	107	
Analytical	45, 16	
<u>Accuracy (% REC)</u>	99	50 - 160
<u>Completeness (%)</u>	100	95

Table 7-5 provides the results of a blank analysis showing no levels above the method detection limit. Tables 7-6 and 7-7 contain the results of replicate analyses for sludge samples analyzed by GC/FID for volatile organics.

Review of these results indicates the greater variability involved in the sampling and analysis of sludge material versus liquid samples. The sample collection precision result is over the anticipated goal of 75 percent RSD. The main reason for this lesser precision is thought to be the more complex nature of the sludge material itself and how the sample matrix is affected by the sample collection procedure. The sludge was found to be much more concentrated than the liquid samples. Variation in the production process at FCC would contribute to wide variations in the settleable organics in the lagoon over time. By nature, the sludge is a non-homogeneous material due to its accumulation over time via deposition. Thus, it is likely that the sludge material is composed of layers of varying concentration which are disturbed by the sampling process itself. This unavoidable disturbance contributes increased variability to the sludge sample concentrations. When these dynamics are considered, the low precision appears reasonable.

The analytical precision is reported for two samples, one as part of a full QC set 45 percent RSD, and one additional random sample analyzed in triplicate, 16 percent RSD. Both of these values are within the stated goals.

TABLE 7-5

GC/FID VOLATILE ORGANIC ANALYSES, SLUDGE SAMPLES
BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	Benzene (mg/l)	Toluene (mg/l)
BLANK	V5448	<130	<55

TABLE 7-6

GC/FID VOLATILE ORGANICS, SLUDGE SAMPLES
REPLICATE ANALYSES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	QC SET ALIQUOT NUMBER	Benzene (mg/kg)	Toluene (mg/kg)
E-5	Sludge	46415	1	1300	350
E-5	Sludge	46416	2	760	180
E-5	Sludge	46417	3	380	98
E-5	Sludge	46418	4	300	<85
			14	190	<85
			15	130	<85
			16	120	<85
E-5	Sludge	46419	5	220	<65
E-5	Sludge	46420	6	76	<65
E-5	Sludge	46421	7	320	<85
E-5	Sludge	46422	8	270	<60
E-5	Sludge	46423	9	650	200
E-5	Sludge	46423	10	450	110
E-5	Sludge	46424	11	<210	85
E-5	Sludge	46425	12	300	<50
E-5	Sludge	46426	13	480	<65
MEASUREMENT (1-13)		AVERAGE		459	171
		SUM (x_i^2)		3,676,876	223,829
		(SUM x_i) ²		30,316,036	1,046,529
		STD.DEV.		323	109
		REL. STD.DEV.		70%	64%
SAMPLE COLLECTION (1-7)		AVERAGE		479	171
		SUM (x_i^2)		2,658,576	171,729
		(SUM x_i) ²		11,262,736	508,369
		STD.DEV.		418	129
		REL. STD.DEV.		87%	126%
ANALYTICAL (4,14,15,16)		AVERAGE		185	NA
		SUM (x_i^2)		157,400	NA
		(SUM x_i) ²		547,600	NA
		STD.DEV.		83	NA
		REL. STD.DEV.		45%	NA

TABLE 7-7

GC/FID VOLATILE ORGANICS, SLUDGE SAMPLES
REPLICATE ANALYSES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	Benzene (mg/kg)	Toluene (mg/kg)	
F-5	Sludge	46455	2,000	510	
			2,800	670	
			2,300	560	
ANALYTICAL			AVERAGE	2367	580
			SUM (x_i^2)	17,130,000	1,022,600
			(SUM x_i) ²	50,410,000	3,027,600
			STD.DEV.	404	82
			REL.STD.DEV.	17%	14%

The magnitude of the percent recovery for the MS and MSD results reported in Table 7-8, is useful as an indicator of the method accuracy. The 91 percent to 108 percent recoveries for the two samples indicate acceptable method accuracy.

GC/FID Semivolatile Organics - Liquid Samples

Extractable organics determinations were performed on liquid samples collected from the lagoon. Quality control samples analyzed included blanks, surrogate spikes on every sample, replicates, and a matrix spike and matrix spike duplicate. The overall precision, accuracy, and completeness results are listed below:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Overall measurement	35	≤50
Sample collection	36	
Analytical	36	
Surrogates	48	
<u>Accuracy (% REC)</u>	107	10 - 130
Surrogates	50	
<u>Completeness (%)</u>	100	95

The results of the analysis of blank samples are provided in Table 7-9. No results above the detection limit are reported for either the field-biased blanks (FBB) or the laboratory method blanks.

Table 7-10 provides the results of a full QC set of analyses conducted on samples collected at location B-1. A total of five compounds are reported, of which only three were identified at levels above the detection limits. The

TABLE 7-8

GC/FID VOLATILE ORGANIC ANALYSES, SLUDGE SAMPLES
MATRIX SPIKE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/kg)	TRUE VALUE (mg/kg)	PERCENT RECOVERY
F-5	46455	Liquid-MS	Benzene	10,100	10,000	101%
		Liquid-MSD		10,800	10,000	100%
		Liquid-MS	Toluene	9,100	10,000	91%
		Liquid-MSD		9,700	10,000	97%
				AVERAGE		99%

TABLE 7-9

SEMI-VOLATILE ORGANIC ANALYSES,
LIQUID SAMPLES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	2,4-Dinitrotoluene (mg/l)	Nitrobenzene (mg/l)	2-Nitrophenol (mg/l)	2,4-Dinitrophenol (mg/l)	4,6-Dinitro-o-cresol (mg/l)
FBB1-20	46449	<10	<10	<3	<50	<10
FBB1-20	46450	<10	<10	<3	<50	<10
BLANK	QC 1566	<10	<10	<3	<50	<10
BLANK	QC 1567	<10	<10	<3	<50	<10
BLANK	QC 1568	<10	<10	<3	<50	<10

