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AP-42 Section	_____	AP-42 Section	10.8
Reference	_____	Reference	13
Report Sect.	4	Report Sect.	4
Reference	15	Reference	10

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IX

75 Hawthorne Street
San Francisco, Ca. 94105-3901

August 19, 1992

Gene Crumpler
OAQPS (MD-13)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Crumpler,

Per your request, I am enclosing a copy of the Final Emission Data Report - Emissions Testing Program (December 1989). This report was prepared as part of the Remedial Investigation at the Koppers Superfund Site in Oroville, California.

Shortly after talking with you today, I received a call from Gwen Smith at RTI (919/541-6456), who was also calling to request a copy of this report. I told her that I was sending a copy to you and that you were planning to forward it to RTI. She said she would call you to confirm which person at RTI was to receive the report.

Please feel free to contact me (at 415/744-2365) if you have any further questions about the report.

Sincerely,

Frederick K. Schauffler
Remedial Project Manager (H-7-2)
Superfund Enforcement Branch

Enclosure

EPA WORK ASSIGNMENT NUMBER: 187-9L43
EPA CONTRACT NUMBER: 68-01-7250
EBASCO SERVICES INCORPORATED

- NOT ORIGINAL TEST REPORT
- CAN ONLY ASSUME AN AVG. ESTIMATED WEIGHT / CYCLE
- COULD ASSUME SOME AVG. WOOD DENSITY TO CALCULATE G+3 WOOD / CYCLE

**FINAL
EMISSION DATA REPORT
EMISSION TESTING PROGRAM
KOPPERS SUPERFUND SITE
OROVILLE, CALIFORNIA**

DECEMBER 1989

REVISION 1

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency (EPA) under REM III Contract No. 68-01-7250 to Ebasco Services Incorporated (Ebasco). This document has been formally released by Ebasco to the EPA. However, this document does not represent the EPA's position or policy and has not been formally released by the EPA.

EPA WORK ASSIGNMENT NUMBER: 187-9L43
EPA CONTRACT NUMBER: 68-01-7250.
EBASCO SERVICES INCORPORATED

FINAL
EMISSION DATA REPORT
EMISSION TESTING PROGRAM
KOPPERS SUPERFUND SITE
OROVILLE, CALIFORNIA

AUGUST 1989



P. Michael Schwan
Site Manager
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1.0 SUMMARY AND DISCUSSION

1.1 SUMMARY

The objective of this project was to measure and/or estimate the emission rates of toxic compounds that are emitted from the Koppers Industries, Inc. wood treatment facility in Oroville, California. This work was conducted by Ebasco Services, Incorporated on behalf of EPA Region 9 as part of the REM III program. The estimated emission rates will be used by contractors to EPA Region 9 as part of risk assessment studies for the facility. The key steps involved in the project were as follows:

- o A literature review was conducted to establish the best methods to measure the stack emissions and fugitive emissions.
- o EPA emission factors were obtained to estimate the emission rates from those sources that could not be directly sampled. The emission factors are described in Chapter 5.0.
- o A program of ambient air quality monitoring and meteorological monitoring was conducted at the site in October, 1988 to measure the evaporative emissions from the treated wood storage area. The methods that were used are described in Section 5.7, and the results are presented in Section 6.3.
- o A stack sampling and wastewater sampling program was conducted at the site in February, 1989. Three of the key stack emission sources were sampled for trace metals, volatile organic compounds (VOCs) and semi-volatile organic

compounds (SVOCs). The stack sampling methods are described in Chapter 4.0. Process chemicals and wastewater streams were sampled for trace metals, VOCs and SVOCs. The results of the liquid stream sampling are given in Section 5.1. The process piping was inventoried to provide data for input to emission factor equations. The results of the process piping inventory are given in Section 5.6.

The estimated annual emission rates for organic compounds are presented in Table 1-1 and the estimated annual emission rates for inorganic compounds are presented in Table 1-2.

1.2 DISCUSSION

The emission rates listed in Tables 1-1 and 1-2 should not be considered as precise engineering values that might be used for design purposes, because many of the listed rates are based on assumptions that provide conservatively high values. The emission rates calculated in this report are intended only for use as input to screening models that will be used to roughly estimate the public health impacts of the toxic pollutant emissions. If the screening models indicate the threat of unacceptable public health risks, then additional actions will be needed to address the emissions.

The significance of the emission rates cannot be determined until the air quality risk assessment is complete. However, two preliminary conclusions can be drawn based on the results in this report:

- o The greatest predicted emissions of organic chemicals was from the steam cycles and storage yard fugitive emissions. The total estimated PAH emissions (stack and fugitive) from

cylinder operations was 3470 kg/yr (21 lbs/day). There are no current standard limits for Hydrocarbons and PAH emissions. However, the 21 lbs/day is higher than the 15 lbs/day that agencies have established for new industrial facilities. The impact of the benzene emissions can only be established when the air modeling is completed.

- o The storage yard is a potential source for large quantities of PAH compounds to be emitted into the ambient air. Based on the measured PAH compounds found in the ambient air and the assumed flux rate, approximately 28,000 kg/yr are released. This is 1.6% of the total amount of PAH compounds found in the process chemical used per year.

NO TESTS ON
CYLINDER
NO. 3
see p. 6-8

TABLE 1-1
SUMMARY OF EMISSION SOURCES
(Emission Rates in kg/year)

X CREOSOTE
CCA

Organic Compound	Cylinder No. 3		Cylinder No. 4		Total General Fugitive Emissions	Wood Storage Yard	Total Emission Rate ⁵	Maximum Possible Emissions
	Total Stacks	Total Fugitive Emissions	Total Stacks	Total Fugitive Emissions				
Benzene	1.3 P	2.4 P	66.1 P	26.1 P	2.7 P	**	99	130
Toluene	3.2 P	2.3 P	73.6 P	24.5 P	2.2 P	**	106	362
Pyridine	**	**	**	**	**	**	0	<24000
Cresols	208.9 <P	29.5 <M	48.6 <P	453.9 <M	17.6 <P	194.0 <M	953	<24000
Napthalene	264.5 P	13.9 M	867.9 P	149.5 M	16.8 P	9500.0 M	10813	106000
2-Methylnapthalene	194.5 P	15.8 M	1023.2 P	171.1 M	20.4 P	86000.0 M	87425	320000
Acenaphthene	33.4 P	1.8 M	263.3 P	22.3 M	2.8 P	5900.0 M	6223	144000
Fluorene	11.9 P	4.9 M	72.2 P	5.4 M	0.7 P	3300.0 M	3395	84000
Phenanthrene	15.9 P	2.5 <M	47.2 P	5.5 M	0.9 P	2100.0 M	2172	384000
Other Detected PAHs PAHs Below Detection Limits in Gas Stream	18.4 <P	0.4	25.9 <P	5.0 M	0.3 P	454.0 M	460	1060900
		0.0 <M		0.2 <M	0.0 P	400.0 <M	445	

1/ "P" Means that the listed value was predicted.

2/ "M" Means that the listed value was based on stack measurements.

3/ "<" Prefix indicates that the listed value is partially based on the Method Detection Limit.

4/ "****" Means that the compound predictions based on MDL were out of reasonable range.

5/ Total emission rates are the sum of all values based on detected concentrations and the method detection limit for samples where compounds are not detected.

CCA
CYLINDER

TABLE 1-2
SUMMARY OF EMISSION SOURCES
(Emissions Rates in kg/year)

Inorganic Compound	Cylinder No. 2 Vacuum Exhaust	Cylinder No. 2 Working Tank Vent	Cylinder No. 2 Unloading	Total Emission Rate ⁵
Arsenic	OK → 9.4E-05 <M	1.2E-01 P	7.7E-05 <P	1.2E-01
Chromium (VI)	----- "	1.0E-01 P	3.6E-05 <P	1.0E-01
Total Chromium	OK → 2.4E-04 M	1.4E-01 P	1.8E-04 P	1.4E-01
Copper	OK → 3.3E-04 M	7.8E-02 P	3.5E-04 P	7.9E-02

- 1/ "p" Means that the listed value was predicted.
- 2/ "M" Means that the listed value was based on stack measurements.
- 3/ "<" Prefix indicates that the listed value is partially based on the Method Detection Limit.
- 4/ "M" Sample exceeded the 24 hour analysis holding time and was not useable.
- 5/ Total emission rates are the sum of all values based on detected concentrations and the method detection limit for samples where compounds are not detected.

2.0 INTRODUCTION

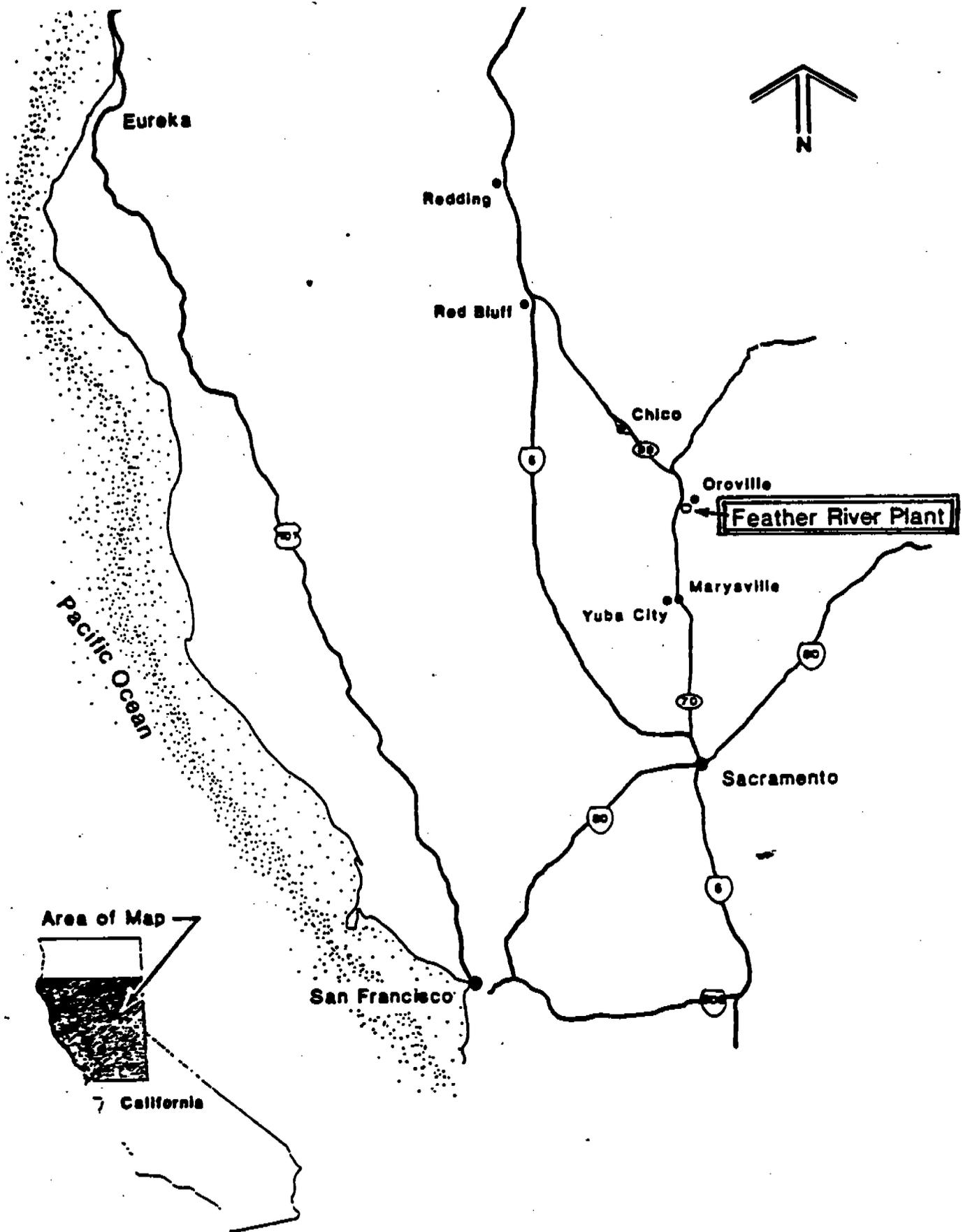
2.1 PROJECT BACKGROUND

The Koppers Industries, Inc. plant in Oroville, California (Figure 2-1) is on EPA's National Priorities List for remediation under the Superfund program. EPA Region 9 is interested in characterizing hazardous substance releases from wood treating operations in order to determine if these emissions may pose public health risks. REM III is conducting a comprehensive risk assessment for the Koppers facility. That risk assessment will include evaluation of the inhalation pathways. This report summarizes the emission rates of key toxic compounds from the stack sources and fugitive sources at the facility. REM III will perform air quality modeling to estimate the ambient concentrations of those compounds around the facility. The results of the air dispersion modeling will be used to estimate the off-site risks associated with the vapor inhalation exposure pathways. The modeling will account for adsorption of the emitted vapors onto atmospheric particles. However, the modeling is not intended to address the emissions of contaminated fugitive dust from the facility.

2.2 PROJECT OBJECTIVES AND APPROACH

The objectives of this project were as follows:

- o Measure or estimate the emission rates of the following contaminants that are emitted from stack sources and fugitive sources:



Not to Scale

FIGURE 2-1 SITE LOCATION MAP

Volatile Organic Compounds

Benzene
Toluene
Pyridine

Semi-Volatile Organic Compounds

Cresols
Phenol
Total PAHs
Speciated PAHs

Inorganic Components

Arsenic
Copper
Total Chromium
Hexavalent Chromium

The above list of components was compiled by EPA's contractor for their risk assessment. The focus of this investigation was on these compounds. The above listed chemicals are normal components of the process chemicals except for pyridine. Pyridine is a by-product which originates in the wood and is leached out of the wood during the creosote treatment process. It is recognized that the wood treating processes at the Koppers facility are likely to emit more components than those listed above, but the list includes those components which are likely to pose the most significant potential public health risks from plant operations.

- o For those sources at the Koppers plant where direct emission measurements are not practical, use emission factors to predict the emission rates.

- o Present the estimated emission rates in a format that REM III can readily use as input to their computer dispersion models.

The emission measurements and estimates were performed using the following approach:

- 1) A literature review was conducted to identify previous studies of emissions from creosote wood treating operations, and to compile appropriate emission factor equations.
- 2) The following technical plans were prepared and approved by EPA Region 9: Work Plan (Ebasco 1988a); Sampling and Analysis Plan or SAP (Ebasco, 1988b); Emission Estimation Plan or EEP (Ebasco, 1988c); Health and Safety Plan (Ebasco, 1988d); and Quality Assurance Project Plan (Ebasco, 1988e).
- 3) A program of ambient air quality and meteorological monitoring was performed at the site in October, 1988 to measure the evaporative emission rates from the treated wood storage yard.
- 4) Stack sampling and sampling of liquid streams (process chemicals and wastewater) was performed in February, 1989 to obtain a snapshot of emissions.

In some cases, site-specific conditions were encountered during the testing which required revisions to the methods specified in the SAP and EEP. Those revisions are noted in the appropriate sections of this report.

3.0 DESCRIPTION OF KOPPERS FACILITY

3.1 WOOD TREATING OPERATIONS AT THE KOPPERS FACILITY

The Koppers Feather River Plant is a wood treatment facility located in Butte County, roughly 65 miles north of Sacramento, California (Figure 2-1). The facility treats wood for use as telephone poles, railroad ties, dock pilings, and fence posts. Logs are shaved on site and then treated in high-pressure, high-temperature vessels. Following treatment, the logs are spread out on pallets in the log yard to dry. Of the wood treatment process currently used at the Koppers plant, the following are considered to be probable sources of toxic air emissions:

- o The chromated copper arsenate (CCA) process;
- o The creosote process; and
- o The diluent process (creosote plus oil solvents).

The simplified process flow diagram for each of these processes is shown in Figure 3-1. A layout of the Koppers Facility is shown in Figure 3-2. The locations of the potential air pollution emission sources are also shown in those figures. Each of the processes are described below.

3.1.1 Chromated Copper Arsenate Process

The Koppers facility treats an estimated 7,000 metric tons per year (420 loads per year) using the CCA process. The CCA process operates by exposing the wood to a high pressure

(roughly 145 psi) solution of water soluble chromium, arsenic and copper. The process is unheated. The treatment process is done in Cylinder No. 2 (a large above-ground cylinder roughly 7 feet in diameter by 50 feet long). After the cylinder is filled with wood and sealed, the cylinder is evacuated and then filled with a dilute CCA solution. No vapors are emitted during the filling process. After the wood is pressure treated with the CCA solution, the solution is drained from the cylinder and "blown back" to the CCA Working Tank. During the blowback cycle, headspace vapors from the CCA Working Tank are vented to the atmosphere through Stack SS-8. After the cylinder is drained, a 22-inch Hg vacuum is drawn on the cylinder for roughly 1/2 hour to remove all excess solution from the pores of the wood. During that vacuum cycle, the gas, which may contain aqueous mists containing arsenic, chromium and copper, is vented directly to the atmosphere through the vacuum exhaust (Stack Source SS-3). Finally, aqueous mists may be released to the atmosphere when the cylinder door is opened for unloading the wood (Fugitive Source FS-2).

The aqueous CCA solution is stored in a working tank adjacent to the treatment cylinder No. 2. Releases of volatilized arsenic from the tank are possible, because the head space in the tank is vented to the atmosphere during filling. Similar emissions occur during venting of the concentrated CCA storage tank.