TABLE 7-10

GC/FID VOLATILE ORGANICS, LIQUID SAMPLES
REPLICATE ANALYSES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	QC SET ALIQUOT NUMBER	2,4-Dinitro-toluene (mg/l)	Nitro-benzene (mg/l)	2-Nitro-phenol (mg/l)	2,4-Dinitro-phenol (mg/l)	4,6-Dinitro-o-cresol (mg/l)
B-1	Liquid	46396	1	<11	320	8.2	100	24
B-1	Liquid	46397	2	<10	510	<16	330	45
B-1	Liquid	46398	3	<10	580	<16	210	23
B-1	Liquid	46399	4	<10	530	<16	250	33
			14	<10	580	<16	89	56
			15	<10	500	<16	120	24
B-1	Liquid	46400	5	<10	650	<16	82	46
B-1	Liquid	46401	6	<10	530	<16	190	27
B-1	Liquid	46402	7	<10	820	<16	89	33
B-1	Liquid	46403	8	<10	630	<16	160	42
B-1	Liquid	46404	9	<10	560	<16	180	27
B-1	Liquid	46405	10	<10	780	<16	84	25
B-1	Liquid	46406	11	<10	830	<16	62	39
B-1	Liquid	46407	12	<20	830	<43	190	53
B-1	Liquid	46408	13	<20	750	<43	280	59
MEASUREMENT (1-13)		AVERAGE		--	640	--	179	37
		SUM (x_i^2)		--	5,614,800	--	459,645	19,082
		(SUM x_i) ²		--	69,222,400	--	4,870,849	226,576
		STD. DEV.		--	155	--	84	12
		REL. STD. DEV.		--	24%	--	50%	32%
SAMPLE COLLECTION (1-7)		AVERAGE		--	563	--	179	33
		SUM (x_i^2)		--	2,355,600	--	276,245	8,153
		(SUM x_i) ²		--	15,523,600	--	1,565,001	53,361
		STD. DEV.		--	152	--	94	9
		REL. STD. DEV.		--	27%	--	52%	28%
ANALYTICAL* (4,14,15)		AVERAGE		--	537	--	153	38
		SUM (x_i^2)		--	867,300	--	84,821	4,801
		(SUM x_i) ²		--	2,592,100	--	210,681	12,769
		STD. DEV.		--	40	--	85	17
		REL. STD. DEV.		--	8%	--	56%	44%

precision estimation results for these three compounds average out to the reported 35 percent RSD, 36 percent RSD, and 37 percent RSD for the overall measurement, sample collection and analytical procedures, respectively. The overall measurement precision is better than that proposed in the QA plan goals.

Table 7-11 provides the results of the recovery percentages for the MS and MSD samples. Based on these results, an estimate of the method accuracy is determined to be 107 percent. This result can be further interpreted when considered with the average surrogate recovery percentage of 50 percent, derived from data included in Table 7-12. Both of these results are within the goals originally proposed for this analytical technique. Also, a relative standard deviation calculation based on the surrogate recovery data indicates an overall 51 percent RSD for the analytical technique.

GC/FID Semivolatile Organics - Sludge Samples

The results of quality control analyses conducted on lagoon sludge samples for semivolatile organics are summarized below:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Overall measurement	70	≤ 75
Sample collection	88	
Analytical	4	
Surrogates	25	
<u>Accuracy (% REC)</u>	69	10 - 150
Surrogates	70	
<u>Completeness (%)</u>	100	95

TABLE 7-11

GC/FID SEMI-VOLATILE ORGANIC ANALYSES, LIQUID SAMPLES
MATRIX SPIKE RECOVERIES, SAMPLE B-1, 46396

PARAMETER	MS QC 1577			MSD QC 1578			AVERAGE PERCENT RECOVERY
	AMOUNT REPORTED (mg/l)	AMOUNT SPIKED (mg/l)	PERCENT RECOVERY	AMOUNT REPORTED (mg/l)	AMOUNT SPIKED (mg/l)	PERCENT RECOVERY	
1,2,4-Trichlorobenzene	8.3	10	83	13.0	10	130	107
Acenaphthene	14.0	10	140	12.8	10	128	134
2,4-Dinitrotoluene	12.2	10	122	11.0	10	110	116
Pyrene	14.2	10	142	14.2	10	142	142
n-Nitroso-di-n-propylamine	<1.0*	10	NA	<1.0*	10	NA	NA
1,4 Dichlorobenzene	<1.0*	10	NA	7.2	10	72	36
Pentachlorophenol	30.0	20	150	27.6	20	138	144
Phenol	11.0	20	55	12.0	20	60	58
Chlorophenol	20.0	20	100	21.2	20	106	103
4-Chloro-e-methylphenol	21.4	20	107	24.4	20	122	115
4-Nitrophenol	22.4	20	112	24.2	20	121	117
						TOTAL	107

* chromatographic interference

TABLE 7-12

GC/FID SEMI-VOLATILE ORGANIC ANALYSES,
LIQUID SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	2-Fluorobiphenyl %	Terphenyl-d14 %	2-Fluorophenol %
A-1	46373	80	48	27
A-2	46370	77	106	27
A-3	46371	82	98	27
A-4	46372	58	65	60
B-1(1)	46396	76	41	48
B-1(2)	46397	62	60	27
B-1(3)	46398	64	72	20
B-1(4)	46399	59	50	10
		72	80	20
B-1(5)	46400	103	20	50
B-1(6)	46401	96	30	50
B-1(8)	46402	97	30	25
B-1(9)	46403	38	91	20
B-1(10)	46404	68	10	25
B-1(11)	46405	112	30	25
B-1(12)	46406	75	20	50
B-1(13)	46407	30	14	0
B-1(14)	46408	14	30	17
B-2	46409	21	50	33
E-1	46447	65	35	47
E-2	46433	68	77	18
E-3	46434	50	44	27
F-1	46476	64	59	40
F-2	46473	14	50	27
F-3	46474	52	56	33
FBB1-20	46449	89	101	25
FBB2-20	46450	95	57	25
BLANK	QC 1566	49	62	28
BLANK	QC 1567	29	63	40
BLANK	QC 1568	29	66	50
SPIKE	QC 1577	73	36	42
SPIKE	QC 1578	114	38	39
AVERAGE RECOVERY in %		65	53	31
SUM(x_i^2)		157,505	108,777	36,972
(SUM x_i) ²		4,305,625	2,852,721	1,004,004
STD.DEV. of RECOVERY %		32	28	16
REL.STD.DEV. in %		49%	54%	50%

Table 7-13 contains the results of blank analyses conducted on distilled water carried through the extraction procedure. No results above the detection limit were reported.

Replicate analyses were conducted on a full QC set of samples from location E-5, documented in Table 7-14. Review of the results again indicates that the sludge sample collection technique is an imprecise operation. The high relative standard deviations (RSD) calculated for the overall measurement and sample collection in conjunction with the low RSD calculated for the analytical technique support this conclusion.

Accuracy, estimated as the percent recovery of the matrix spike and matrix spike duplicate, and surrogate spiked compounds are presented in Tables 7-15 and 7-16. Overall values of 69 percent and 70 percent were reported. The relative standard deviation of the surrogate recoveries, averages 25 percent. This result can be compared with the analytical precision estimated from the replicate sample analyses.

GC/MS Volatile Organics - Liquid Samples

Quality control samples analyzed via this method included blanks, a matrix spike and matrix spike duplicate, and spiked surrogate compounds. No QC set replicate analyses were conducted on samples via GC/MS to keep the sample load manageable. Therefore, only overall method precision estimates can be made. The precision and accuracy indicators and completeness results are summarized below. All results indicate acceptable method performance.

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Surrogates	4	≤ 50

TABLE 7-13

SEMI-VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	2,4 Dinitrotoluene (mg/kg)	Nitrobenzene (mg/kg)	2-Nitrophenol (mg/kg)	2,4-Dinitrophenol (mg/kg)	4,6-Dinitro-o-cresol (mg/kg)
BLANK	QC 1591	<50	<50	<15	<250	<50
BLANK	QC 1598	<50	<50	<15	<250	<50

TABLE 7-14

GC/FID SEMI-VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLE REPLICATES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	QC SET ALIQUOT NUMBER	2,4-Dinitro-toluene (mg/l)	Nitro-benzene (mg/l)	2-Nitro-phenol (mg/l)	2,4-Dinitro-phenol (mg/l)	4,6-Dinitro-o-cresol (mg/l)	
E-5	Sludge	46435	1	230	7,000	110	4,400	2,000	
E-5	Sludge	46436	2	410	13,000	6,400	7,800	3,000	
E-5	Sludge	46437	3	380	12,000	200	7,700	2,800	
E-5	Sludge	46438	4	<200	14,000	410	9,200	3,800	
			14	<200	15,000	440	8,800	3,400	
			15	<200	15,000	440	9,100	3,500	
E-5	Sludge	46439	5	<400	8,400	220	5,700	2,200	
E-5	Sludge	46440	6	<200	20,000	560	12,000	4,400	
E-5	Sludge	46441	7	240	31,000	800	22,000	6,000	
E-5	Sludge	46445	8	<400	6,800	<1,000	4,200	1,700	
E-5	Sludge	46446	9	<400	10,000	290	6,400	2,900	
E-5	Sludge	46432	10	<400	6,800	3,500	4,000	2,300	
E-5	Sludge	46442	11	<400	15,000	390	11,000	3,400	
E-5	Sludge	46443	12	<400	15,000	390	11,000	3,200	
E-5	Sludge	46444	13	<400	20,000	490	16,000	4,200	
MEASUREMENT (1-13)		AVERAGE		315	13,769	1,147	9,338	3,223	AVERAGE
		SUM (x_i^2)		423,000	303,204,000	55,060,600	1,457,220,000	151,510,000	
		(SUM x_i) ²		1,587,600	32,041,000,000	189,337,600	14,737,960,000	1,755,610,000	
		STD.DEV.		158	6,876	1,837	5,192	1,171	
		REL.STD.DEV.		50%	50%	160%	56%	36%	70%
SAMPLE COLLECTION (1-7)		AVERAGE		315	15,057	1,243	9,829	3,457	
		SUM (x_i^2)		423,000	1,989,560,000	42,182,200	884,520,000	95,480,000	
		(SUM x_i) ²		1,587,600	11,109,160,000	75,690,000	4,733,440,000	585,640,000	
		STD.DEV.		181	8,191	2,287	5,894	1,403	
		REL.STD.DEV.		57%	54%	184%	60%	41%	88%
ANALYTICAL (4,14,15)		AVERAGE		--	14,667	430	9,033	3,567	
		SUM (x_i^2)		--	646,000,000	555,300	344,890,000	3,825,000	
		(SUM x_i) ²		--	1,936,000,000	1,664,100	734,410,000	114,490,000	
		STD.DEV.		--	577	17	208	208	
		REL.STD.DEV.	--	--	4%	4%	2%	6%	4%

TABLE 7-15

GC/FID SEMI-VOLATILE ORGANIC ANALYSES, SLUDGE SAMPLES
MATRIX SPIKE RECOVERIES, SAMPLE E-5, 46435

PARAMETER	MS QC 1589			MS QC 1590			AVERAGE PERCENT RECOVERY %
	AMOUNT REPORTED (mg/kg)	AMOUNT SPIKED (mg/kg)	PERCENT RECOVERY %	AMOUNT REPORTED (mg/kg)	AMOUNT SPIKED (mg/kg)	PERCENT RECOVERY %	
Phenol	715.0	1,100	65	605.0	1,100	55	60
2-4-Dinitrotoluene	440.0	550	80	401.5	550	73	77
					AVERAGE		69

TABLE 7-16

GC/FID SEMI-VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	2-Fluorobiphenyl %	Terphenyl-d14 %	2-Fluorophenol %
A-5	46374	47	37	61
B-5	46410	95	73	82
E-5(1)	46435	68	59	77
E-5(2)	46436	73	58	85
E-5(3)	46437	72	54	84
E-5(4)	46438	72	57	88
	46438B	79	47	98
	46438C	78	50	83
E-5(5)	46439	75	50	87
E-5(6)	46440	77	43	87
E-5(7)	46441	79	46	94
E-5(11)	46442	79	55	88
E-5(12)	46443	78	49	84
E-5(13)	46444	87	55	97
E-5(8)	46445	76	88	25
E-5(9)	46446	83	63	79
E-5(10)	46432	112	109	103
F-5	46475	55	65	29
BLANK	QC 1591	36	41	50
BLANK	QC 1598	76	88	80
SPIKE	QC 1589	68	59	80
SPIKE	QC 1590	63	54	75
AVERAGE RECOVERY in %		74	59	78
SUM(x_i^2)		125,468	82,974	142,316
(SUM x_i) ²		2,650,384	1,690,000	2,944,656
STD.DEV. of RECOVERY %		15	17	20
REL.STD.DEV. in %		21%	29%	26%

<u>Accuracy (% REC)</u>	<u>Actual (%)</u>	<u>Goals (%)</u>
MS and MSD	86	60 - 145
Surrogates	98	
<u>Completeness (%)</u>	100	95

The blank results are provided in Table 7-17, and indicate that field-biased blanks and laboratory method blanks contained no data above the detection limits. Tables 7-18 and 7-19 contain the matrix spike and matrix spike duplicate recoveries and surrogate compound recoveries. The averaged recoveries presented on these two tables estimate accuracy as 86 percent and 98 percent, respectively.

A rough indication of the method precision is provided by determining the relative standard deviation of the surrogate recovery percentage. The 4 percent value reported on Table 7-19 indicates good precision. The lack of replicate sample aliquots precludes a better estimate of this parameter.