3.1.2 Creosote Process

The creosote process is conducted in either of two large above-ground treatment cylinders (Nos. 3 and 4). The Koppers facility treats an estimated 11,000 metric tons per year (200 loads per year) in Cylinder No. 4 and an estimated

7,000 metric tons per year (120 loads per year) in Cylinder No. 3. The cylinders are roughly 7 feet in diameter by 140 feet long. Wood is pressure treated using pure creosote with the following steps:

- o The cylinder is charged with wood and filled with creosote. This process takes roughly 1/2 hour. The head space vapors are emitted to the atmosphere through SS-4 and SS-6.
- o The wood is "Boultonized" between 4-8 hours by exposing the wood and creosote to a 22-inch Hg vacuum at 200°F. Vapors from the vacuum pumps are treated using a vapor condensor and emitted through SS-5 and SS-7.
- o The cylinder is drained and the creosote is "blown back" to the creosote working tank. This cycle lasts 1/2 hour. The organic components in the headspace vapors from the creosote work tank are recovered using a water cooled vapor condensor. The treated headspace gas is emitted through SS-1.
- o The cylinder is refilled with creosote again, under pressure this time. This cycle takes about 45 minutes. No vapors are emitted during this phase of the process.
- o The cylinder is heated to 135°F at 30 psi pressure for 3/4 hour. No vapors are emitted during this cycle.

- o The pressure is reduced to atmospheric and the temperature is raised to 210°F for roughly three hours. No vapors are emitted during this phase of the process.
- o The creosote is again "blown back" to the working tank. This cycle takes roughly 1/2 hour. Treated vapors are emitted through SS-1.
- o The drained cylinder is exposed to a 22-inch Hg vacuum for roughly 1/2 hour. Treated vapors are emitted from Cylinder 3 through SS-5 and from Cylinder 4 through SS-7. This process pulls additional creosote from wood pores.
- o Residual creosote is "stripped," or pumped from the bottom of the cylinder back to the working tank. This process takes roughly 45 minutes. Treated vapors are emitted through SS-1.
- o The treated logs are heated by direct contact with pressurized steam at 240°F for roughly one hour. Treated vapors are emitted through SS-1.
- o Two additional one-hour "final vacuum" cycles at 22-inch Hg vacuum are done to pull the last amounts of creosote from the wood. Treated vapors are emitted from Cylinder 3 through SS-5 and from Cylinder 4 through SS-7.
- o The cylinder is opened and the wood is removed. Residual vapors inside the cylinder are released to the atmosphere as Fugitive Sources FS-3 and FS-4.

3.1.3 Diluent Process

The Koppers facility treats an estimated 9,000 metric tons per year (150 loads per year) using the diluent process. This process is identical to the Creosote Process described in Section 3.1.2, except that the wood is treated using a mixture of creosote plus No. 6 fuel oil. This process is done using only Cylinder 3, which is identical to Cylinder 4. The diluent working tank is heated. Headspace vapors from the diluent working tank are vented through Stack SS-1 along with the vapors from the creosote working tank.

3.1.4 Wastewater Collection and Treatment

The water from the vacuum exhaust vapor condensers and the residual creosote and diluent streams that drain from the cylinders after the cylinders are opened are collected in small sumps ("door pits") and periodically pumped to a central oil/water separator. Each of the door pits of Cylinders 3 and 4 are roughly 5 feet in diameter and 5 feet deep. The sumps are drained every few days. The oil/water separator divides the waste stream into three parts:

- o The fuel oil fraction of the diluent floats, and is skimmed from the separator and pumped back to the diluent storage tank.
- o The creosote fraction sinks, and is scraped from the bottom of the separator and is pumped back to the creosote storage tank.
- o The aqueous phase that neither floats nor sinks is pumped to a separate wastewater treatment process.

The oil/water separator handles roughly 5 gallons per minute (gpm) for six hours per day. It is an open vessel roughly 25 feet long and 8 feet wide.

3.1.5 Rail, Truck and Tank Car Unloading

The CCA concentrate is delivered to the site as a 50 percent solution in tank trucks. Roughly 8,800 gallons per year of concentrate are purchased and offloaded to the CCA Concentrate Storage Tank. Head space vapors are emitted through SS-9 when the concentrate Storage Tank is filled.

Rail tank cars containing pure creosote are offloaded about 2-4 times per month. Each tank car contains about 20,000-30,000 gallons of creosote resulting in approximately 800,000 gallons per year of creosote being purchased. The creosote in the tank car is first heated for 2 days by using steam coils built into the car. Then, the creosote is pumped from the car over a 4-6 hour period. The creosote is pumped from the top of the car through a standard filling cap that is open to the atmosphere. Fugitive emissions from tank car unloading are designated FS-1.

Diluent oils (No. 6 fuel oil) are delivered to the plant in tank trucks at a frequency of less than once per month. Roughly 115,000 gallons per year are purchased. The unloading process for the diluent oils is similar to that for the creosote, except that the tanker trucks are not heated.

3.1.6 Treated Wood Storage

The treated wood is stored at the plant until it is sold and shipped off-site. A load of treated wood is typically stored for 2-4 weeks before it is sold. Telephone poles treated by the Creosote Process are stored in a roughly 5-acre area northeast of the treating facility. Railroad ties treated by the Diluent Process are stored in a 1-acre area south of the treating facility.

3.2 POTENTIAL AIR POLLUTION EMISSION SOURCES

Table 3-1 lists the air pollution emission sources at the Koppers plant that are considered to be possible sources of toxic air pollutants. Each of the emission sources are shown in the process flow diagram in Figure 3-1. The emission sources labeled FS-1 through FS-10 are fugitive sources. The emission sources labeled SS-1 through SS-9 are individual exhaust stacks.

A description of the stacks designated as SS-1 through SS-9 is given in Table 3-2. Most of the stacks are shown in the plant layout given in Figure 3-2. Stacks SS-8 and SS-9 are not shown in Figure 3-2 and are located roughly 150 feet southeast of Cylinder No. 2.

TABLE 3-1

SUMMARY OF AIR POLLUTION EMISSION SOURCES

Source Number	Description	Contaminants ^{1/}	Source Type	Method for Emission Estimate ^{2/}
FS-1	Raft Tank Car Unloading	Organics	Fugitive	EPA emission factors
FS-2	Cylinder No. 2 Unloading	Metals	Fugitive	Mtl. balance based on SS-3 tests
FS-3	Cylinder No. 3 Unloading	Organics	Fugitive	Mtl. balance based on SS-7 tests
FS-4	Cylinder No. 4 Unloading	Organics	Fugitive	Mtl. balance based on SS-7 testing
FS-5	Product Storage Evaporation	Organics	Fugitive	Ambient Measurements
FS-6	Cylinder No. 3 Sump	Organics	Fugitive	Emission factor, based on LSP-4
FS-7	Cylinder No. 4 Sump	Organics	Fugitive	Emission factor, based on LSP-4
FS-8	Oil/Water Separator	Organics	Fugitive	Emission factor, based on LSP-4
FS-9	Cylinder No. 3 Piping	Organics	Fugitive	Emission factor, based on LSP-2
FS-10	Cylinder No. 4 Piping	Organics	Fugitive	Emission factor, based on LSP-2
SS-1	Creosote Working Tank Vent	Organics	Stack	Direct measurement, SS-1
SS-3	Cylinder 2 Vacuum Exhaust	Metals	Stack	Direct measurement, SS-3
SS-4	Cylinder 3 Fill Vent	Organics	Stack	Emission factor, based on LSP-2
SS-5	Cylinder 3 Vacuum Exhaust	Organics	Stack	Emission factor, based on SS-7
SS-6	Cylinder 4 Fill Vent	Organics	Stack	Emission factor, based on LSP-1
SS-7	Cylinder 4 Vacuum Exhaust	Organics	Stack	Direct measurement
SS-8	CCA Working Tank Vent	Metals	Stack	Emission factor, based on LSP-3
SS-9	CCA Concentrate Tank Vent	Metals	Stack	Emission factor, based on LSP-3

^{1/} "Organics" and "metals" are defined as those compounds listed in Section 2.2.

^{2/} Designations for stack sources, fugitive sources and sampling points are given in Figure 3-1.

TABLE 3-2

DESCRIPTION OF EMISSION STACKS

Stack No.	Source Description	Stack Height (ft)	Pipe Diameter (inches)
SS-1/2	Creosote and Diluent Working Tank Vent	15	8
SS-3	Cylinder No. 2 Vacuum Exhaust	ground level	2
SS-4	Cylinder No. 3 Fill Vent	15	3
SS-5	Cylinder No. 3 Vacuum Exhaust	15	3
SS-6	Cylinder No. 4 Fill Vent	15	3
SS-7	Cylinder No. 4 Vacuum Exhaust	10	3
SS-8	CCA Work Tank Vent	25	6
SS-9	CCA Concentrate Tank Vent	8	3

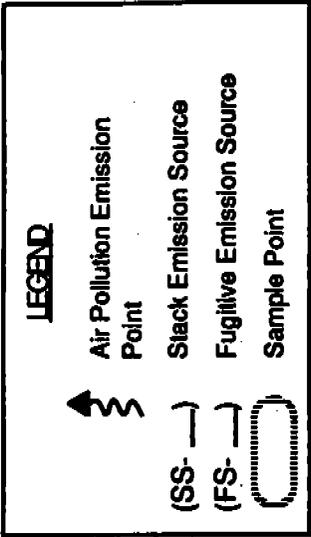
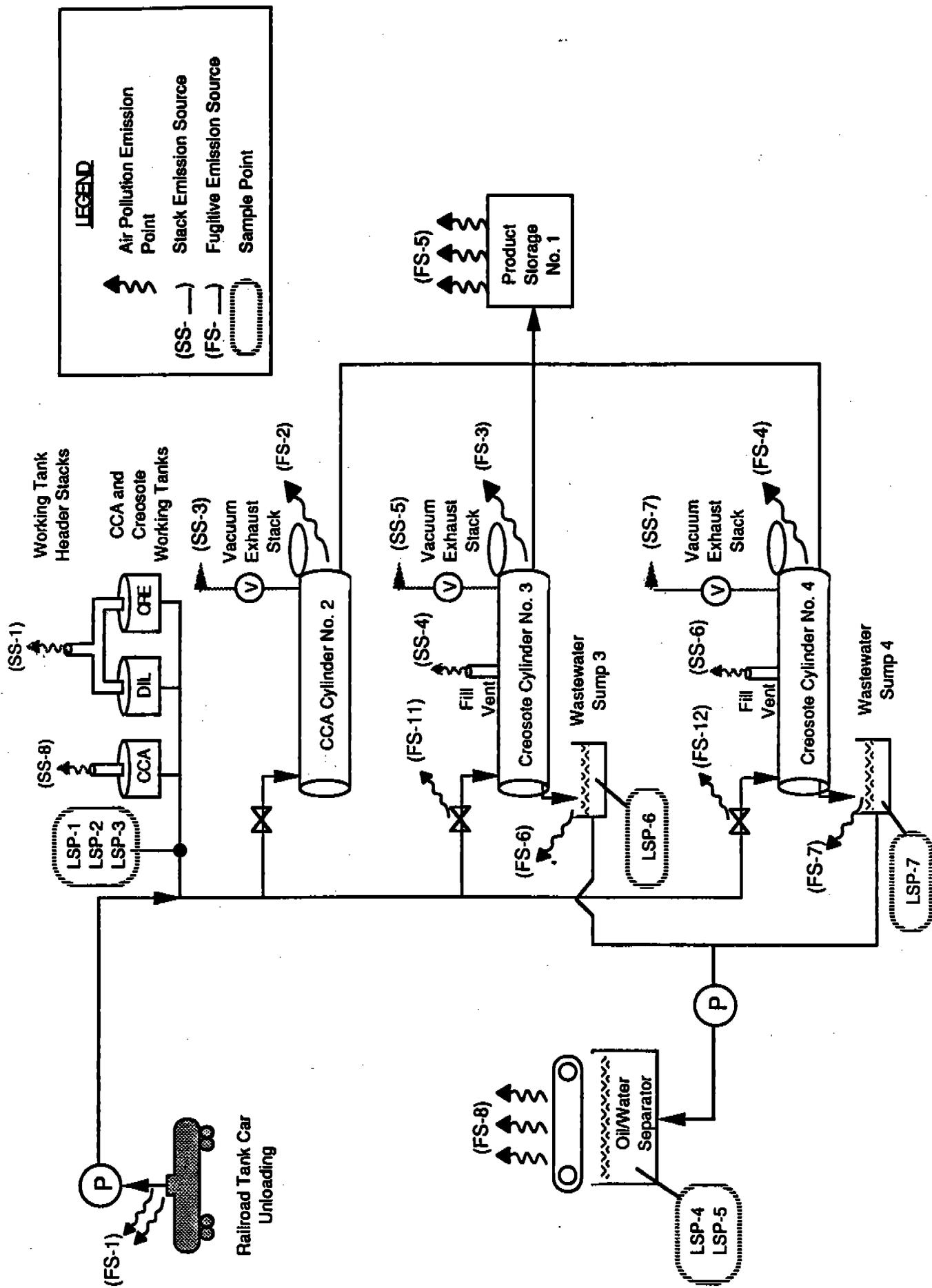


FIGURE 3-1. KOPPERS PROCESS FLOW DIAGRAM

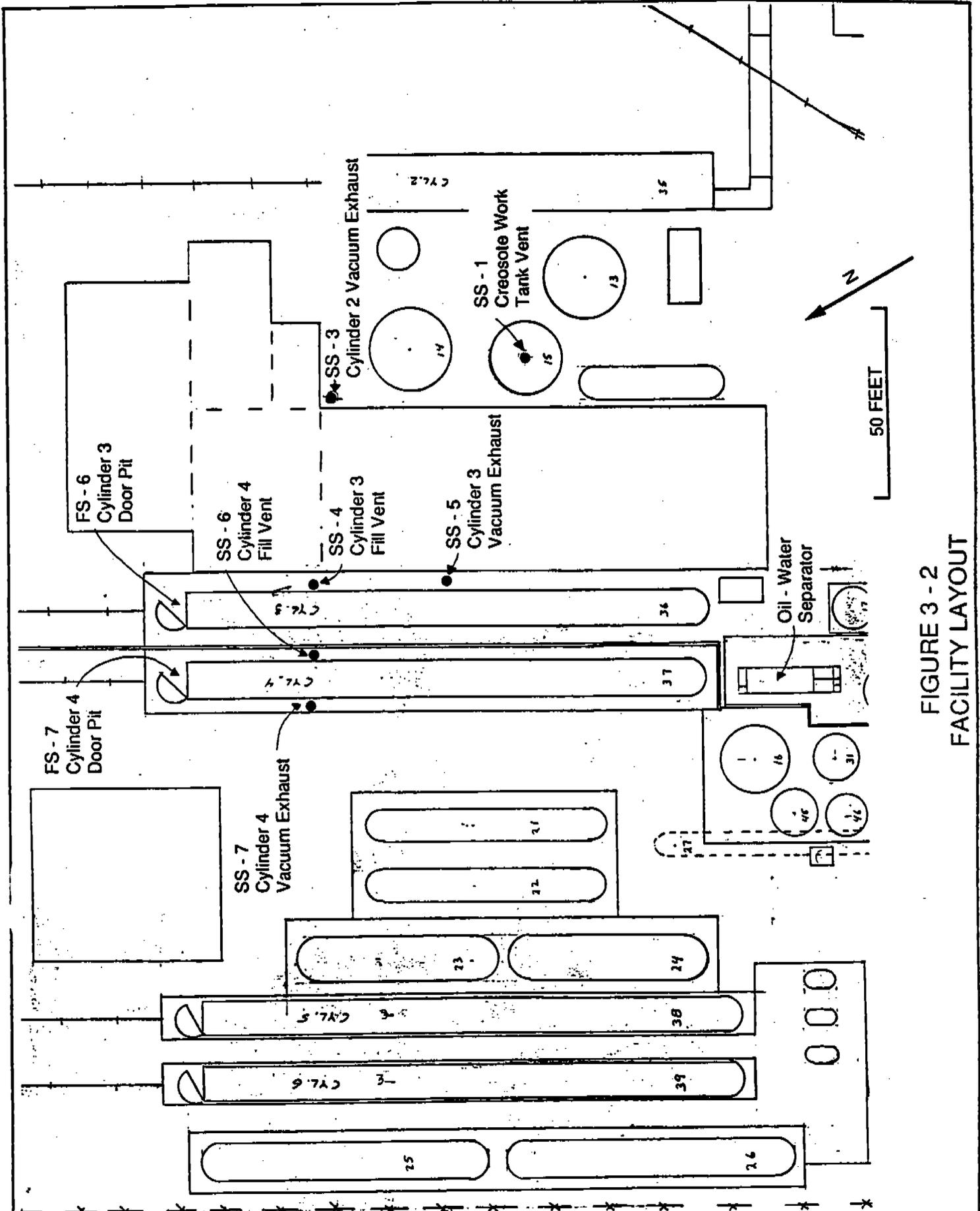


FIGURE 3 - 2
FACILITY LAYOUT

4.0 STACK SAMPLING METHODOLOGY

4.1 STACK SAMPLING APPROACH

The stack sampling was performed to measure trace organic emissions from the full cycle of the Creosote Process described in Section 3.1.2, and to measure trace metal emissions from the vacuum cycle of the CCA Process described in Section 3.1.1. The following types of stack samples, which are described in detail in Section 4.2, were taken:

- o EPA Method 5 samples were taken at the Cylinder No. 2 vacuum exhaust, to measure particulate and vapor phase metals.
- o Volatile Organic Sampling Train (VOST) samples were taken at the exhaust from Cylinder No. 4 to measure the concentrations of benzene, toluene and pyridine.
- o Semi-Volatile Organic Sampling Train (Semi-VOST) samples were taken at the exhaust from Cylinder No. 4 to measure phenol, cresol, and PAH concentrations.