GC/MS Volatile Organics Analyses - Sludges

QC sample analyses for sludges were conducted on blanks, a matrix spike and a matrix spike duplicate, and spiked surrogate compounds. Results of these analyses are useful as indicators of precision and accuracy, as well as the completeness result are presented below:

<u>Precision (% RSD)</u>	<u>Actual (%)</u>	<u>Goals (%)</u>
Surrogates	2	≤ 75
<u>Accuracy (% REC)</u>		
MS and MSD	110	50 - 160
Surrogates	100	
<u>Completeness (%)</u>	100	95

TABLE 7-17

VOLATILE ORGANIC ANALYSES,
LIQUID SAMPLES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	Benzene (mg/l)	Toluene (mg/l)	Nitro- Benzene* (mg/l)	Unknown (1) (mg/l)	Unknown (2) (mg/l)	Sum of Cpds. Reported	Sum of the Integrated Chromatograph
FBB-19	46395	<5	<1	<10	<10	<10	<10	<100
FBB-19	46431	<5	<1	<10	<10	<10	<10	<100
BLANK	V5480	<5	<1	<10	<10	<10	<10	<100
BLANK	V5478	<5	<1	<10	<10	<10	<10	<100

* Calculated relative to internal standard

TABLE 7-18

GC/FID VOLATILE ORGANIC ANALYSES, LIQUID SAMPLES
MATRIX SPIKE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/l)	TRUE VALUE (mg/l)	PERCENT RECOVERY %
F-5	46368	Liquid-MS	Benzene	235	250	94%
		Liquid-MSD		185	250	74%
		Liquid-MS	Toluene	220	250	88%
		Liquid-MSD		220	250	88%
					AVERAGE	86%

TABLE 7-19

GC/FID VOLATILE ORGANIC ANALYSES,
LIQUID SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	Toluene-dB %	BFB %	1,2-Dichloro- ethane-dB %	
A-1	46368	100	97	98	
	MS 46368	98	97	96	
	MSD 46368	97	99	100	
B-1	46379	95	99	101	
E-1	46412	95	98	101	
F-1	46452	91	100	104	
FBB-19	46395	102	96	102	
FBB-20	46431	101	97	95	
BLANK	V5480	101	99	97	
BLANK	V5478	99	85	88	
					AVERAGE
AVERAGE RECOVERY in %		98	98	98	98%
SUM(x_i^2)		95,951	95,475	96,620	
(SUM x_i) ²		958,441	954,529	964,324	
STD.DEV. of RECOVERY %		3	2	5	
REL.STD.DEV. in %		4%	2%	5%	4%

Table 7-20 provides the results for the sludge blank sample analysis. This sample was distilled water which was carried through the sludge extraction procedure. No compounds were present at levels above the stated detection limits.

Table 7-21 lists the matrix spike and matrix spike duplicate results. The results indicate the method accuracy, as an average of 110 percent recovery.

Recoveries of surrogate compounds are reported in Table 7-22 for seven sludge sample analyses. The average percent recovery of 100 percent is a further indicator of method accuracy. The relative standard deviation, 2 percent, of the recovery percentages serves as an indicator of analytical precision.

GC/MS Semivolatile Organics - Liquids

QC sample analyses included matrix spike, matrix spike duplicate, and spiked surrogate compounds analyses. No sample blanks or duplicate samples were analyzed by this method. This procedure was used as confirmation of the GC/FID results, rather than as a primary analysis for the stratification study. Since the GC/FID blank samples were below detection limits, no GC/MS analysis for blanks were performed. The precision and accuracy indicators and calculation of completeness are listed below:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Surrogates	17	≤50
<u>Accuracy (% REC)</u>		
MS and MSD	92	10 - 130
Surrogates	109	
<u>Completeness (%)</u>	100	95

TABLE 7-20

GC/MS VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	Benzene (mg/kg)	Toluene (mg/kg)	Nitro- Benzene* (mg/kg)	Unknown (1) (mg/kg)	Unknown (2) (mg/kg)	Sum of Cpds. Reported	Sum of the Integrated Chromatograph
BLANK	V5448	<30	<30	<100	<100	<100	<100	<1000

* Calculated relative to internal standard

TABLE 7-21

GC/MS VOLATILE ORGANIC ANALYSES, SLUDGE SAMPLES
MATRIX SPIKE RECOVERIES

SAMPLE LOCATION	GCA CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/kg)	TRUE VALUE (mg/kg)	PERCENT RECOVERY
F-5	46455	Sludge-MS	Benzene	12,200	10,000	122%
		Sludge-MSD		8,800	10,000	88%
		Sludge-MS	Toluene	13,000	10,000	130%
		Sludge-MSD		10,000	10,000	100%
					AVERAGE	110%

TABLE 7-22

GC/MS VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	Toluene-dB %	BFB %	1,2-Dichloro-ethane-dB %	
A-5	46362	102	99	103	
B-5	46392	100	99	99	
E-5	46415	99	100	102	
F-5	46455	97	101	102	
	MS 46455	95	100	106	
	MSD 46455	98	101	101	
BLANK	V5448	103	100	101	
					AVERAGE
AVERAGE RECOVERY in %		99	100	102	100%
SUM(x_i^2)		68,852	70,004	72,856	
(SUM x_i) ²		481,636	490,000	509,796	
STD.DEV. of RECOVERY %		3	1	2	
REL.STD.DEV. in %		3%	1%	2%	2%

Table 7-23 provides the results of the matrix spike and matrix spike duplicate results for the GC/MS semivolatile organic analysis of liquid samples. The average percent recovery of 92 percent provides an indication of the method accuracy.

The surrogate spike recovery results, presented in Table 7-24, provide indicators of both precision and accuracy. The average surrogate recovery of 109 percent serves as an accuracy indicator and the 17 percent relative standard deviation of the surrogate recovery percentages provides an estimation of the method precision.

GC/MS Semivolatile Organics - Sludge Samples

Blank samples, matrix spike and matrix spike duplicates, and surrogate spiked compounds were used to assess method precision and accuracy. The QC results are summarized below:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Surrogates	40	<75
<u>Accuracy (% REC)</u>		
MS and MSD	68	10 - 150
Surrogates	77	
<u>Completeness (%)</u>	100	95

Table 7-25 provides the results of the blank sample analysis, revealing no levels above the stated detection limits. Results of the analysis of matrix spike and matrix spike recoveries appear in Table 7-26. The average percent recovery of 68 percent serves as an indicator of method accuracy. The results of three compounds were invalidated by high matrix interference and were not included in the average percent recovery calculation.