The original Sampling and Analysis Plan (Ebasco, 1988b) specified that trace organic emissions from the Diluent Process would also be measured. However, the Diluent Process was unexpectedly not operated during the testing period, so emissions from that process could not be measured. Instead, as described in Section 4.5, the emission rates from the Diluent Process were estimated based on the results of the measured emission rates from the Creosote Process.

The stack sampling was performed by AM Test, Inc. of Redmond, WA. Stack emission tests were performed during the 24-hr operating cycle on February 15-16, 1989. Table 4-1 lists the number of tests for each stack, in addition to the number and type of QC samples taken at each location.

Figure 4-1 shows the 24-hour Creosote Process Cycle at Cylinder No. 4 and the timing of the stack tests performed on that process. As shown in that figure, the timing of the stack tests at the working tank vent stack (SS-1) and the Cylinder No. 4 vacuum exhaust stack (SS-7) was designed to sample emissions from each of the key emission events:

- o Emissions from the Cylinder No. 4 vacuum exhaust (SS-7) during the long Boultonizing Cycle.
- o Emissions from the working tank vent stack (SS-1) when the treatment cylinder is drained and the creosote is "blown back" to the working tank.
- o Emissions from the working tank vent stack (SS-1) during the Steam Cycle, when the creosote-impregnated logs are heated with live steam.
- o Emissions from the vacuum exhaust stack (SS-7) during the final vacuum cycle.

TABLE 4-1

SUMMARY OF STACK EMISSION TESTS

Stack No.	Test Method	Environmental Samples	Field Blanks	Trip Blanks	Total Samples
SS-1 (Creosote Tank Vent)	Method 5	0	0	0	0
	VOST	2	1	1	4
	Semi-VOST	2	1	1	4
SS-3 (CCA Vacuum Exhaust)	Method 5	2	1	0	3
	VOST	0	0	0	0
	Semi-VOST	0	0	0	0
SS-7 (Cyl. 4 Vacuum Exhaust)	Method 5	0	0	0	0
	VOST	3	1	0	4
	Semi-VOST	3	1	0	4

3223K

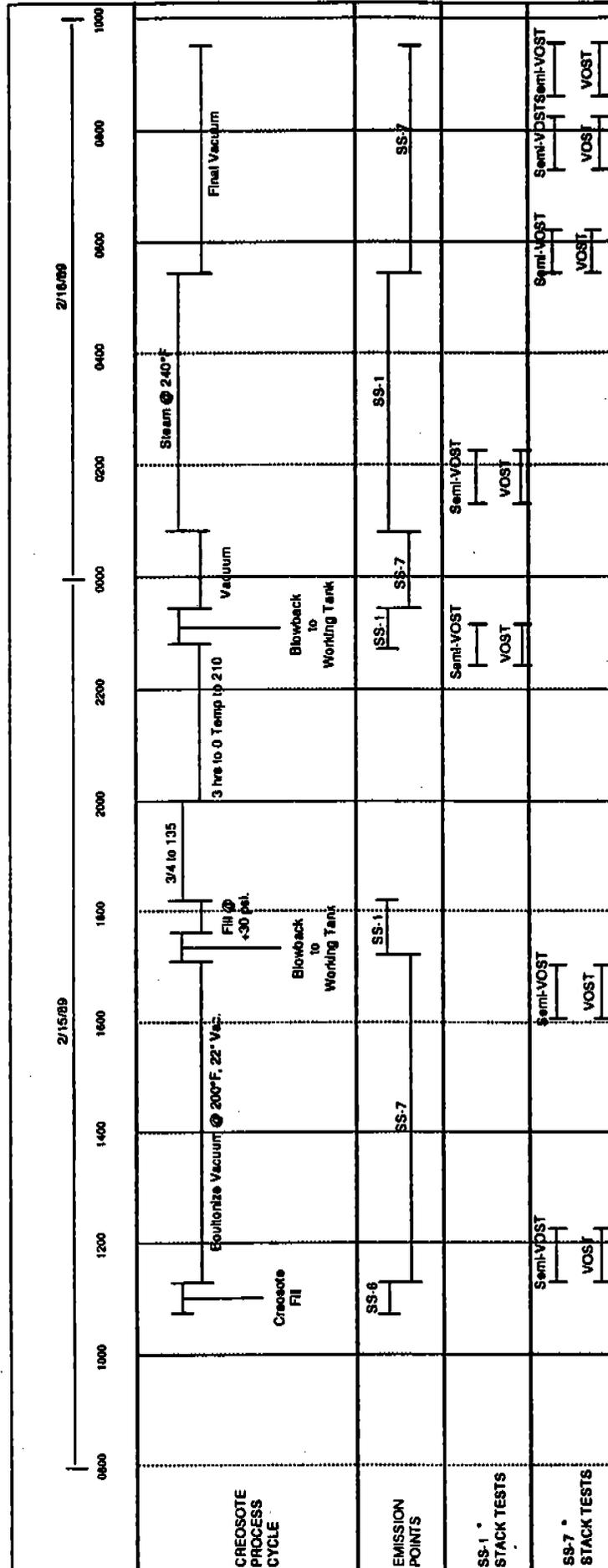


Figure 4-1 Creosote Wood Treating Cycle at Cylinder No. 4

* Indicates when the specified samples were taken at each stack.

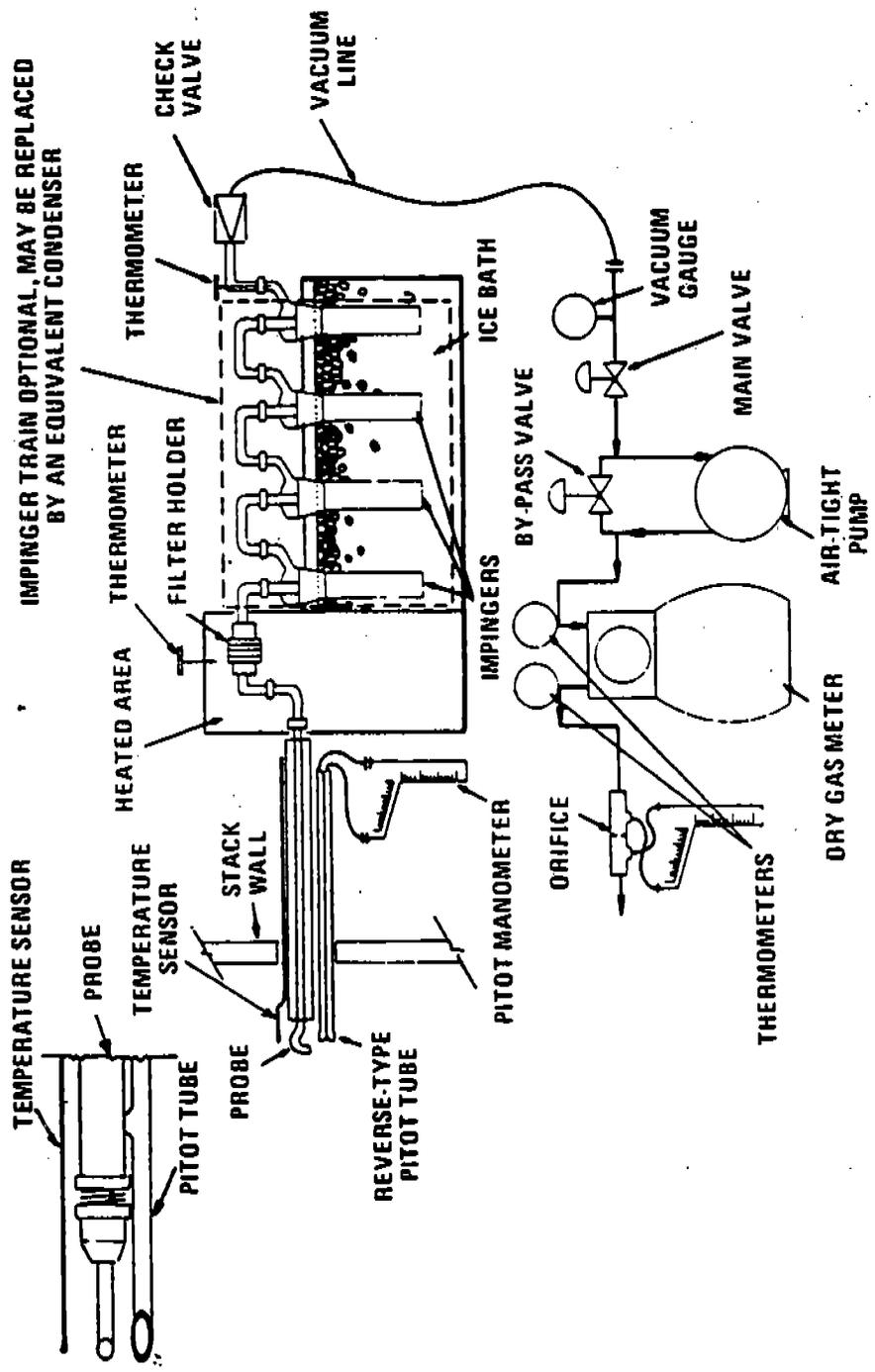
4.2 STACK SAMPLING METHODS (STACKS SS-1, SS-3 AND SS-7)

4.2.1 CCA Cylinder Vacuum Exhaust Pipe (SS-3)

The CCA cylinder vacuum exhaust is a 2-inch galvanized pipe which discharges downward into a ground level sump. The exhaust pipe was modified for the stack tests by inserting a 2-inch PVC pipe "tee" to serve as a sampling port. The exhaust gas was sampled as it traveled downward.

The exhaust gas was sampled for particulate trace metals and arsenic vapors by using an EPA Method 5 Sampling Train (Figure 4-2), which was modified in accordance with California Air Resources Board (CARB) Method 425 to allow sampling of arsenic vapors (CARB, 1988). That modification consisted of using dilute sodium hydroxide in one of the impingers, instead of using water as specified for regular Method 5 sampling. The stack test method allowed measurement of both the vapor-phase and particle-phase emission rates.

The gas sample was collected by inserting the sample nozzle and pitot tube into the center of the pipe. Each test run lasted 30 minutes. The sampling flowrate was adjusted every 5 minutes, so that the sampling flowrate was proportional to the exhaust gas flowrate. Because it was anticipated that the exhaust gas flowrate would vary so much that isokineticity could not be maintained without changing the sample nozzle during the test, the sampling contractor was not required to satisfy strict isokinetic conditions that are normally required for a Method 5 test. This deviation from the Method 5 protocol is not considered significant, because any aerosols in the exhaust gas are expected to be of submicron size and are therefore not affected by non-isokinetic sampling.



Source: 40 CFR, Part 60, Appendix A

FIGURE 4-2 METHOD 5 SAMPLING TRAIN

The annual emission rates for the stack emissions were calculated using the following equation:

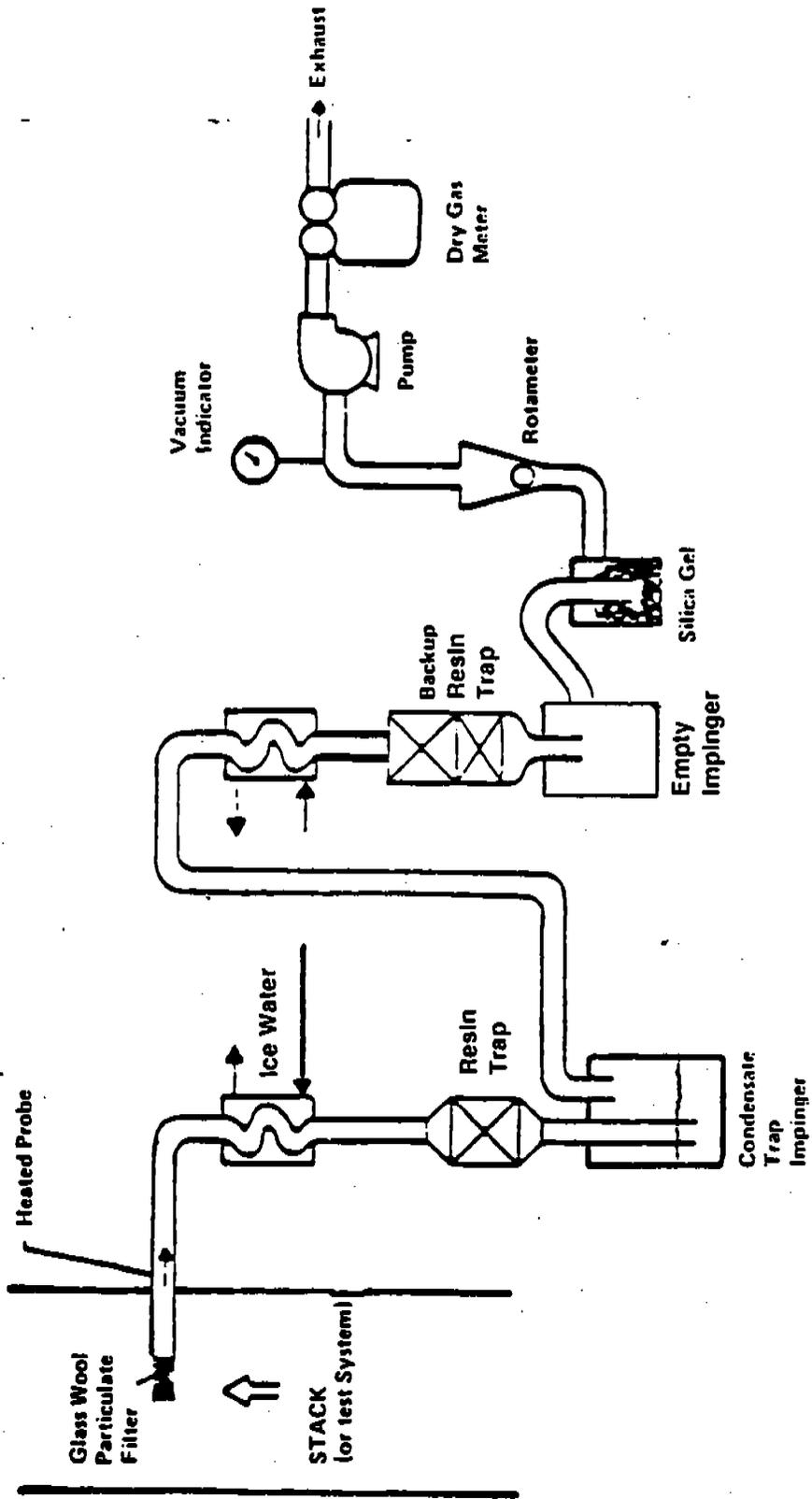
$$E_{\text{Annual}} = (E_i) (N) (t) \frac{1 \text{ kg}}{10^6 \text{ mg}} \quad (4-1)$$

where E_{Annual} is the annual emission rate (kg/yr), E_i is the instantaneous emission rate measured by the stack test (mg/hr), N is the number of loads per year, and t is the number of hours that stack emissions occur during each load.

4.2.2 Working Tank Vent Stack (SS-1)

The working tank vent stack is a 6 foot long, 8-inch diameter vertical steel pipe mounted on top of a small working tank. Headspace vapors from the Creosote working tank are vented through that stack after they are first treated for product recovery by a vapor condenser. The stack was modified for this project by installing a 3-inch threaded nipple to serve as a sampling port.

The exhaust gases were sampled simultaneously for volatile organics by using the Volatile Organic Sampling Train (VOST Train) and for semi-volatile organics by using the Semi-VOST Train. The VOST Train is shown in Figure 4-3. The VOST sampling protocol is given as EPA Method 0030 in SW-846 (EPA, 1986a). The VOST Train uses water-cooled condensers to cool the sampled gas and Tenax adsorbent to collect the volatile organic components. After sampling, the Tenax cartridges were thermally desorbed using EPA Method 5040 and the volatile components were analyzed by Gas Chromatography/Mass Spectrometer (GC/MS).



Source: EPA, 1986a

FIGURE 4-3 VOST SAMPLING TRAIN

As described in Chapter 6.0, the concentrations of benzene and toluene in the stacks were too high to quantify by EPA Methods 0030 and 5040. The air concentration of the VOCs in Stacks SS-1 and SS-7 were therefore estimated based on the measured emission rate of naphthalene (NPTH), which is the most volatile of the compounds that were successfully measured:

$$E_i = E_{NPTH} \times \frac{X_i P_i^O}{X_{NPTH} P_{NPTH}^O} \times \frac{Mw_i}{Mw_{NPTH}} \quad (4-2)$$

where E_i is the estimated air concentration of the VOCs (benzene, toluene, pyridine) in mg/M^3 ; E_{NPTH} is the measured naphthalene air concentration in mg/M^3 ; P_i^O and P_{NPTH}^O are the pure component vapor pressures in psia at the process temperatures; x_i and X_{NPTH} are the mole fractions of the process liquids. The pure component vapor pressures were calculated from literature values (EPA 1987b). The use of Equation 4-2 assumes that the VOCs and naphthalene are in vapor equilibrium at the process temperatures and the composition of the condensate is related to the vapor equilibrium over the tank liquids. Preliminary calculations were performed using stack temperatures and was determined that the estimated values did not correspond with the measured components, therefore, it is assumed that the vapor equilibrium was more closely related to process temperatures rather than stack temperatures.

The above assumptions cannot be tested without knowing the composition of the vapor condensates. The predicted benzene and toluene emissions are 5-10 times greater than maximum values reported by the laboratory.

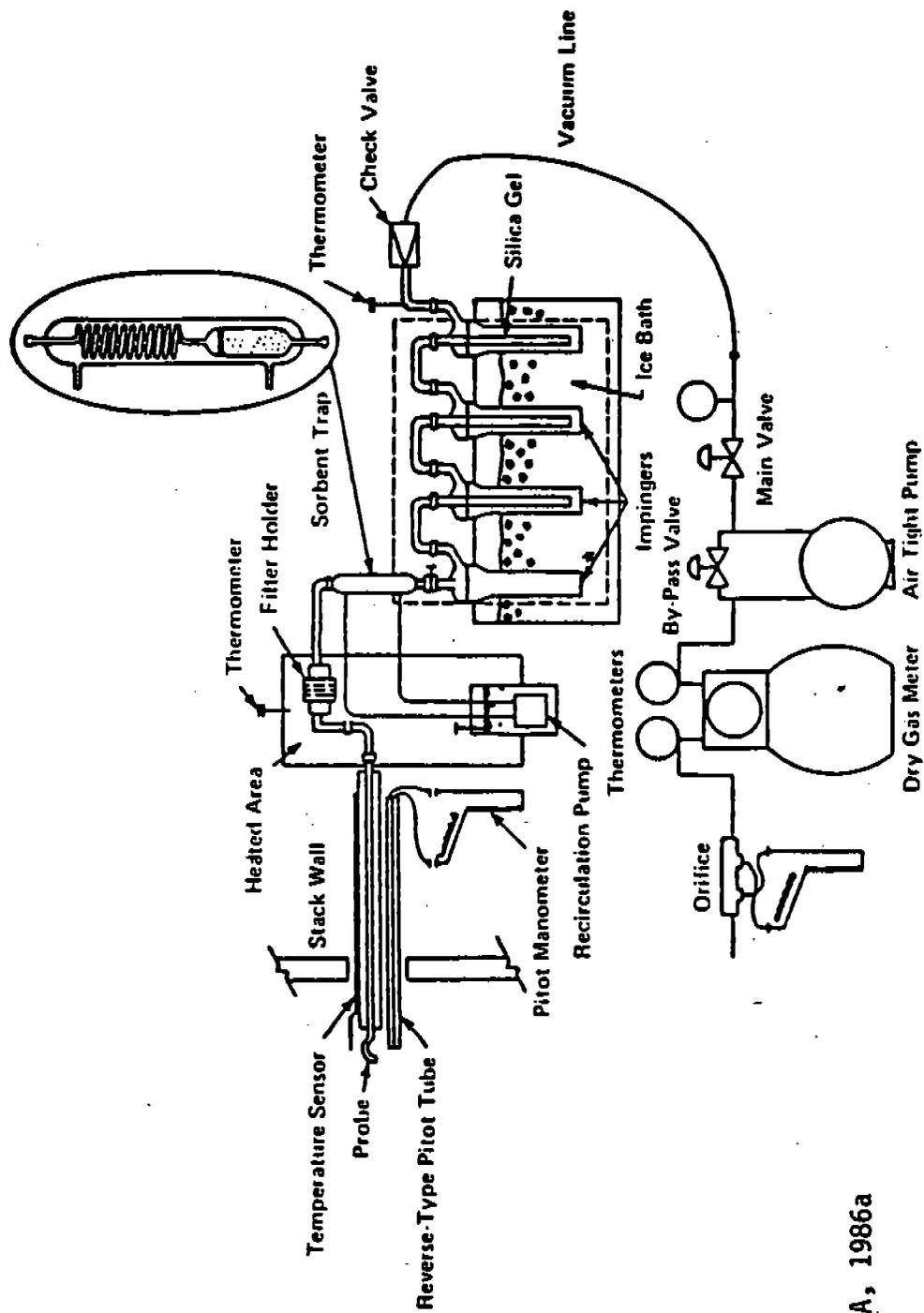
The Semi-VOST sampling train is shown in Figure 4-4. The Semi-VOST method is specified as EPA Method 0010 in SW-846 (EPA, 1986a). The Semi-VOST train uses a heated filter similar to that used for the Method 5 train. Water-cooled condensers are used downstream of the filter to cool the sample gas, and an XAD-2 sorbent cartridge is used to collect the semi-volatile organic components. After sampling, the filter, probe wash and XAD-2 cartridge were combined and chemically desorbed using methylene chloride solvent. The extract was analyzed by using EPA Method 8270 (GC/MS).

The gas samples for both the VOST and Semi-VOST trains were collected by inserting the sample probes into the center of the stack. The gas temperature and exhaust gas velocity were measured by using a calibrated low-flow hot wire anemometer that was inserted into the stack roughly two feet upstream of the sampling port. Each test run lasted roughly 20 minutes. The sample flowrate on the VOST Train was fixed at 1.0 liter per minute in accordance with EPA Method 0030. The sample flowrate on the Semi-VOST Train was adjusted every five minutes to maintain isokinetic flow.

The stack tests measured the instantaneous emission rates (in mg/hr). The annual emission rates were calculated using Equation 4-1 in Section 4.2.1.

4.2.3 Cylinder No. 4 Vacuum Exhaust Pipe (SS-7)

The exhaust pipe is a 3-inch diameter vertical pipe. For the sampling, the pipe was modified by adding an elbow to create a five foot long horizontal section into which the sampling probes were inserted.



Source: EPA, 1986a

FIGURE 4-4 SEMI-VOST SAMPLING TRAIN

The VOST and Semi-VOST sampling probes were inserted into the center of the pipe through adjacent sample ports that were drilled into the horizontal pipe section. The gas temperature and the exhaust gas velocity were measured downstream of the sampling points. Each test run lasted 20 minutes. The VOST Train sampling rate was set at 1.0 liters/minute in accordance with EPA Method 0030. The sampling rate on the Semi-VOST Train was adjusted every 5 minutes to approximate isokinetic flow. Strict isokinetic conditions could not be maintained because the exhaust gas flowrate varied so much during each test that the sampling nozzle would have had to be changed during the test to maintain isokineticity. However, this deviation from the Semi-VOST protocol is not considered significant because any aerosols in the gas stream are expected to be of submicron size and therefore not affected by non-isokinetic sampling.

The stack tests measured the instantaneous emission rates (in mg/hr). The annual emission rates were calculated using Equation 4-1 in Section 4.2.1.

4.3 ESTIMATION OF EMISSIONS FROM NON-SAMPLED STACKS

It was not practical to sample many of the known stack sources. The emission rates from those stacks were estimated using the methods described in the following sections.

4.3.1 Cylinder No. 3 Fill Vent (SS-4)

The emissions from the treatment cylinder fill vent were calculated using the emission factor equations (EPA, 1987b):

TABLE 4-2
SATURATION FACTORS^{a/}

Cargo Carrier	Mode of Operation	S Factor
Tank Trucks and Tank Cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedicated service	1.45
	Submerged loading: dedicated vapor balance service	1.00
	Splash loading: dedicated vapor balance service	1.00

^{a/} Compilation of Air Pollutant Emission Factors, AP-42,
Table 4.4-1 (EPA 1977).

$$L_i = \frac{12.46 (S) (P_i) (MW_i)}{T} \quad (4-4)$$

where L_i = release of component i in pounds/1,000 gal of liquids loaded.

P_i = partial pressure of component i in psia.

MW_i = molecular weight of component i in lb/lb-mole.

T = liquid temperature, °R.

S = 1.0 saturation factor (see Table 4-2).

12.46 = emission factor constant

The partial pressure P_i was calculated for each chemical of concern using Raoult's Law.

$$P_i = P_i^{\circ} X_i \quad (4-5)$$

where P_i° = vapor pressure of pure component i in psia

X_i = mole fraction of component i in the liquid phase.

The mole fraction X_i was calculated knowing the concentration of i in the liquid phase, the molecular weight of i, the density of the liquid, and the average molecular weight of the liquid:

$$X_i = \frac{C_i / MW_{ave}}{d_{oil} / MW_{ave}} \quad (4-6)$$

where C_i = concentration of compound i in the liquid phase, lb/ft³.

d_{oil} = density of the oily liquid phase, lb/ft³.

MW_{ave} = average molecular weight of the oily liquid phase, lb/lb-mole.

The saturation factor, S, depends on the mode of loading the tank. A listing of typical saturation factors is shown in Table 4-2. A saturation factor of 1.00 was used.

The annual emission rate was calculated using the following equation:

$$E_i = \frac{(L_i) (Q)}{(1,000 \text{ gallons})} \times \frac{1 \text{ kg}}{2.2 \text{ lbs}} \quad (4-7)$$

where E_i = annual emission rate, kg/yr.

L_i = release rate of component i, lbs/1,000 gallons

Q = annual volume of liquid pumped into the treatment cylinder, gal/yr

4.3.2 Cylinder No. 4 Fill Vent (SS-6)

The emissions were calculated using equations identical to those used to calculate the emissions from the Cylinder No. 3 Fill Vent (Section 4.3.1).

4.3.3 Cylinder No. 3 Vacuum Exhaust (SS-5)

Cylinder No. 3 treats wood using both the Creosote Process and the Diluent Process. The emission rate (in grams/second) from Cylinder No. 3 during the Creosote Process were assumed to be identical to those that were measured for the Creosote Process in Cylinder No. 4 (SS-7). The emission rate from the Cylinder No. 3 vacuum exhaust during the Diluent Process were scaled from the measured results for the vacuum exhaust from the Creosote Process, as follows:

$$E_i \text{ (Diluent)} = E_i \text{ (Creosote)} * \frac{P_i \text{ (Diluent)}}{P_i \text{ (Creosote)}} \quad (4-8)$$

$$= E_i \text{ (Creosote)} * \frac{X_i \text{ (Diluent)}}{X_i \text{ (Creosote)}} \quad (4-9)$$

- E_i (Diluent) = calculated emission rate of component i from Cylinder No. 3 vacuum exhaust, mg/hr.
- E_i (Napthalene) = measured emission rate of component i from Cylinder No. 4 vacuum exhaust, mg/hr.
- P_i (Diluent) = calculated equilibrium vapor pressure over diluent solution, psia
- P_i (Napthalene) = calculated equilibrium vapor pressure over napthalene, psia
- X_i (Diluent) = measured mole fraction of component i in liquid diluent.
- X_i (Napthalene) = measured mole fraction of component i in liquid napthalene.

After the instantaneous emission rate was calculated by Equations 4-8 and 4-9, the annual emission rate (in kg/yr) was calculated using Equation 4-1.

4.3.4 CCA Concentrate Tank Vent (SS-9)

Emissions of arsenic from the CCA tank fill vent were estimated using the following procedure. Only emissions of arsenic are considered since arsenic is the only volatile component of the CCA solution. Furthermore, aerosol formation, which could lead

to emission of the other two metallic components, is highly unlikely in the CCA tank because the filling process does not create much turbulence.

The arsenic concentration in the vapor space of the CCA tank was assumed to be saturated during filling. This assumption provides a conservatively high emission estimate, because the vapors inside the tank could be below saturation. The saturated concentration of arsenic was calculated using Raoult's law:

$$P_{As} = X_{As} \times P_{As}^{\circ} \quad (4-10)$$

where P_{As} = arsenic saturation vapor pressure, atm

X_{As} = mole fraction of arsenic in the CCA concentrate

P_{As}° = Arsenic pure component vapor pressure at ambient conditions = 1.3×10^{-3} atm (EPA 1987a).

The saturated vapor emission rate was calculated using the known volume of CCA concentration pumped into the storage tank each year:

$$E_{As} = \frac{Q_{CCA} \times P_{As} \times MW_{As}}{V_M} \quad (4-11)$$

V_M

where E_{As} = annual arsenic emission rate, kg/yr

Q_{CCA} = annual CCA concentrate purchase =
33 m³/yr

MW_{As} = arsenic atomic weight = 75 g/gmole

V_m = molar gas volume = 0.025 m³/gmole

4.3.5 CCA Working Solution Tank Vent (SS-8)

Emissions from the CCA Working Tank Vent were estimated by assuming that the arsenic concentration in the head space vapors is the saturation equilibrium value. The emission rates were calculated using Equations 7 and 8. It was assumed that 560,000 ft³/yr of working solution was cycled through the treatment cylinder and into the working tank.

5.0 FUGITIVE EMISSION ESTIMATION METHODOLOGY

5.1 SAMPLING OF PROCESS CHEMICALS AND WASTEWATER

The emission factor equations used to predict the fugitive emissions described in Sections 5.2 through 5.6 required that the composition of the process chemicals and the wastewater streams be known. The liquid samples listed in Table 5-1 were collected on February 15, 1989. The samples were collected, shipped and analyzed as follows:

- o The samples were obtained by collecting the liquid in a prewashed 1-liter glass beaker, then carefully transferring aliquots to the sample containers. A separate glass beaker was used for each liquid sample.
- o The sample jars were sealed with custody seals, placed inside resealable plastic bags, sealed inside of vermiculite-filled paint cans, then shipped to the laboratory in ice chests filled with vermiculite and blue ice. Each ice chest was sealed with custody seals and was accompanied by a chain of custody form.
- o One aliquot of LSP-3 (CCA concentrate solution) was analyzed for hexavalent chromium by Weston Laboratory in Stockton, California. The remaining liquid samples were analyzed by Aqua Tech Inc. in South Burlington, Vermont.

Note that the concentrations of some compounds were less than the method detection limits (MDLs). The MDLs for pyridine and phenol in the pure creosote and diluent mix (Samples LSP-1 and LSP-2) were unexpectedly higher than the detection limits

specified in the SAP. The high MDLs probably resulted from matrix effects caused by the high concentrations of total hydrocarbons in those process chemicals. Compounds listed in Table 5-1 that were not found at concentrations above the MDL are indicated as "less than" their MDL.

5.2 RAIL TANK CAR UNLOADING (SOURCE FS-1)

A procedure for estimating emissions during rail tank car unloading was not found in the literature. Only an estimation method for liquid storage tank filling was located. The emissions are expected to be higher during loading than unloading, because more contaminated vapors will be physically displaced during loading as the liquid level in the car rises. As a conservative estimate, the rail car emissions were calculated using the emission factor equations for tank filling, which were listed in Section 4.3.1. A "saturation" factor of 0.5 was assumed (see Table 4-2).

5.3 TREATMENT CYLINDER UNLOADING

5.3.1 Cylinder No. 2 Unloading (FS-2)

During the "vacuum cycle," gas emitted from the vacuum exhaust stack (SS-3) was sampled and the stack gas concentrations (both vapor-phase and particulate-phase) of chromium, arsenic, and copper were measured. The concentration of chromium, arsenic, and copper in the gas inside cylinder No. 2 before the cylinder door is opened was assumed to be identical to the concentration measured during the vacuum exhaust. Assuming that all the gas within the cylinder is released to the atmosphere when the cylinder door is opened, the average emission rate on a yearly basis during wood unloading was estimated using the following equation:

TABLE 5-1

SUMMARY OF PROCESS CHEMICAL AND WASTEWATER SAMPLE RESULTS

ANALYTE	LSP-1 Working Creosote (mg/l)	LSP-2 Diluent Mix (mg/l)	LSP-3 CCA Conc. (mg/l)	LSP-4 Oil/Water Sep. (mg/l)	LSP-5 Oil/Water Sep. (mg/l)	LSP-6 Cyl No. 3 Sump (mg/l)	LSP-7 Cyl. No. 4 Sump (mg/l)
Benzene	43	0.8	NA	0.061	0.53	18	0.44
Toluene	119	5	NA	0.094	0.7	13	2.7
Pyridine	<6,600	<9,800	NA	2.3	2.4	1.5	<660
Phenol	<6,600	<9,800	NA	18	17	0.3	<660
Cresols	<6,600	<9,800	NA	18.5	19.6	1.3	<660
Napthalene	33,000	15,000	NA	8.8	8.9	14	6,100
1-Methylnapthalene	29,000	10,000	NA	6.6	8.1	14	7,700
2-Methylnapthalene	71,000	26,000	NA	2.7	3.4	5.3	2,900
Acenapthene	45,000	18,000	NA	<0.9	0.6	0.1	<660
Acenapthalene	710	<9,800	NA	2.6	3.5	5.6	1,600
Dibenzofuran	20,000	8,800	NA	1.1	1.7	2.8	580
Fluorene	26,000	12,000	NA	1.2	7.1	3.5	440
Phenanthrene	120,000	44,000	NA	4.1	3	1.2	480
Anthracene	8,000	8,100	NA	0.5	0.8	1.6	<660
Fluoranthene	63,000	21,000	NA	1.6	2.2	6.3	<660
Pyrene	50,000	16,000	NA	1.2	2.2	5.2	<660
Benzo(a)anthracene	11,000	4,500	NA	0.3	0.3	1.2	<660
Chrysene	9,300	4,900	NA	0.2	0.3	1.1	<660
Benzo(b)fluoranthene	4,400	2,900	NA	<.9	<.6	0.5	<660
Benzo(k)fluoranthene	4,900	2,900	NA	<.9	<.6	0.5	<660
B(a)P	4,400	3,000	NA	<.9	<.6	0.4	<660
1H-Indene	5,600	<9,800	NA	4.9	<.6	10	2,000
Other Detected PAHs	121,170	13,100	NA	5.9	8	9.3	7,800
PAHs Below Detection	40,000	39,000	NA	<.9	<.6	0.98	<660
Quinolines	13,000	<9,800	NA	49	41	1.7	400
Methyl Pyridines	<9,800	<9,800	NA	27.1	26.2	5.32	<660
Arsenic	NA	NA	51,300	NA	NA	NA	NA
Copper	NA	NA	33,300	NA	NA	NA	NA
Cr-Total	NA	NA	60,300	NA	NA	NA	NA
Cr-Hexavalent	NA	NA	43,800	NA	NA	NA	NA

(1) NA - Not analyzed for in the specified sample.

(2) "<" Means that the listed value is less than the Method Detection Limit.

$$E_i^Y = \frac{V C_i^{cyl} N}{1,000 \text{ g/kg}} \quad (5-1)$$

where

E_i^Y = annual average emission rate for component i

V = volume of void space in the cylinder, m^3

C_i^{cyl} = concentration of component i in the cylinder, g/m^3
 = concentration of contaminant i in the vacuum exhaust, g/m^3

N = number of door openings per year, yr^{-1}

It is assumed that the total volume of the empty cylinder, rather than the smaller void space of the wood-filled cylinder is completely displaced during each cylinder loading. This assumption provides a conservatively high estimate of the emission rates.