TABLE 7-23

GC/MS SEMI-VOLATILE ORGANIC ANALYSES, LIQUID SAMPLES
MATRIX SPIKE RECOVERIES, SAMPLE B-1, 46396

PARAMETER	QC 1577			QC 1578			AVERAGE PERCENT RECOVERY
	AMOUNT REPORTED (mg/l)	AMOUNT SPIKED (mg/l)	PERCENT RECOVERY	AMOUNT REPORTED (mg/l)	AMOUNT SPIKED (mg/l)	PERCENT RECOVERY	
1,2,4-Trichlorobenzene	8.3	10	83	8.8	10	88	85.5
Acenaphthene	7.9	10	79	9.2	10	92	85.5
2,4-Dinitrotoluene	7.3	10	73	8.4	10	84	78.5
Pyrene	6.4	10	64	7.0	10	70	67.0
n-Nitroso-di-n-propylamine	7.4	10	74	8.1	10	81	77.5
1,4 Dichlorobenzene	7.9	10	79	9.2	10	92	85.5
Pentachlorophenol	27.2	20	136	25.8	20	129	132.5
Phenol	8.4	20	42	7.6	20	38	40.0
Chlorophenol	17.2	20	86	15.6	20	78	82.0
4-Chloro-e-methylphenol	20.4	20	102	18.6	20	93	97.5
4-Nitrophenol	18.0	20	90	17.2	20	86	88.0
						AVERAGE	92.0

TABLE 7-24

GC/MS SEMI-VOLATILE ORGANIC ANALYSES,
LIQUID SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	2-Fluorobiphenyl %	Terphenyl-d14 %	2-Fluorophenol %	
A-1	46373	112	70	48	
B-1	46396	94	60	90	
E-1	46447	100	64	92	
F-1	46476	130	128	90	
FBB1-20	46449	108	72	84	
FBB2-20	46450	104	66	80	
BLANK	QC 1566	104	78	94	
BLANK	QC 1567	102	80	86	
BLANK	QC 1568	106	74	86	
BLANK	QC 1588	100	100	100	
SPIKE	QC 1577	94	60	96	
SPIKE	QC 1578	104	60	88	
SPIKE	QC 1589	81	42	88	
SPIKE	QC 1590	42	54	80	
					AVERAGES
AVERAGE RECOVERY in %		126	92	109	109%
SUM(x_i^2)		141,193	78,360	105,156	
(SUM x_i) ²		1,907,161	1,016,064	1,444,804	
STD. DEV.		20	21	17	
REL.STD.DEV. in %		16%	23%	11%	17%

TABLE 7-25

GC/MS SEMI-VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	Nitro- benzene (mg/kg)	2-Nitro- phenol (mg/kg)	2,4-Dinitro- phenol (mg/kg)	4,6-Dinitro- o-cresol (mg/kg)	4-Nitro- phenol (mg/kg)	Benzoic Acid (mg/kg)
BLANK	QC 1586	<330	<330	<1650	<1650	<1650	<1650

TABLE 7-26

GC/MS SEMI-VOLATILE ORGANIC ANALYSES, SLUDGE SAMPLES
MATRIX SPIKE RECOVERIES (SAMPLE 46435)

PARAMETER	MS QC 1589			MSD QC 1590			AVERAGE PERCENT RECOVERY
	AMOUNT REPORTED (mg/kg)	AMOUNT SPIKED (mg/kg)	PERCENT RECOVERY	AMOUNT REPORTED (mg/kg)	AMOUNT SPIKED (mg/kg)	PERCENT RECOVERY	
Nitrobenzene (1)	7,900	1,100	718%	8,300	1,300	638%	678%
1,2,4-trichlorobenzene	270	550	49%	310	630	49%	49%
Acenaphthene	330	550	60%	320	630	51%	55%
2,4-Dinitrotoluene	500	1,100	45%	1,200	1,300	92%	69%
Pyrene	220	550	40%	580	630	92%	66%
4-Chloro-m-cresol	770	1,100	70%	1,200	1,300	92%	81%
1,4 Dichlorobenzene	300	550	55%	310	630	49%	52%
Pentachlorophenol	810	1,100	74%	1,600	1,300	123%	98%
Phenol	560	1,100	51%	810	1,300	62%	57%
Chlorophenol	520	1,100	47%	990	1,300	76%	62%
2-Nitrophenol	110	1,100	10%	170	1,300	13%	12%
4-Nitrophenol	2,000	1,100	182%	1,600	1,300	123%	152%
2,4-Dinitrophenol (1)	25,000	1,100	2273%	10,600	1,300	815%	1544%
4,6-Dinitro-o-cresol (1)	3,800	1,100	345%	2,800	1,300	215%	280%
	AVERAGE		62%			75%	68%

(1) High matrix interference invalidated these compounds.

The surrogate compounds recovery data are presented in Table 7-27. The average percent recovery result of 77 percent provides a further measure of method accuracy. The 40 percent relative standard deviation of the surrogate recovery percentages provides an estimate of the method precision.

Total Organic Carbon (TOC) Analyses

The total organic carbon analysis included typical QC sample analyses for the estimation of method precision and accuracy. The following values were determined for this method:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>TOC - LIQUIDS</u>		
<u>Precision (% RSD)</u>		
Duplicates	2	≤15
<u>Accuracy (% REC)</u>		
MS	96	85 - 115
EMSL spike	99	
<u>Completeness (%)</u>	100	95
<u>TOC - SLUDGES</u>		
<u>Precision (% RSD)</u>		
Duplicates	7	≤25
<u>Accuracy (% REC)</u>		
EMSL spike	96	75 - 125
<u>Completeness (%)</u>	100	95

The data from which these estimates were calculated are provided in Table 7-28, blank results; Table 7-29, duplicate results for liquid samples;

TABLE 7-27

GC/MS SEMI-VOLATILE ORGANIC ANALYSES,
SLUDGE SAMPLES SURROGATE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	2-Fluorobiphenyl %	Terphenyl-d14 %	2-Fluorophenol %	
A-5	46374	68	45	69	
B-5	46410	123	115	90	
E-5	46435	41	27	83	
F-5	46475	160	68	46	
SPIKE	QC 1589	81	42	88	
SPIKE	QC 1590	42	54	80	
BLANK	QC 1588	100	100	100	
					AVERAGES
AVERAGE		68	64	79	77%
SUM(x_i^2)		65,359	35,283	46,010	
(SUM x_i) ²		378,225	203,401	309,136	
STD.DEV.		43	32	18	
REL.STD.DEV.		49%	50%	22%	40%

TABLE 7-28

TOC ANALYSES METHOD BLANK RESULTS

CONTROL NO.	SAMPLE TYPE	PARAMETER	mg/m ³ of carbon
DI H2O	BLANK	TOC	0.477
DI H2O	BLANK	TOC	0.302

TABLE 7-29

TOC ANALYSES, LIQUID SAMPLES REPLICATE RESULTS

SAMPLE LOCATION	CONTROL NUMBER	SAMPLE ANALYSES (mg/m ³ of carbon)	AVERAGE CONCENTRATION (mg/m ³ of carbon)	RELATIVE STANDARD DEVIATION
A-1	46360	1,471 1,415 1,426	1,436	2%
B-1	46394	1,327 1,280 1,318	1,304	2%
E-1	46430	1,202 1,157 1,166	1,180	2%
F-1	46460	1,167 1,168 1,189	1,173	1%
			AVERAGE	2%

Table 7-30, duplicate results for sludge samples; Table 7-31, matrix spike results; and the results of EMSL - QC sample analyses in Tables 7-32 and 7-33.