5.3.2 Cylinder No. 4 Unloading (FS-4)

The procedure used for estimating emissions during cylinder No. 4 unloading was identical to the procedure used for cylinder No. 2 (see Section 3.1.2). Cylinder No. 4 is used just for creosote operations. The contaminant concentrations measured in the vacuum exhaust stack (SS-7) were; in this case; benzene, toluene, cresol, phenol, pyridine, and PAHs.

5.3.3 Cylinder No. 3 Unloading (FS-3)

Cylinder No. 3 is used for both creosote and diluent operations. It was assumed that the emission rates during unloading of creosote-treated wood are the same regardless of whether the wood is treated in Cylinder No. 3 or Cylinder No. 4.

Emissions from cylinder No. 3 during the unloading of creosote-treated wood were therefore estimated using the procedure for Cylinder No. 4 described in Section 5.3.2. The contaminant concentrations in the Cylinder No. 3 vacuum exhaust stack (SS-5) were assumed to be identical to the concentration of contaminants measured in the Cylinder No. 4 vacuum exhaust stack (SS-7) for the creosote operations. Emissions from cylinder No 3 during the unloading of diluent treated wood were estimated using the following procedure.

Contaminant concentrations in the Cylinder No. 3 vacuum exhaust stack (SS-5) during diluent operations were not measured and therefore could not be used for estimating emissions from Cylinder No. 3 during diluent treated wood unloading. Instead, the contaminant concentrations measured in the Cylinder No. 4 vacuum exhaust (SS-7) during creosote operations were used to estimate emissions from Cylinder No. 3 unloading during diluent operations by taking into account the known differences in the diluent and creosote composition. The mole fractions for each contaminant of concern in the diluent and in the creosote were known from samples LSP-1 and LSP-2. The concentration of the contaminant in the Cylinder No. 3 exhaust stack during diluent operations was then estimated using the following equation:

$$C_{iD} = C_{iC} * \frac{X_{iD}}{X_{iC}} \quad (5-2)$$

where: C_{iD} = estimated vapor-phase concentration of contaminant i in the Cylinder No. 3 vacuum exhaust during diluent operation
 C_{iC} = measured vapor-phase concentration of contaminant i in the cylinder No. 4 vacuum exhaust during creosote operations

X_{iD} = Mole fraction of contaminant i for diluent
 X_{iC} = Mole fraction of contaminant i for creosote

Once the concentration of contaminants in the Cylinder No. 3 vacuum exhaust was estimated, equation (5-1) was used to estimate the average emission rate on a yearly basis.

5.4 TREATMENT CYLINDER DOOR PITS (Sources FS-8 and 9)

5.4.1 Cylinder No. 3 Sump (FS-6)

The emissions from the treatment cylinder sumps were calculated by assuming that the sumps are equivalent to a large, open-top dumpster. The following equation for open-top dumpster emissions was used (EPA 1987b):

$$E_i = \frac{2 P_i MW_i W}{RT} \frac{D_i W U_x^{1/2}}{x} \quad (5-3)$$

$$P_i = X_i P_i^0 \quad (5-4)$$

E_i = emission rate, g/sec

P_i = equilibrium vapor pressure of component "i" over sump contents, mmHg

MW_i = molecular weight, g/gmole

W = sump width, 200 cm

R = gas constant, 62,300 mmHg-cm³/gmole-K

T = annual average temperature, 290 K

D_i = air diffusivity of component i, cm²/sec

U_x = annual average wind speed, cm/sec

X_i = mole fraction of component i in sump content
(LSP-6)
 P_i^o = pure component vapor pressure, mmHg

The values for D_i and P_i^o were taken from literature sources (EPA 1987b).

E_i = annual emission rate of component i, kg/yr
 Q_L = annual wastewater volume, 60,000 gallons
 C_{iL} = concentration of component i in wastewater, mg/l

5.4.2 Cylinder No. 4 Sump (FS-7)

The emissions from the Cylinder No. 4 sump were estimated using the procedures for the Cylinder No. 3 sump described in Section 5.4.1. The wastewater composition from LSP-7 was used.

5.5 OIL/WATER SEPARATOR (FS-8)

The emissions from the oil/water separator were estimated using the procedure described for the Cylinder No. 3 sump in Section 5.4.1. The average wastewater composition from samples LSP-4 and LSP-5 was used.

5.6 PROCESS PIPING

An inventory of process piping around Treatment Cylinders 3 and 4 was conducted on February 14, 1989. The purpose of the inventory was to count the valves, flanges and seals along the process piping that could cause fugitive vapor emissions. The results of the piping inventory are given in Table 5-2.

TABLE 5-2
RESULTS OF PROCESS PIPING INVENTORY

Item	Cylinder 3		Cylinder 4		Cylinders 3 and 4
	Fill and Drain	Pressure Cycle	Fill and Drain	Pressure Cycle	Common Piping
<u>Valves</u>					
Leaking ^{1/}	7	2	11	6	6
Nonleaking	1	2	2	0	4
<u>Flanges</u>					
Leaking ^{1/}	14	6	32	19	14
Nonleaking	5	10	5	0	9
<u>Pump Seals</u>					
Leaking ^{1/}	1	0	1	1	1
Nonleaking	0	1	0	0	0

^{1/} Determined by visual inspection.

5.6.1 Cylinder No. 3 Piping (FS-9)

The piping serving cylinder No. 3 was separated into two different systems to estimate emissions. One system is used to fill and drain cylinder No. 3 and the other system is used for the pressure cycle. Both piping systems are used for creosote and diluent operations. The following method was used to calculate emissions from both piping systems during both creosote and diluent operations.

The accepted method of estimating releases from leaking seals, valves, and other process piping equipment is emission factors (EPA 1987a). The total emission rate is calculated by summing the contributions of individual pieces of equipment. Thus, the total emission rate was calculated using the following equation:

$$E = \sum N_j \times EF_j \quad (5-5)$$

where

E = Total Emission Rate, lb/hr
EF_j = Emission Factor for Process Equipment Type j
N_j = Total number of type j equipment in the process piping

Emission factors for leaking and nonleaking process equipment are listed in Table 5-3.

To estimate the emission rate of contaminant i, the total emission rate was multiplied by the partial pressure of contaminant i divided by the sum of the partial pressures for all the contaminants. This procedure ensures that the highest emissions are attributed to the contaminants with the highest vapor pressure.

TABLE 5-3

PROCESSING PIPING FUGITIVE EMISSION FACTORS^{a/}
(lbs/hour)

Fugitive Emission Source	Leaking (>10,000 ppm) Emission Factor	Nonleaking (<10,000 ppm) Emission Factor
Pump Seals		
Light Liquids	0.96	0.026
Heavy Liquids	0.85	0.030
Valves (in-line)		
Gas	0.099	0.0011
Light Liquid	0.19	0.0038
Heavy Liquid	0.00051	0.00051
Gas Safety-Relief Valves	3.72	0.098
Open-ended Lines	0.0263	0.0033
Flanges	0.083	0.00013
Sampling Connections	-	-
Compressor Seals	3.54	0.20

^{a/} Source: Emission Factors for Equipment Leaks of Volatile Organic Compounds and Hazardous Air Pollutants, EPA-450/3-86-002, January 1986, Table 3-3 (EPA 1986b).

$$E_i = \frac{E P_i}{P_i} \times 454 \text{ g/lb} \quad (5-6)$$

where E_i = emission rate of component i, g/hr
 P_i = partial pressure of component i, atm
 $\quad = P_i^O X_i$
 P_i^O = pure component vapor pressure
 X_i = mole fraction of component i

The average emission rate on a yearly basis was then calculated using the following equation:

$$E_i^Y = E_i \times N \times t \times \frac{1 \text{ kg}}{1,000 \text{ g}} \quad (5-7)$$

where

E_i^Y = average emission rate for component i on a yearly basis, kg/yr
 N = number of transfers per year or number of pressure cycles per year, yr⁻¹
 t = time required for each transfer or time wood is treated with pressure cycle, hr

5.6.2 Cylinder No. 4 Piping (FS-10)

The piping serving cylinder No. 4 was also separated into two different systems to estimate emissions. One system is used to fill and drain cylinder No. 4 and the other system is used for the pressure cycle. Both piping systems are used just for creosote operations since cylinder No. 4 is only used for creosote operations. The method described in Section 5.6.1 was used for estimating emissions from the two piping systems.

5.6.3 Cylinders No. 3 and No. 4 Common Piping (FS-11)

The emissions from this piping were estimated using the procedure described in Section 5.6.1. This piping is used for both creosote and diluent transfers from railroad cars or tank trucks to the storage tanks.

5.7 TREATED WOOD STORAGE AREA EVAPORATIVE EMISSIONS

5.7.1 General Methodology

Ebasco found no previous studies that could be used to predict the evaporation rates of organic components from the treated log storage yards. The evaporative emission rates were therefore measured in the field using the following approach:

- o Ambient air quality measurements were taken in October 1988, while daytime temperatures were moderate and evaporative emissions were expected to be representative of the entire year.
- o As shown in Figure 5-1, a network of ambient air sampling stations and an electronic meteorological station were placed around the creosote-treated telephone pole storage area. One sampling station was roughly upwind and the other stations were roughly downwind of the storage area. The upwind and downwind sampling locations on the first sampling day were established based on historical prevailing wind directions. The sampling locations on the subsequent days were selected based on inspection of the previous day's measured wind direction.

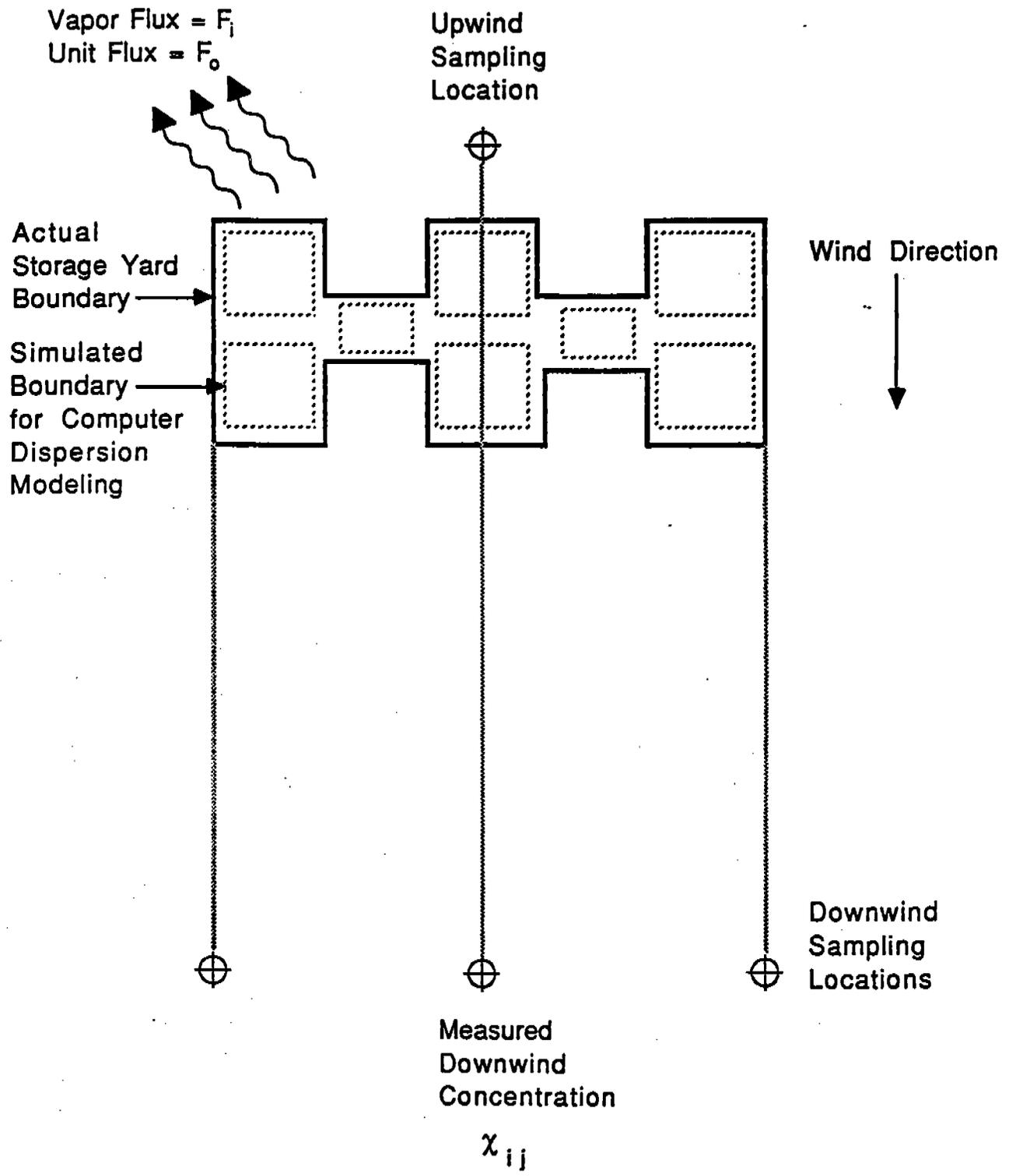


Figure 5-1 Schematic of Wood Storage Area Ambient Sampling

- o Each sampling station measured the ambient concentrations (X_{ij}) of each contaminant of concern (i) at each sampling location (j). The units for the ambient concentrations were in grams/cubic meter.
- o During each sampling period, an electronic meteorological station measured wind data suitable for use with the Industrial Source Complex Short-Term (ISC-ST) computer dispersion model. That model was used to predict the "downwind dispersion factor" at each of the sampling stations, $(X/F_0)_j$, which is the concentration at each sampling location j that would have resulted from a "Unit Vapor Flux" (F_0) of 1.0 grams per second in the storage yard and the vapor flux is based on the area of a 4 x 40 foot pallet pile equaling 1,600 ft² (148.6m²). The assumed vapor flux was calculated as follows:

$$\begin{aligned} \text{Vapor Flux } (F_0) &= \frac{1 \text{ g/sec}}{148.6\text{m}^2} \\ &= 6.7 \times 10^{-3} \text{ g/sec/m}^2 \end{aligned}$$

The units for the "downwind dispersion factor" are (g/m³)/(g/sec/m²). The ISCST modeling results are given in Appendix F. For example, for the 10/19/88 sampling day the modeling was done using 50 square area sources at the locations shown in Figure 5-2, each with an assumed vapor flux of 6.7 x 10⁻³ g/sec/m². Based on the seven hours of meteorological data for 10/19/88, the calculated ambient concentration at Sample Point A was 7.95 x 10⁻⁴ g/m³. The dispersion factor (X/F_0) for Sample Point A on 10/19/88 was therefore calculated as follows:

$$\begin{aligned} (X/F_0) &= \frac{7.95 \times 10^{-4} \text{ g/m}^3}{6.7 \times 10^{-3} \text{ g/sec/m}^2} \\ &= 0.118 \text{ (g/m}^3\text{)/(g/sec/m}^2\text{)} \end{aligned}$$

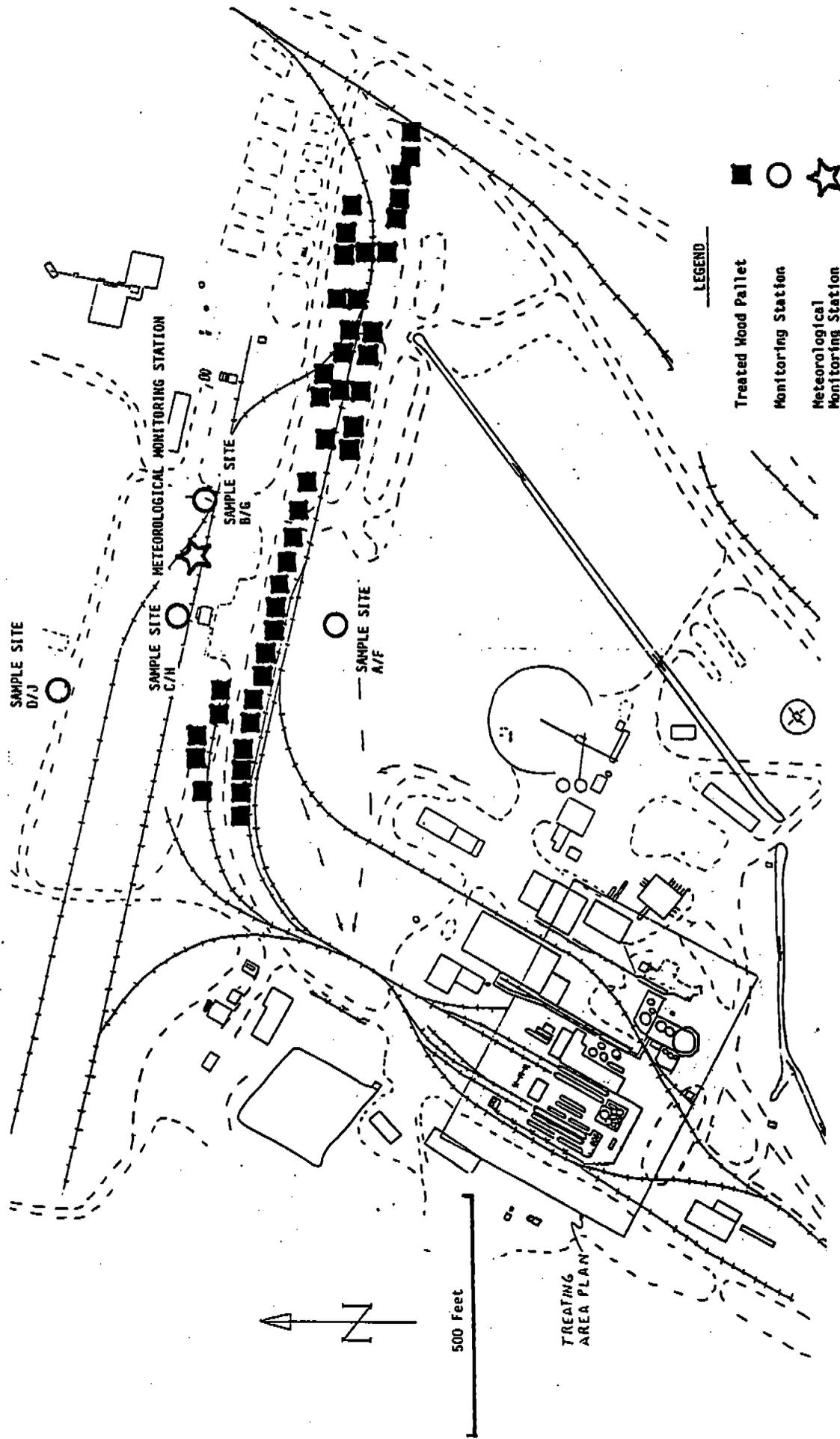


FIGURE 5-2 AMBIENT AIR SAMPLE SITES FOR 10/19/88

Note that the dispersion factor on any given day depends on both the wind patterns and the locations of the treated wood pallets on that day.