Purgeable Organic Carbon (POC) Analyses

Performance standards for the analysis of purgeable organic carbon, POC, in liquid samples were not available at the time this method was proposed for use in this project. Because this procedure has not reached EPA standard method status or acceptance and lacks EPA standard method development results, standards for precision and accuracy are not obtainable. The research into the use of POC as a surrogate analytical parameter for liquid samples provided the following results:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Measurement	3	NA
Sample collection	3	NA
Analytical	4	NA
<u>Accuracy (% REC)</u>		
MS	90	NA
EMSL spike	89	NA
<u>Completeness (%)</u>	100	95

The actual QC sample results from which these precision and accuracy determinations were made are provided in the following tables. Table 7-34 provides blank results, Table 7-35 provides the results of the QC set of replicate analyses, Table 7-36 provides matrix spike results, and Table 7-37 provides the EMSL spike results.

TABLE 7-30

TOC ANALYSES, SLUDGE SAMPLES DUPLICATE RESULTS

SAMPLE LOCATION	CONTROL NUMBER	SAMPLE ANALYSES (mg/m ³ of carbon)	AVERAGE CONCENTRATION (mg/m ³ of carbon)	RELATIVE STANDARD DEVIATION
E-5	46448	39,938 34,829 35,794	36,854	7%

TABLE 7-31

TOC ANALYSES MATRIX SPIKE RESULTS

SAMPLE LOCATION	GCA CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/m ³ of carbon)	TRUE VALUE (mg/m ³ of carbon)	PERCENT RECOVERY
F-1	46460	Liquid	TOC	87.9	91.5	96.1

TABLE 7-32

TOC ANALYSES, LIQUID SAMPLES
EMSL QC SAMPLE RESULTS

SAMPLE NUMBER	PARAMETER	AMOUNT REPORTED (mg/m ³ of carbon)	TRUE VALUE (mg/m ³ of carbon)	PERCENT RECOVERY
WP782-4	TOC	92.44	91.5	101.0
WP782-4	TOC	91.37	91.5	99.9
WP782-4	TOC	85.86	91.5	93.8
WP782-4	TOC	91.75	91.5	100.3
WP782-4	TOC	89.18	91.5	97.5
			AVERAGE	98.5%

TABLE 7-33

TOC ANALYSES, SLUDGE SAMPLES
EMSL QC SAMPLE RESULTS

SAMPLE NUMBER	PARAMETER	AMOUNT REPORTED (mg/m ³ of carbon)	TRUE VALUE (mg/m ³ of carbon)	PERCENT RECOVERY
EPA QC	TOC	216.4	225.7	95.9

TABLE 7-34

POC ANALYSES BLANK RESULTS

GCA CONTROL NO.	SAMPLE TYPE	PARAMETER	mg/m ³ of carbon
DI H ₂ O	BLANK	POC	0.009
DI H ₂ O	BLANK	POC	0.008

TABLE 7-35

POC ANALYSES, LIQUID SAMPLES
REPLICATE ANALYSES

SAMPLE LOCATION	SAMPLE TYPE	CONTROL NO.	QC SET ALIQUOT NUMBER	POC (mg/m ³ of carbon
F-1	Liquid	46460	1	150
				146
F-1	Liquid	46461	2	154
				143
F-1	Liquid	46462	3	146
				140
				136
F-1	Liquid	46463	4	139
				140
F-1	Liquid	46464	5	147
				145
F-1	Liquid	46465	6	149
				145
F-1	Liquid	46466	7	149
				147
F-1	Liquid	46467	8	147
				146
F-1	Liquid	46468	9	151
				151
				142
F-1	Liquid	46469	10	143
				145
F-1	Liquid	46470	11	144
F-1	Liquid	46471	12	141
F-1	Liquid	46472	13	142
MEASUREMENT (1-13)		AVERAGE		145
		SUM (x_i^2)		526,930
		(SUM x_i) ²		13,162,384
		STD.DEV.		4
		REL.STD.DEV.		3%
SAMPLE COLLECTION (1-7)		AVERAGE		145
		SUM (x_i^2)		315,984
		(SUM x_i) ²		4,734,976
		STD.DEV.		5
		REL.STD.DEV.		3%
ANALYTICAL (3,14,15)		AVERAGE		141
		SUM (x_i^2)		59,412
		(SUM x_i) ²		178,084
		STD.DEV.		5
		REL.STD.DEV.		4%

TABLE 7-36

POC ANALYSES MATRIX SPIKE RESULTS

SAMPLE LOCATION	CONTROL NO.	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/m ³ of carbon)	TRUE VALUE (mg/m ³ of carbon)	PERCENT RECOVERY
F-1	46470	Liquid	POC	8.23	10	82.3
F-1	46471	Liquid	POC	10.11	10	101.1
F-1	46472	Liquid	POC	8.73	10	87.3
AVERAGE						90.2%

TABLE 7-37

POC ANALYSES EMSL QC SAMPLE RESULTS

SAMPLE NUMBER	SAMPLE TYPE	PARAMETER	AMOUNT REPORTED (mg/m ³ of carbon)	TRUE VALUE (mg/m ³ of carbon)	PERCENT RECOVERY %
WP782-4	SPIKE	POC	81.16	91.5	88.7

GC/PID Volatile Organics Analysis

Quality control samples for the GC/PID analysis of samples collected during the composite syringe field trials included blanks, duplicates, matrix spikes and EMSL spikes. The results presented in this section indicate that the analytical methodology performed well for this study. Table 7-38 shows no detectable level of benzene or toluene in the field-biased syringe blank. Since these compounds were the only analytical parameters selected for this field study, no sample contamination is indicated to have occurred.

All syringe samples were analyzed in triplicate. The results of these analyses and the calculated relative standard deviations are presented in Tables 7-39 and 7-40. Also, summarized in Table 7-41 are the results of two grab samples which were analyzed in duplicate. Table 7-42 provides the results of spiked sample analyses. In summary, the precision and accuracy estimates for these procedures are indicated by the following results:

	<u>Actual (%)</u>	<u>Goals (%)</u>
<u>Precision (% RSD)</u>		
Syringe with pump	2	≤75
Syringe with capillary	2	
<u>Accuracy (% REC)</u>	96	60 - 145
<u>Completeness (%)</u>	100	95

In order to assess the accuracy of the GC/PID methodology, a matrix spike and an EMSL QC sample were analyzed. The results ranged from 85 percent to 112 percent recovery. These results are well within the goal stated in the QAPP of 60 to 145 percent.

TABLE 7-38

GC/PID VOLATILE ORGANIC ANALYSES BLANK RESULTS

SAMPLE LOCATION	CONTROL NO.	Benzene (mg/l)	Toluene (mg/l)
SYRINGE FBB	46487	0.5	<0.5

TABLE 7-39

DUPLICATE ANALYSES, GC/PID VOLATILE ORGANIC ANALYSES

CONTROL NUMBER	SAMPLE LOCATION	SAMPLE TYPE	PARAMETER	CONCENTRATION (mg/l)			AVERAGE	RELATIVE STANDARD DEVIATION
				A	B	C		
46408	S-1	Syringe Pump	Benzene	23	23	23	23.0	0.0%
			Toluene	2.9	2.8	2.8	2.8	2.0%
46489A	S-1	Syringe Pump	Benzene	26	27	27	26.7	2.9%
			Toluene	3.8	3.7	3.8	3.8	1.5%
46489B	S-1	Syringe Pump	Benzene	24	25	24	24.3	2.4%
			Toluene	3.2	3.1	3.0	3.1	3.2%
AVERAGE REL. STD. DEV.							1.9%	

TABLE 7-40

DUPLICATE ANALYSES, GC/PID VOLATILE ORGANIC ANALYSES

CONTROL NUMBER	SAMPLE LOCATION	SAMPLE TYPE	PARAMETER	CONCENTRATION (mg/l)			AVERAGE	RELATIVE STANDARD DEVIATION
				A	B	C		
46491	S-1	Syringe Capillary	Benzene	25	24	24	24.1	3.4%
			Toluene	2.6	2.5	2.5	2.5	3.2%
46490	S-1	Syringe Capillary	Benzene	17	17	17	17.1	0.0%
			Toluene	1.3	1.2	1.3	1.3	1.1%
AVERAGE REL. STD. DEV.							1.9%	

TABLE 7-41

DUPLICATE ANALYSES, GC/PID VOLATILE ORGANIC ANALYSES

CONTROL NUMBER	SAMPLE LOCATION	SAMPLE TYPE	PARAMETER	CONCENTRATION in mg/l		AVERAGE	RELATIVE STANDARD DEVIATION
				A	B		
46481	S-3	Grab	Benzene	28	29	28.5	2.5%
			Toluene	2.8	2.8	2.8	0.0%
46480	S-2	Grab	Benzene	36	36	36.0	0.0%
			Toluene	4.3	4.3	4.3	0.0%
						AVERAGE REL. STD. DEV.	0.2%

TABLE 7-42

GC/PID VOLATILE ORGANIC ANALYSES MATRIX SPIKE RECOVERIES

SAMPLE LOCATION	CONTROL NO.	PARAMETER	AMOUNT REPORTED (mg/l)	TRUE VALUE (mg/l)	PERCENT RECOVERY
EPA-EMBL-QC	WP879	Benzene	26	30.6	85%
		Toluene	4.6	4.1	112%
S-2	46479	Benzene	9.1	10	91%
		Toluene	9.5	10	95%

7.3 On-Site Analyses

The precision and accuracy of the onsite analytical methods were assured by adhering to the procedures and guidelines of the methods discussed in Section 5. No actual QC sample analyses were conducted in the field.

7.4 Calibration Procedures and Frequency

Laboratory Instruments

All analytical instruments, including the GC/FID, GC/MS, GC/PID, TOC and POC systems, were calibrated in accordance with the procedures listed in the QAPP, and following the guidelines of the referenced EPA methodology.

Onsite Instrumentation

Field instruments were used at First Chemical Corporation following procedures outlined in U.S. EPA Methodology EPA-600/4-84-017 "Methods for Chemical Analysis of Water and Wastes." The field instruments were tested and calibrated following manufacturers specifications and the frequency table listed in the program QAPP.

7.5 Sample Custody

The purpose of chain-of-custody procedures is to document the identity of the sample and its handling from its first existence as a sample until analysis and data reduction are completed. Sample custody procedures and the forms used at First Chemical Corporation are discussed in this section. Sample bank custody procedures will also be discussed.

Field Chain-of-Custody Record Sheets

A two-part carbonless copy custody record was used following the NEIC format. Samples obtained from First Chemical Corporation were recorded daily

on the custody forms, signed by the sampler, and relinquished by the field team leader. Copies of the forms are included in Appendix A.

Sample Identification

Each sample, including replicates and field-biased blanks have a field sample tag completely filled in with analysis requested, sampler and sample location. The tag is printed on a waterproof, tear-resistant paper which insures legibility.

Custody Seals and Shipped Samples

Samples collected at First Chemical Corporation were shipped on a daily basis back to the contractor laboratory by a Air Carrier (e.g., Federal Express). Shipments were made following DOT protocols in steel-lined coolers. Each cooler contained a chain-of-custody record of the samples within. The package was then closed with strapping tape and custody seals, so that the carrier is transporting a sealed container.

Sample Bank Custody

A Division Sample Bank was maintained to implement chain-of-custody procedures and to provide proper storage for all samples submitted to the Division.

Upon receipt at the Sample Bank, each shipment was inspected to assess the condition of the shipping container and the samples within. The enclosed chain-of-custody forms were cross-referenced with all the samples in the shipment. The records were signed by the Sample Bank Assistant and recorded in the bound master Sample Log under a Control Number.