The vapor flux (F_{ij}) for each component "L" was calculated using the ambient monitoring data for each station "j" using the following equation:

$$F_{ij} = \frac{X_{ij} - (0.9 * (X_i^{Upwind}))}{(X/F_0)_j} \quad (5-8)$$

where F_{ij} is the calculated vapor flux in grams/sec/m², X_{ij} is the measured concentration of component "i" at station "j" in grams/m³, X_i^{upwind} is the ambient concentration of component "i" at the upwind monitoring station, and $(X/F_0)_j$ is the wind dispersion factor for station "j".

Theoretically, the vapor flux calculated for each of the sampling stations should be identical, if the vapor emission rate from each of the numerous log pallets stored was identical. In actuality the emission rates from each of the pallets was expected to differ slightly. Since the ambient concentrations of each of the monitoring stations are mainly influenced by the pallets nearest the station, the vapor flux calculated using the ambient data for each station is also expected to differ from the other stations. The average vapor flux (F_i) from the entire storage yard was therefore calculated by averaging the calculated vapor fluxes determined for each of the sampling stations.

5.7.2 Ambient Monitoring Methods

Sampling Schedule and Sample Locations

Ambient monitoring was conducted on three consecutive days during mid-October, when the daily temperatures were expected to be near the annual average (see Section 6.3.1 for a discussion of the measured meteorological conditions). The original plan called for two sample sets to be taken during the daytime and a third set to be taken at night, to give emission estimates under different temperature ranges. However, the nighttime wind speeds during the test period were too low to allow adequate use of the ISCST computer model to back-calculate the emission rates. The original sampling plan was therefore modified to include only daytime sampling for all three test days.

The sampling locations for October 19, 20 and 21, 1988 are shown in Figures 5-2, 5-3 and 5-4. The sampling locations were chosen to allow measurement of ambient organic compound concentrations both upwind and downwind of the log storage yard.

Ambient Air Sampling Methods

A listing of the types of ambient samples and QA/QC samples taken each day is given in Table 5-4.

Ambient VOCs - Ambient volatile organic compounds (VOCs) including benzene, toluene and naphthalene were sampled using NIOSH Method 1501. Granular activated carbon sorbent tubes were obtained from SKC Incorporated. Each sorbent tube contained two separate sections of carbon, containing 200 mg and 100 mg, respectively. The air samples were drawn through

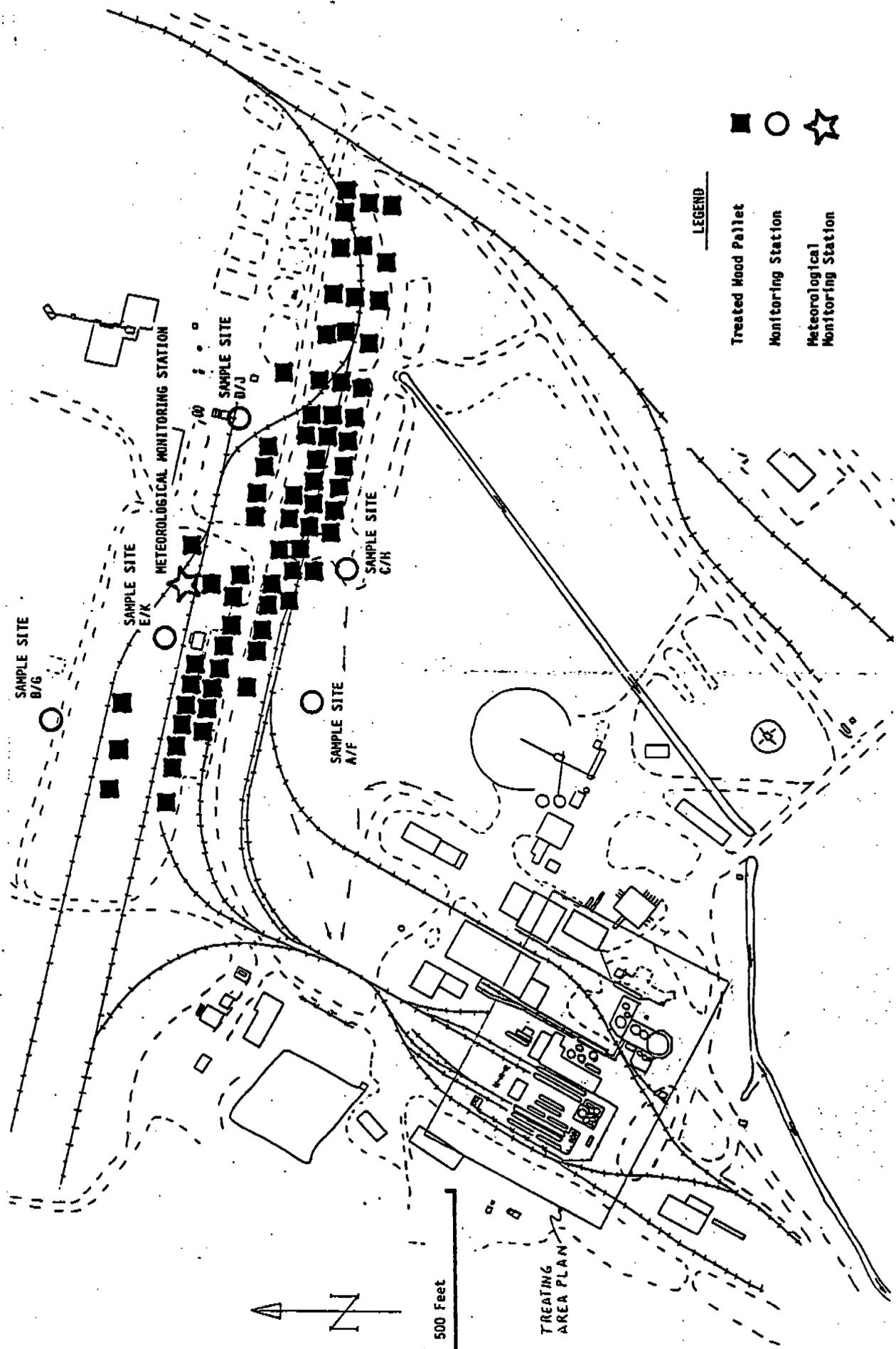


FIGURE 5-3 AMBIENT AIR SAMPLING SITES FOR 10/20/88

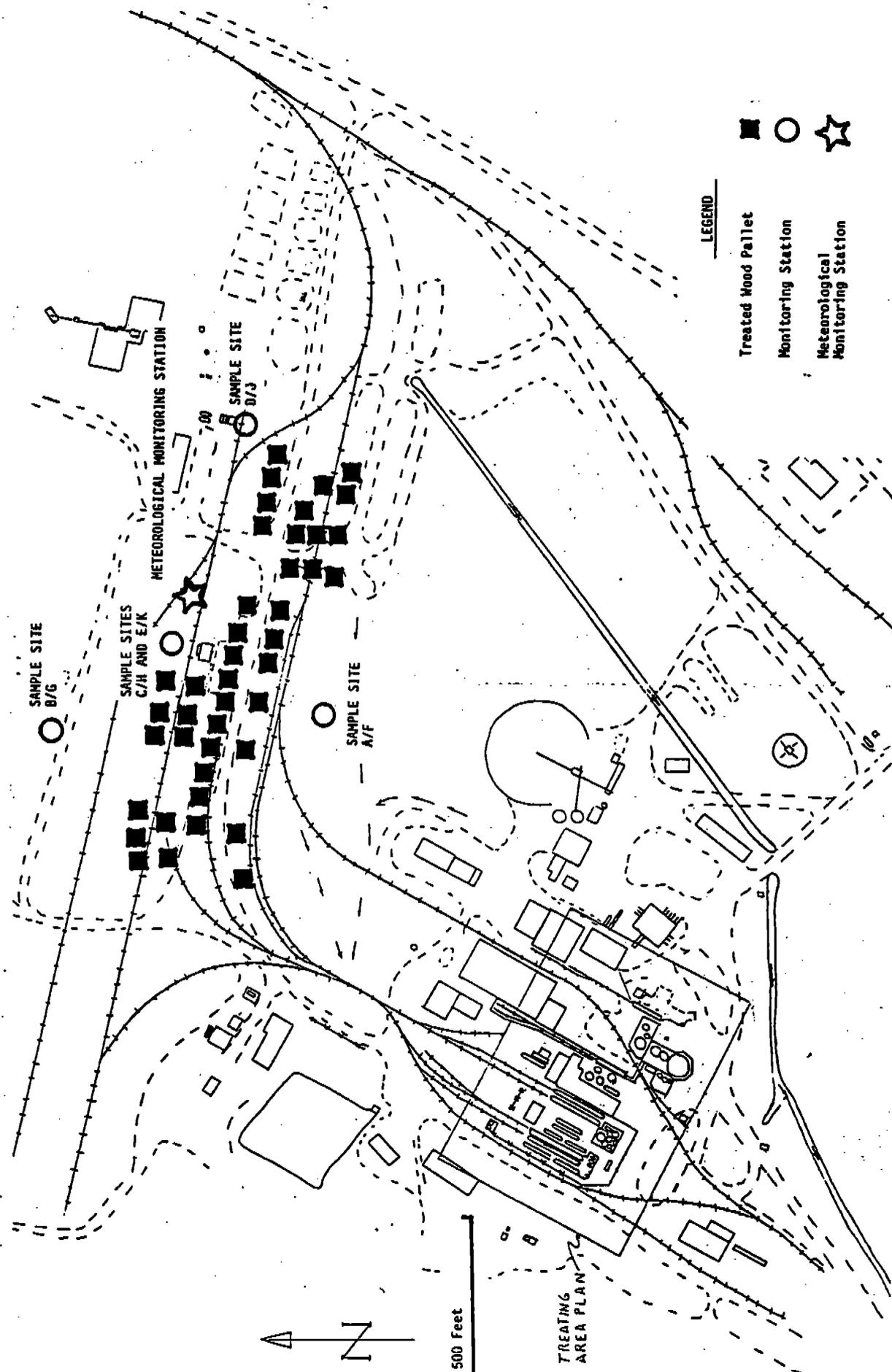


FIGURE 5-4 AMBIENT AIR SAMPLING SITES FOR 10/21/88

TABLE 5-4
SUMMARY OF AMBIENT AIR QUALITY SAMPLES

	Environmental Samples	Duplicate Samples	Trip Blanks	Field Blanks
<u>October 19, 1988</u>				
VOCs (NIOSH Method 1501)	4	0	1	0
Pyridine (NIOSH 1613)	4	0	1	0
PAHs (NIOSH 5515)	4	0	1	0
<u>October 20, 1988</u>				
VOCs	5	0	1	0
Pyridine	5	0	1	0
PAHs	5	0	1	0
<u>October 21, 1988</u>				
VOCs	4	1	1	1
Pyridine	4	1	1	1
PAHs	4	1	1	1
Total Suspended Particulates	1	1	0	0
Ambient Particle Size Distribution	1	1	0	0

the sorbent tubes at a nominal 200 cc/min flowrate. The tubes were mounted inside of Gillian sorbent tube housings. The sample flowrate was adjusted using needle valves, and calibrated rotameters were used to record the sample flowrate several times during each test run. Field data forms for the ambient sampling are given in Appendix C. Sampling commenced at mid-morning each sampling day, and continued until late afternoon. Line-powered electric pumps were used at two of the stations that were located near electrical outlets. Battery powered Gillian Model HFS-113 personal sampling pumps were used at the remaining stations. The tube housings were taped to the top of steel fence posts that were driven into the ground at each sampling site. The sampling height was typically four feet above ground.

Ambient Pyridine - Ambient pyridine was sampled using NIOSH Method 1613. Activated carbon sorbent tubes identical to those used for the VOC sampling were used. The sample flowrate was a nominal 200 cc/min. The pump arrangement was the same that was used for the VOC samples.

Ambient PAHs - Ambient PAHs were sampled using NIOSH Method 5515. Field data forms are given in Appendix C. Prepared sorbent tubes containing 200/100 mg amounts of XAD-2 resin were obtained from Supelco Company. The sorbent tubes were placed into Gillian housings. 37 mm PTFE filters in plastic cartridges were used upstream of the XAD-2 sorbent to collect particulate PAHs. The sorbent tube housings and the filter cartridges were wrapped in foil to prevent photodegradation of the collected samples. Air samples were taken at a nominal 2,000 cc/min flowrate. Line-powered electric pumps were used at the sampling sites that were near electrical outlets. Battery-powered Gillian Model HFS-113 sampling pumps were used

at the remaining sites. The sample flow was adjusted using needle valves, and was measured using a calibrated rotameter several times during the sample period. The sample housings were taped onto steel fence posts that were driven into the ground at the sample sites, with a nominal four foot sample height above ground.

Particle Concentration - The ambient particle concentration and particle size distribution was measured using two collocated samples on 10/21/88. NIOSH Method 0500 was used to collect the samples. Two collocated samples for particle concentration were collected at Sampling Point E. Plastic cartridges with 37-mm glass fiber filters were used to collect the samples. The samples were collected for roughly 8 hours at a nominal 2,000 cc/min flowrate, which was adjusted using a needle valve and measured using a calibrated rotameter. The collected particle mass was measured by dessicating and weighing the filters before and after sampling.

Particle Size Distribution - The particle size distribution was measured using two collocated samplers on 10/21/88. Particle samples were collected at Sample Point E using 37-mm Nucleopore filters in plastic cartridges. The sampling flowrate was a nominal 1,000 cc/min. The particle size distributions on the filters were determined by taking an electron photomicrograph of the exposed filters, then manually counting the collected particles shown on the photograph.

Packaging and Shipping of Ambient Air Samples

After sampling, the spent carbon and XAD-2 sorbent tubes were sealed by using the plastic end caps provided by the manufacturers of the tubes. The PTFE filters used to collect

PAHs were removed from their plastic housings, then carefully folded in half so that their exposed sides were together. The folded filters were then placed inside a glass test tube, and the end of the tube was sealed with foil. The sorbent tubes and the exposed filters were sealed inside of individual ziplock baggies. Sample labels were attached to each baggie. The baggies were then sealed inside of glass canning jars and temporarily stored before shipment at a temperature below 4 degrees C.

The samples were shipped to the analytical laboratory inside of ice chests that were packed with vermiculite and cooled with blue ice. Chain of custody forms were placed inside of each ice chest. The lid on the ice chests were sealed using custody seals. The ice chests were delivered to laboratory by overnight courier service.

Analyses of Ambient Air Samples

The ambient air samples for VOCs, pyridine and PAHs were analyzed by Data Chem, Inc. of Salt Lake City, Utah. The analytical report summaries are given in Appendix D. The samples were analyzed and validated in accordance with Data Quality Objective (DQO) Level IV.

The VOC samples were analyzed by NIOSH Method 1501 for benzene, toluene and naphthalene. Each of the two carbon sections in the sorbent tubes were analyzed separately. The carbon was desorbed using carbon disulfide. The extract was analyzed using gas chromatography (GC/FID). Standards were spiked onto the sorbent tubes before desorption.

pallets for different applications, and loaded into trucks and shipped off-site. Therefore, it was impossible to get an accurate "snapshot" of the number of logs in the yard during each of the sampling periods. Instead, the location of each of the pallets was noted, and whenever possible the number of logs in an individual palette was determined. Model input parameters included the location of each palette. For this analysis, it was assumed that each pallet was a square area source with a dimension of 40 feet per side.

Limitations of Evaporative Emission Measurement Method

The evaporative emission rates measured for this project are subject to the following limitations:

- o It is assumed that the age distribution of the treated logs stored in the yard on each of the three sampling days was representative of the entire year. On each sampling day, freshly treated logs (which are expected to have high emissions) were spread in the yard while the older logs (which should have low emissions) were removed. Note that the emission rate on any given day would depend on the relative ages of the stored logs on that day.

- o It is assumed that the sunlight intensity on the sampling days in October was representative of the entire year. It is presumed that solar intensity, in addition to air temperature, is an important factor because intense sunlight could cause the surface temperature of the black logs to be higher than the surrounding air temperature.

6.0 RESULTS

This chapter presents the estimated emission rates as follows:

- o Section 6.1 gives the Maximum Quantifiable Emission Rates, which are the highest annual-average emission rates that could have occurred if the process conditions that existed during the February 1989 sampling period existed for the entire year.
- o Section 6.2 gives the results of the actual stack tests.
- o Section 6.3 gives the estimate emission rates from the non-sampled stacks, calculated by either comparison with the emission rates measured at the sampled stacks or by use of emission factor equations.
- o Sections 6.4 to 6.8 give the estimated fugitive emissions, calculated using emission factor equations based on the liquid process chemical and wastewater samples.
- o Section 6.9 gives the measured ambient particle mass concentrations and size distributions.

6.1 MAXIMUM QUANTIFIABLE EMISSION RATES

The emission rates measured or estimated for this project represent a "snapshot" based on the process conditions that existed on the day that the stack samples and wastewater samples were collected. It is assumed that the process conditions that occurred on the sampling days were representative of the conditions that apply for the entire

year. This assumption was checked with the Koppers plant operators, who indicated that the wood treating processes were operating normally during the sampling period.

The emission rates that were measured during the sampling period also depend on the concentrations of the contaminants that were present in the working creosote and working diluent on the sampling day. The emission rates clearly cannot exceed the amount of contaminant in the process chemicals. The Maximum Quantifiable Emission Rate based on the measured data taken on February 16, 1989 is therefore calculated as follows:

$$(E_i)_{\max} = Q_{\text{chem}} \times C_i \times 10^{-6} \times \frac{3.7851}{\text{gal}} \quad (6-1)$$

where $(E_i)_{\max}$ is the maximum quantifiable emission rate (kg/yr), Q_{chem} is the annual quantity of process chemicals imported to the Koppers facility (800,000 gal/yr for creosote and 115,000 gal/yr for diluent), and C_i is the contaminant concentration (mg/l) measured in the process chemical samples on February 15, 1989 (See Table 5-1).

The Maximum Quantifiable Emission Rates are listed in Table 6-1. Note that the values in that table represent only the maximum emission rates that are quantifiable based on the February 15, 1989 test data. It is possible that the actual annual emissions for the volatile components could be higher than the values listed in Table 6-1, because it is expected that the fresh creosote and diluent that are imported to the facility contain higher contaminant concentrations than the working creosote and working diluent that were sampled on February 15, 1989. Fresh creosote and diluent oil are imported 2-4 times per month. The emission rates for the volatile

TABLE 6-1

MAXIMUM QUANTIFIABLE ANNUAL EMISSIONS
 BASED ON PROCESS CHEMICAL CONCENTRATIONS

Component	Quantity in 800,000 gal/yr Working Creosote ^{1/} (kg/yr)	Quantity in 115,000 gal/yr Working Diluent ^{1/} (kg/yr)	Total Annual Quantity (kg/yr)
Benzene	130	0.35	130
Toluene	360	2.1	362
Pyridine	<20,000 ^{2/}	<4,300	<24,000
Cresols	<20,000	<4,300	<24,000
Phenol	<20,000	<4,300	<24,000
Methylnapthalene	303,000	16,000	320,000
Napthalene	100,000	6,500	106,000
Acenapthalene	2,200	430	2,600
Acenapthene	136,000	7,900	144,000
Fluorene	79,000	5,200	84,000
Phenanthrene	365,000	19,000	384,000
Fluoranthene	190,000	9,200	199,000
Pyrene	150,000	7,000	157,000
B(a)Pyrene	13,000	1,300	14,300
Dibenzofuran	61,000	3,800	65,000
Other Detected PAHs	610,000	13,000	623,000

^{1/} Based on creosote and diluent concentrations listed in Table 5-1.

^{2/} "Less than" indicates that calculated value is based on the MDL detection limit concentration.

components would be expected to be highest immediately after a fresh shipment of creosote or diluent oil was added to the working solutions in the storage tanks.

6.2 RESULTS OF STACK EMISSION TESTS

6.2.1 Stack Testing Chemical Analyses

The stack testing at the Koppers facility was performed by Am Test, Inc. of Redmond, WA. The emission test report is under separate cover (AM Test, 1989). The stack test results are summarized in Appendix G. The stack testing analytical data have been validated by EPA for use as CLP Level IV. CLP Level IV analytical data is subject to rigorous QA/QC protocols and documentation and provides qualitative and quantitative analytical data which is suitable for any RI/FS purposes.

The method detection limits for the stack testing chemical analyses are listed in Table 6-2. The detection limit stack gas concentrations for the PAHs were higher than the values that were specified in the SAP for the following reasons:

- o The sample durations for the Semi-VOST runs were shortened to less than those specified in the SAP, because it was observed that high concentrations of unknown organic compounds were depositing on the inside of the sampling train. The shortening of the sample durations resulted in lower sample volumes, and hence higher detection limits.
- o The liquid extracts taken from the PAH sorbent tubes had to be diluted more than expected, because the concentrations of the condensable hydrocarbons other than the PAHs of concern were so high that they adversely affected the GC/MS used for the analyses.

TABLE 6-2

METHOD DETECTION LIMITS FOR STACK SAMPLING
(mg/m³)

Compound	Stack SS-3 (Cylinder 2 Vacuum)	Stack SS-1 (Work Tank Vent)	Stack SS-7 (Cylinder 4 Vacuum)	Expected Detection Limit from SAP
Arsenic	2.3	--	--	0.0003
Cr-6	0.76	--	--	0.0003
Cr-Total	0.76	--	--	0.0003
Copper	0.76	--	--	0.0003
Benzene	--	0.02-0.04	0.02-0.04	0.001
Toluene	--	0.02-0.04	0.02-0.04	0.001
Phenol	--	25-50	2.2-4.4	0.005
Cresols	--	25-50	2.2-4.4	0.005
Napthalene	--	25-50	2.2-4.4	0.005
Acenapthene	--	25-50	2.2-4.4	0.005
Acenapthalene	--	25-50	2.2-4.4	0.005
Dibenzofuran	--	25-50	2.2-4.4	0.005
Fluorene	--	25-50	2.2-4.4	0.005
Phenanthrene	--	25-50	2.2-4.4	0.005
Fluoranthene	--	25-50	2.2-4.4	0.005
Pyrene	--	25-50	2.2-4.4	0.005
Benzo(a)Pyrene	--	25-50	2.2-4.4	0.005
Anthracene	--	25-50	2.2-4.4	0.005
B(a)Anthracene	--	25-50	2.2-4.4	0.005
Chrysene	--	25-50	2.2-4.4	0.005
B(b)Fluoranthene	--	25-50	2.2-4.4	0.005
B(k)Fluoranthene	--	25-50	2.2-4.4	0.005
Ideno(1,2,3)pyrene	--	25-50	2.2-4.4	0.005
Dibenz(a,h)anthracene	--	25-50	2.2-4.4	0.005
Benzo(g,h,i)pyrene	--	25-50	2.2-4.4	0.005

3435K

Benzene and toluene concentrations in all of the stack gas samples were too high to quantify using the VOST sampling train in accordance with EPA Method 0030. That method uses Tenax sorbent, which is designed to collect and measure very small quantities of hydrocarbons. By EPA Method 0030, the collected hydrocarbons are thermally desorbed into the GC/MS analyzer. There is no opportunity to sequentially dilute the extracted hydrocarbons to bring the concentrations down to the upper range of the analyzer if the stack concentrations were too high. Unfortunately, the stack gas at Koppers contained much higher concentrations of volatile hydrocarbons than was originally planned. In all cases, the tenax sorbent tubes contained more than the maximum 50,000 ng of hydrocarbons that can be measured by the particular GC/MS used for the analyses. In order to estimate emission rates of benzene and toluene from the stacks, a comparison with the measured emission rates of other compounds was performed. (See Section 4.2.2 for further explanation.) A discussion of the high concentrations of benzene and toluene is given in Appendix G.

6.2.2 Measured Emissions from SS-3 (CCA Cylinder Vacuum Exhaust)

The emission rates from Stack SS-3 are listed in Table 6-3. Copper and total chromium were the major components. Spreadsheets used to calculate the emission rates are given in Appendix A. The concentrations of arsenic and hexavalent chromium were below the method detection limits shown in Table 6-2, and their emission rates are listed as "less than" values based on assumed concentrations equal to the detection limit.

TABLE 6-3

MEASURED EMISSIONS FROM STACK SS-3 (CCA CYLINDER VACUUM EXHAUST)
(Emissions in kg/year)

Component	Emission Rate
Arsenic	$<9.4 \times 10^{-5}$
Cr-6	$<3.1 \times 10^{-5}$ *
Cr-Total	2.4×10^{-4}
Copper	3.3×10^{-4}

* This value is considered to be estimated because the sample exceeded the 24 hour analysis holding time. Value provided would be the lower boundary with the actual Cr-6 value being between 3.1×10^{-5} and CR-Total emission rate.

6.2.3 Emissions from Stack SS-1 (Working Tank Vent)

The emission rates from Stack SS-1 are listed in Table 6-4. Spreadsheets used to calculate the emission rates are given in Appendix A. The concentrations of several compounds in the gas stream (e.g., phenol) were below the method detection limit, and the emission rates of those compounds are indicated as "less than" values based on stack gas concentrations equal to the detection limit.

As shown in Table 6-4, most of the measured emissions consisted of naphthalene, 2-methylnaphthalene and acenaphthene. The bulk of the emissions occur during the steam cycle for both cylinders.

No emission tests were done at Cylinder No. 3. The emission rates from the Cylinder 3 operations were estimated based on the results of the stack tests at Cylinder 4, using the calculations described in Section 4.3. The calculations showed that approximately 25 percent of the naphthalene vapor in the tank exits through the stack.

6.2.4 Emissions from Stack SS-7 (Cylinder No. 4 Vacuum Exhaust)

The emission rates from Stack SS-7 are listed in Table 6-5. Spreadsheets used to calculate the emission rates are given in Appendix A. Most of the measured emissions consisted of cresols, naphthalene and acenaphthene. The stack gas concentrations of some compounds (e.g., phenol) were less than the method detection limits, so their emission rates are indicated as "less than" upper limits.

TABLE 6-4

EMISSION RATES FROM STACK SS-1 (CREOSOTE WORKING TANK VENT)

UNITS ??
K57R ??

Substrate
swirl
Cylinder No. 4

COMPOUND	CYLINDER No. 3		CYLINDER No. 4		Total Emission Rate
	Blowback	Steam Cycle	Blowback	Steam Cycle	
Benzene	0.2 P	0.5 P	2.5 P	55.0 P	58
Toluene	0.5 P	1.2 P	2.8 P	61.3 P	66
Pyridine	46.0 P	107.9 P	0.6 <M	3.4 <M	161
Cresols	50.5 P	118.3 P	1.9 <M	23.5 <M	199
Napthalene	63.3 P	148.4 P	31.6 M	696.0 M	939
2-Methylnapthalene	47.0 P	110.2 P	27.6 M	839.0 M	1024
Acenaphthene	8.1 P	18.9 P	2.0 <M	245.0 M	274
Fluorene	2.6 P	6.2 P	2.0 <M	62.4 <M	73
Phenanthrene	4.1 P	9.5 P	2.0 <M	40.9 M	57
PAHs Below Detection Limits in Gas Stream	4.1 P	9.5 P	2.0 <M	23.5 <M	39

OK
OK

- (1) "P" Means that the listed value was predicted.
- (2) "M" Means that the listed value was based on stack measurements.
- (3) "<M" Means that the listed value was based on MDL values.

TABLE 6-5

EMISSION RATES FROM STACK SS-7 (VACUUM EXHAUSTS)
(Emission Rates in kg/yr)

COMPOUND	SS-7 CYLINDER No. 4 Boil-tonizing	SS-7 CYLINDER No. 4 Vacuum Cycle	TOTAL EMISSION RATE
Benzene	0.8 P	0.4 P	1.2
Toluene	0.9 P	0.4 P	1.3
Pyridine	0.2 <M	0.2 <M	0.4
Cresols	0.2 <M	0.2 <M	0.4
Napthalene	8.4 M	38.4 M	46.8
2-Methylnapthalene	10.3 M	58.7 M	69.0
Acenaphthene	0.2 <M	2.5 M	2.7
Fluorene	0.2 <M	0.2 M	0.4
Phenanthrene	0.2 <M	0.2 M	0.4
PAHs Below Detection Limits in Gas Stream	0.2 <M	0.2 <M	0.4

(1) "P" Means that the listed value was predicted.

(2) "M" Means that the listed value was based on stack measurements.

(3) "<M" Means that the listed value was based on MDL values.

6.2.5 Stack Exhaust Flowrates

The stack heights and stack diameters were listed previously in Table 3-2. For dispersion modeling purposes, the stack gas volumetric flowrates and stack temperatures that were measured during the stack tests at SS-1, SS-3 and SS-7 are listed below:

	<u>Volumetric Flow</u> <u>(actual m³/min)</u>	<u>Temperature</u> <u>(Deg. C)</u>
SS-1	8.2	38
SS-3	3.4	25
SS-7	1.3	31

6.3 ESTIMATED EMISSIONS FROM NONSAMPLED STACKS

As described in Section 4.5, it was not practical to measure the emission rates from all of the stack sources. The emission rates from those stacks were therefore either calculated from EPA emission factors or estimated based on the measured emission rates from Sources SS-1, SS-3 and SS-7. The emission estimation procedures for each of the nonsampled stacks are presented in Section 4.5.

6.3.1 Estimated Emissions from Stack SS-5 (Cylinder No. 3 Vacuum Exhaust)

The estimated emission rates from the Boultonizing Cycle and Vacuum Cycle at Cylinder No. 3 are listed in Table 6-6. The emission rates were calculated by scaling from the rates that were measured at Cylinder No. 4, and adjusting for the number of loads per year at each cylinder and the relative composition of the process chemicals used in each cylinder (see Section 4.5).

TABLE 6-6

EMISSION RATES FROM STACK SS-5 (VACUUM EXHAUSTS)
(Emission Rates in kg/yr)

CONFIDENTIAL

COMPOUND	SS-5 CYLINDER No. 3 Boultonizing	SS-5 CYLINDER No. 3 Vacuum Cycle	TOTAL EMISSION RATE
Benzene	0.0 P	0.5 P	0.5
Toluene	0.0 P	1.2 P	1.2
Pyridine	1.3 P	1.6 P	2.9
Cresols	1.3 P	4.9 P	6.2
Napthalene	1.7 P	8.6 P	10.3
2-Methylnapthalene	1.2 P	4.6 P	5.8
Acenaphthene	0.2 P	0.8 P	1.0
Fluorene	0.1 P	0.3 P	0.4
Phenanthrene	0.1 P	0.4 P	0.5
PAHs Below Detection Limits in Gas Stream	0.1 P	0.3 P	0.4

(1) "P" Means that the listed value was predicted.

The estimated emission rates from the remaining nonsampled stacks are summarized in Table 6-7. The spreadsheets used to calculate the emission rates are given in Appendix A. The emission rates listed in Table 6-7 are annual-average values, that account for the total number of hours per year that the processes causing the emissions are active.

6.3.3 Stack Flowrates for Nonsampled Stacks

The stack heights and stack diameters were listed previously in Table 3-2. The locations of the stacks were shown in Figure 3-2. For dispersion modeling purposes, the estimated stack gas volumetric flowrates and the stack gas temperatures for the nonsampled stacks are listed below:

<u>Stack</u>	<u>Volumetric Flow (actual m³/min)</u>	<u>Temperature (Deg. C)</u>
SS-4	2.7	50
SS-5	1.3	31
SS-6	2.7	50
SS-8	2.7	50
SS-9	2.7	50

TABLE 6-7

CALCULATED EMISSIONS FROM NONSAMPLED STACKS

COMPOUND	CYLINDER	CYLINDER	CYLINDER	CYLINDER	TOTAL
	No. 3 FILL VENT (SS-4) (kg/yr)	No. 4 FILL VENT (SS-6) (kg/yr)	No. 2 TASK VENT (SS-8) (kg/yr)	No. 2 CONC. VENT (SS-9) (kg/yr)	ESTIMATED EMISSIONS (kg/yr)
Benzene	0.1	7.4	NA	NA	7.5
Toluene	0.3	8.2	NA	NA	8.5
Pyridine	30.9	20.8	NA	NA	51.7
Cresols	33.9	22.8	NA	NA	56.7
Napthalene	42.5	93.5	NA	NA	136.0
Methylnapthalene	31.5	87.6	NA	NA	119.1
Acenaphthene	5.4	13.5	NA	NA	18.9
Fluorene	2.7	7.4	NA	NA	10.1
Phenanthrene	1.8	3.9	NA	NA	5.7
Other Detected PAHs	4.4	18.8	NA	NA	23.2
Arsenic	NA	NA	0.12	0.0054	0.1
Copper	NA	NA	NA	NA	0.0
Cr-Total	NA	NA	NA	NA	0.0
Cr-Hexavalent	NA	NA	NA	NA	0.0

(1) NA - Not Analyzed for in the specified sample

6.4 MEASURED EMISSIONS FROM TREATED WOOD STORAGE AREA

6.4.1 Meteorological Conditions During Ambient Sampling

The measured wind speed, wind direction and temperature during the three day ambient monitoring period between October 19 and October 21, 1988 are shown in Figures 6-1, 6-2 and 6-3, respectively. The values shown in those figures are the 15-minute averages that were recorded into the data logger. The sampling periods on each of the sampling days are shown on the figures. The average wind speed and temperature at the site during each of the sampling periods are listed below:

<u>Sampling Day</u>	<u>Wind Speed (meters/sec)</u>	<u>Temperature (deg. C)</u>
10/19/88	1.95	27
10/20/88	1.98	30
10/21/88	1.70	25

The wind speeds and temperatures during the sampling periods in October 1988 were compared with the annual-average values that have been measured at the site by an existing long duration meteorological tower operated under a separate EPA contract. The wind speeds at the Koppers facility during the sampling periods on each of the three sampling days were slightly lower than the historical 2.2 meters/sec average wind speed for the site, while the average temperatures on each of the three days were significantly higher than the historical 17.3 C average temperature.