7.6 Data Reduction

Precision

Precision was determined by the analysis of replicate samples and is expressed as the standard deviation, S, which is determined according to the following equation:

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

where: S = standard deviation
x_i = individual measurement result
N = number of measurements

Relative standard deviation is also reported. It is calculated as follows:

$$RSD = 100 \left(\frac{S}{\bar{x}} \right) \quad (2)$$

where: RSD = relative standard deviation, expressed in percent
S = standard deviation
 \bar{x} = arithmetic mean of replicate measurements

Precision of duplicate samples is expressed as the relative percent difference, which is determined according to the following equation:

$$\text{Relative \% Difference} = \frac{\text{Value 1} - \text{Value 2}}{\text{arithmetic mean of value 1 and 2}} \times 100 \quad (3)$$

Accuracy

Accuracy was estimated from the analysis of spiked samples, or Laboratory Control samples whose true values are known to the Laboratory QC Coordinator. Accuracy is expressed as percent recovery or as relative error. The formulas to calculate these values are:

$$\text{Percent Recovery} = 100 \left(\frac{\text{Measured Value}}{\text{True Value}} \right) \quad (4)$$

$$\text{Relative Error} = 100 \left(\frac{\text{Measured Value} - \text{True Value}}{\text{Trace Value}} \right) \quad (5)$$

Completeness

Completeness is reported as the percentage of all measurements made whose results are judged to be valid. The procedures used for validating data and determination of outliers are contained in Section 8.0 of this QA plan. The following formula was used to estimate completeness:

$$C = 100 \left(\frac{V}{T} \right) \quad (6)$$

where: C = percent completeness
V = number of measurements judged valid
T = total number of measurements

Surrogate Study

Presentation of the surrogate study results included comparisons of the GC/MS compound specific results to those generated by the surrogate analytical parameters, POC and TOC. The volatile surrogate parameter comparison were made according to the following equations using POC and GC/MS VOC data.

$$C_T = \sum_{x=1}^N C_x \left[\frac{W_{C_x}}{MW_x} \right] \quad (7)$$

$$R_i = \frac{C_S}{C_T} \quad (8)$$

$$S = \frac{\left(\sum_{i=1}^y R_i^2 \right) - \frac{1}{y} \left(\sum_{i=1}^y R_i \right)^2}{y-1} \quad (9)$$

where:

- W_{C_x} = weight of carbon per compound
- MW_x = molecular weight of compound
- N = number of compounds identified in GC/MS VOC analysis
- C_T = total carbon-weighted GC/MS VOC concentration, ppm as carbon
- C_x = specific volatile organic compound result from GC/MS scan, ppm
- C_S = POC concentration, ppm of carbon
- R_i = correlation factor between POC surrogate and GC/MS VOC total
- N = number of analytical comparisons
- S = standard deviation of correlation factors

The total organic surrogate parameter comparison were made according to the following equations using the TOC and GC/MS VOC and SVOC results:

$$C_A = \sum_{x=1}^N \left[C_x \left(\frac{W_{C_x}}{MW_{C_x}} \right) \right] \quad (10)$$

$$R_{i2} = \frac{C_B}{C_A} \quad (11)$$

$$S = \sqrt{\frac{\left(\sum_{i=1}^y R_{i2}^2 \right) - \frac{1}{y} \left(\sum_{i=1}^y R_{i2} \right)^2}{y-1}} \quad (12)$$

where: C_A = total carbon weighted GC/MS concentration including both VOC and SVOC results
 N = number of compounds identified in GC/MS VOC and SVOC analysis
 R_i = correlation factor between TOC surrogate and GC/MS VOC and SVOC
 C_B = TOC concentration, ppm carbon

Time-Integrated Syringe VOC Sampler Field Trial

Each of the four field trial sampling runs compared the analytical results from the duplicate composite syringe samples to the average of the four grab samples collected per run. The comparisons were made for each of the selected compounds analyzed. The analytical results were tabulated for each run, and percent differences calculated using the following equation.

$$\% \text{ Difference} = \frac{Y_i - X_i}{X_i} \times 100 \quad (13)$$

Steam Stripper Vent Flow Measurement

An approximate stack velocity was calculated from the basic pitot tube velocity formula:

$$V = \sqrt{\frac{2 \Delta P}{\rho}} \quad (14)$$

where: V = velocity [ft/sec]
 P = pressure [LBF/ft²]
 ρ = density [slugs/ft³]

The smallest readable increment on the manometer was .005 inches H₂O, or 0.026 pounds force per square foot. The density of the stack gas was assumed

to be that of 80°C air at 1 ATM, or .0021 slugs/ft³. The minimum detection limit of the device is then:

$$V = \sqrt{\frac{2 (.026)}{.0021}} \sim 5.0 \text{ feet/sec} \quad (15)$$

Given an inside pipe diameter of 2.0 inches, the minimum detectable flow is 6.5 CFM.

7.7 Deviations from the QA Plan

This section of the quality assurance discussion is meant to identify the deviations which occurred during the program from that which was proposed in the quality assurance project plan. Several issues of this type did occur during the implementation of the lagoon study. One primary deviation was the reduction in the scope of the sampling and analytical activities. This reduction was the result of curtailed sampling necessitated by the hurricane warning conditions imposed by the facility. Four sampling locations were selected instead of the eight which were originally proposed.

Technically, the analytical methodology proposed for the collected samples was implemented consistent with the QAPP. The TOC and POC analyses for the surrogate study and the GC/PID analyses for the syringe composite sampler field trials were completed on schedule. The nature of the samples collected as well as severe instrumental impacts resulted in serious analytical delays for the GC/FID and GC/MS analyses. These delays occurred for many reasons, including:

- The occurrence of unidentified aliphatic (C10) compounds in the sample matrix, necessitated two hour retention time screening runs for all GC/FID and GC/MS analyses. Prior to completion of these sample screening analyses dilution ratios and surrogate compound spiking concentrations could not be determined. This lengthy turnaround time for each sample resulted in analytical delays.
- The complex sample matrix resulted in data reduction complications as well as exaggerated equipment maintenance and repair demands, including; frequent column replacement, syringe failure and autosampler malfunctions. Also, a fault in the software of the GC/MS volatile organic instrument resulted in a period of instrument downtime.
- All semivolatile organic samples were subjected to screening analyses to determine dilution ratios and surrogate compound spiking concentrations. Screening was necessary due to the expected variability in the samples based on the color range of the samples from red to yellow to black. This screening to determine spike levels is not usually required for semivolatile organics analyses and resulted in analytical delays.
- Frequent reanalysis of samples was required when unacceptable surrogate spike recoveries were identified, particularly for some of the phenolic semivolatile organics. Also, retention time shifts due to matrix effects made quantitation of sample results difficult, and caused additional delays.
- The highly organic nature of the sludge samples and the corresponding very low sediment content required a more extensive sample preparation, screening and dilution approach.

Internal GCA corrective action investigations (CA No. 063) were pursued concurrent with the activities required to respond to the conditions identified above. The extensive QC sample load in this field program provides some insight into the precision and accuracy of the analytical work. The effects of the analytical delays incurred are not, however, separable from these overall precision and accuracy estimates.