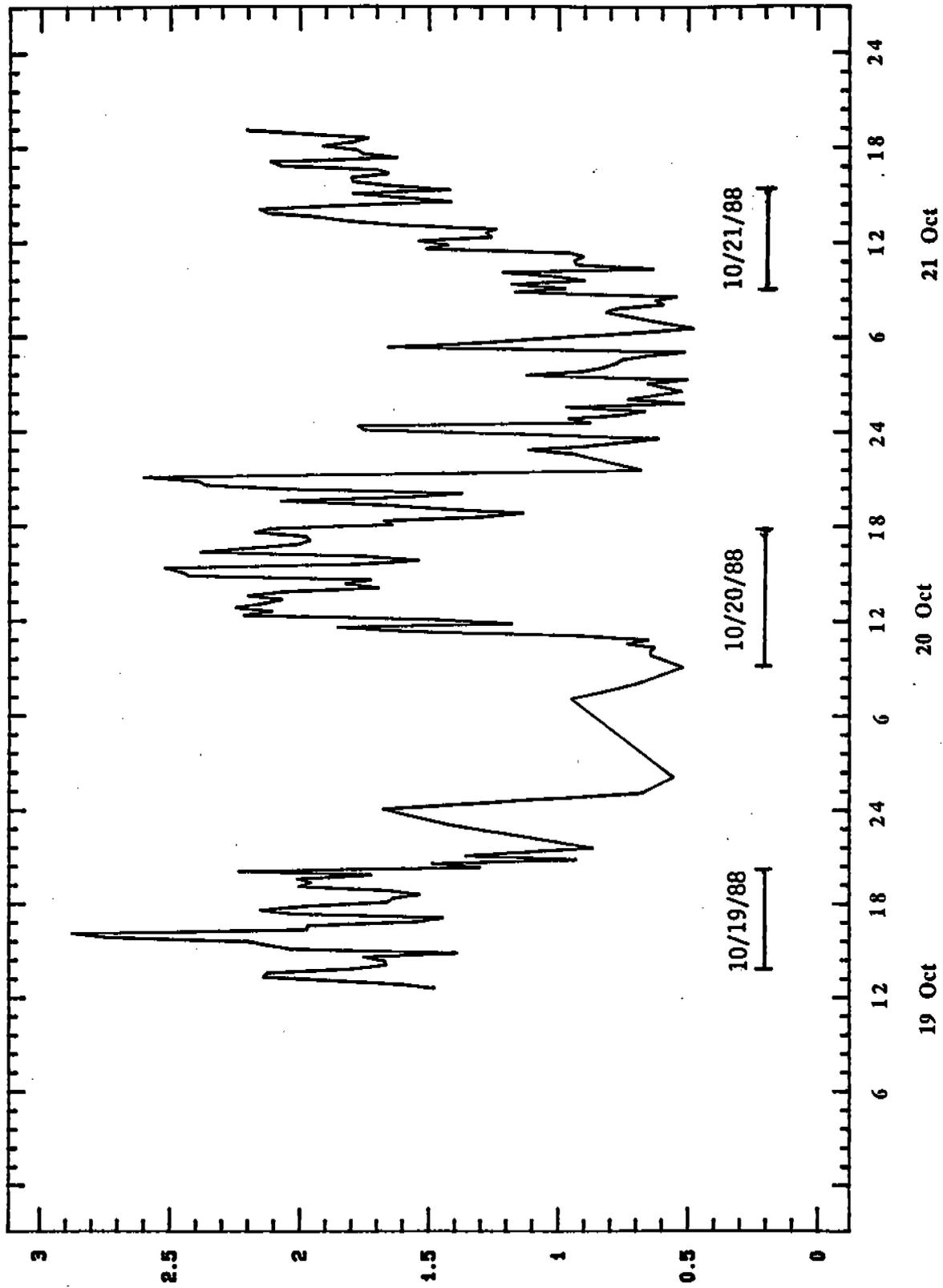


Figure 6-1 Wind Speed During Ambient Sampling

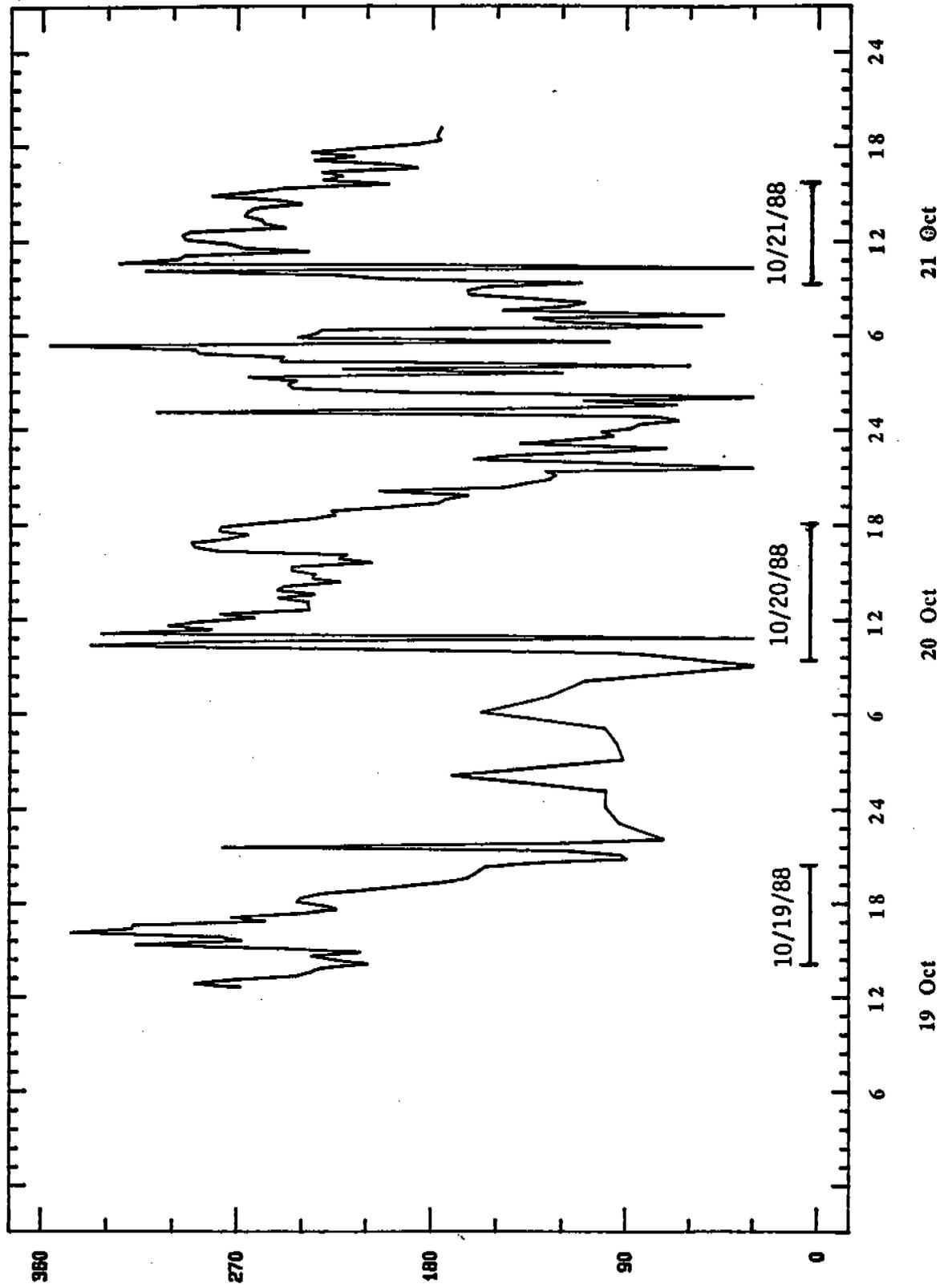


Figure 6-2 Wind Direction During Ambient Sampling

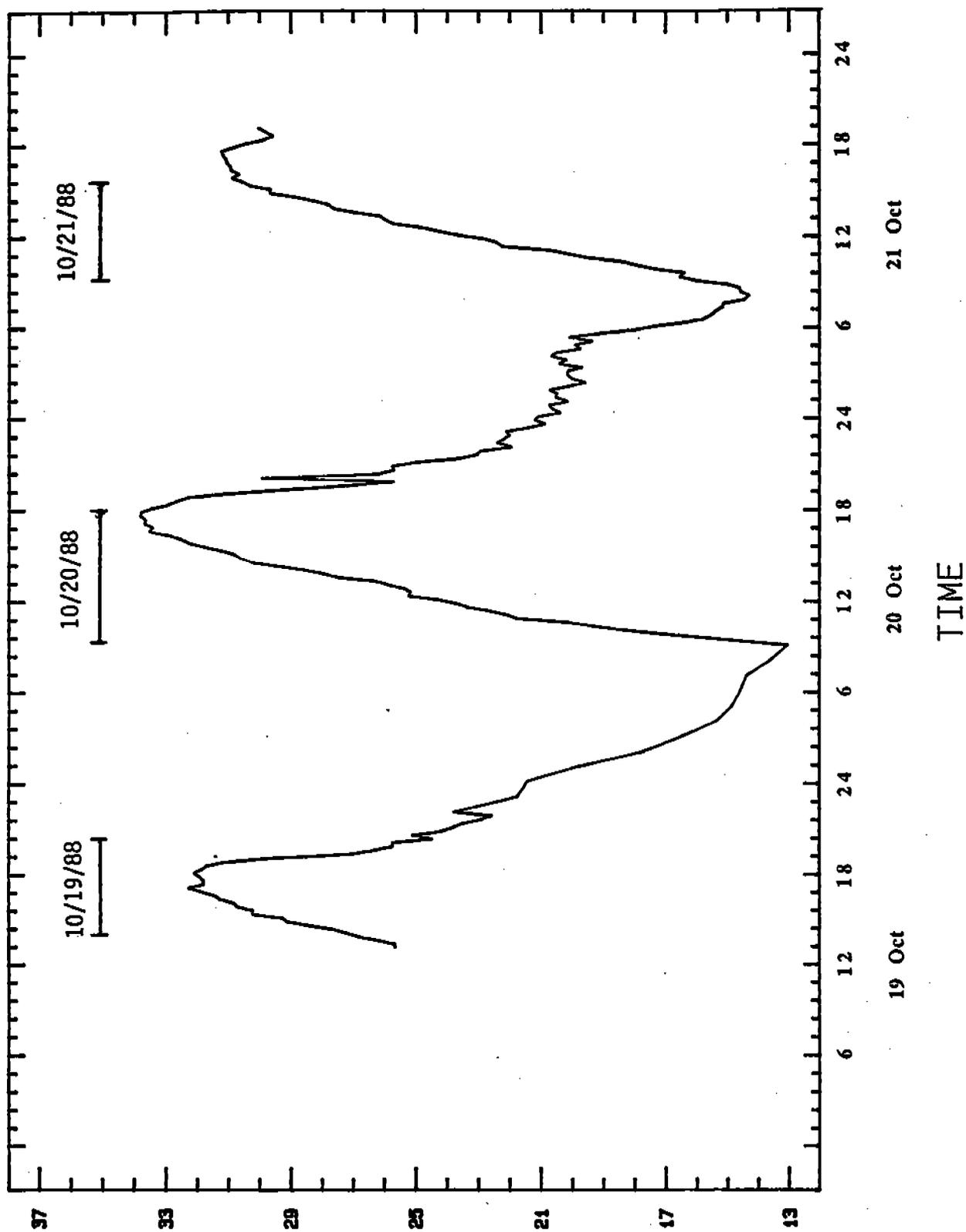


Figure 6-3 Temperature During Ambient Sampling

TABLE 6-8
TYPICAL AMBIENT DETECTION LIMITS

Analyte	Analytical Detection Limit (ug/sample)	Typical Sample Volume (cu. meters)	Typical Ambient Concentration Limit (ug/m ³)	Detection Limit Specified in SAP (ug/m ³)
Benzene	1.0	0.056-0.094	10.6-17.8	50
Toluene	10.0	0.056-0.094	106-178	50
Pyridine	10.0	0.056-0.094	106-178	3,000
Naphthalene (NIOSH 5501)	10.0	0.056-0.094	106-178	50
Naphthalene (NIOSH 5515)	1.0	0.30-0.87	1.1-3.3	50
Acenaphthalene	0.5	0.30-0.87	0.57-1.2	50
Acenaphthene	0.5	0.30-0.87	0.57-1.2	50
Fluorene	0.5	0.30-0.87	0.57-1.2	50
Phenanthrene	0.5	0.30-0.87	0.57-1.2	50
Anthracene	0.5	0.30-0.87	0.57-1.2	50
Fluoranthene	0.5	0.30-0.87	0.57-1.2	50
Pyrene	0.5	0.30-0.87	0.57-1.2	50
B(a)Anthracene	0.5	0.30-0.87	0.57-1.2	50
Chrysene	0.5	0.30-0.87	0.57-1.2	50
B(b)Fluoranthene	1.0	0.30-0.87	1.1-3.3	50
B(e)Pyrene	0.5	0.30-0.87	0.57-1.2	2.5
B(a)Pyrene	0.5	0.30-0.87	0.57-1.2	2.5
Ideno(123-cd)Pyrene	1.0	0.30-0.87	1.1-3.3	2.5
Dibenzo(a,h)anthracene	1.0	0.30-0.87	1.1-3.3	2.5
Benzo(ghi)pyrene	1.0	0.30-0.87	1.1-3.3	2.5

3435K

6.4.2 Results of Ambient Monitoring for VOCs

No volatile organic compounds were detected on any of the charcoal tubes used to measure benzene, toluene and naphthalene by NIOSH Method 1501 and pyridine using NIOSH Method 1613. The field data forms for the VOC sampling are given in Appendix C. Laboratory analytical reports are given in Appendix D. The ambient concentration limits corresponding to the laboratory analytical detection limits for those methods are listed in Table 6-8. The ambient detection limits for the VOCs were lower than the target values specified in the SAP.

The estimated VOC evaporative fluxes measured for October 21, 1988, corresponding to the VOC method detection limits, are given in Table 6-9. That table gives the following information:

- o The sample volume for each sampling site.
- o The MDL detection limit and the corresponding upper-limit ambient concentration.
- o The "downwind dispersion factor" (X/F_0) for each sampling site, calculated using the onsite meteorological data by the ISCST computer model.
- o The calculated upper-limit VOC flux, based on Equation 5-8 in Section 5.7.1.

TABLE 6-9
DETECTION LIMIT VOC EMISSION RATES FROM TREATED WOOD STORAGE PILE (10/21/88)

Sample Date - 10/21/88

Weather Data

Avg. Wind Speed (mps) 1.7
Avg. Temperature (deg K) 25

	Sampling Data	VOCs (NIOSH METHOD 1501)			
		BENZENE	TOLUENE	PYRIDINE	NAPHTHALENE
Location/Sample	A/AAV-12/AAPYR-12				
X/F (g/m3)/(g/m2/sec)	2.16E-01	2.16E-01	2.16E-01	2.16E-01	2.16E-01
Air Vol (m3)	0.076	0.076	0.076	0.076	0.076
Analyte Mass (ug)	0	0	0	0	0
Ambient Conc. (ug/m3)	0.00	0.00	0.00	0.00	0.00
Calc. Flux (g/m2/sec)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Location/Sample	B/AAV-13/AAPYR-13				
X/F (g/m3)/(g/m2/sec)	2.35E-01	2.35E-01	2.35E-01	2.35E-01	2.35E-01
Air Vol (m3)	0.0791	0.0791	0.0791	0.0791	0.0791
Analyte Mass (ug)	-1	-10	-10	-10	-10
Ambient Conc. (ug/m3)	-12.64	-126.42	-126.42	-126.42	-126.42
Calc. Flux (g/m2/sec)	-5.38E-05	-5.38E-04	-5.38E-04	-5.38E-04	-5.38E-04
Location/Sample	C/AAV-14/AAPYR-14				
X/F (g/m3)/(g/m2/sec)	2.32E+00	2.32E+00	2.32E+00	2.32E+00	2.32E+00
Air Vol (m3)	0.0735	0.0735	0.0735	0.0735	0.0735
Analyte Mass (ug)	-1	-10	-10	-10	-10
Ambient Conc. (ug/m3)	-13.61	-136.05	-136.05	-136.05	-136.05
Calc. Flux (g/m2/sec)	-5.86E-06	-5.86E-05	-5.86E-05	-5.86E-05	-5.86E-05
Location/Sample	D/AAV-15/AAPYR-15				
X/F (g/m3)/(g/m2/sec)	3.56E+00	3.56E+00	3.56E+00	3.56E+00	3.56E+00
Air Vol (m3)	0.0781	0.0781	0.0781	0.0781	0.0781
Analyte Mass (ug)	-1	-10	-10	-10	-10
Ambient Conc. (ug/m3)	-12.80	-128.04	-128.04	-128.04	-128.04
Calc. Flux (g/m2/sec)	-3.60E-06	-3.60E-05	-3.60E-05	-3.60E-05	-3.60E-05
Location/Sample	E/AAV-16/AAPYR-16				
X/F (g/m3)/(g/m2/sec)	2.32E+00	2.32E+00	2.32E+00	2.32E+00	2.32E+00
Air Vol (m3)	0.072	0.072	0.072	0.072	0.072
Analyte Mass (ug)	-1	-10	-10	-10	-10
Ambient Conc. (ug/m3)	-13.89	-138.89	-138.89	-138.89	-138.89
Calc. Flux (g/m2/sec)	-5.99E-06	-5.99E-05	-5.99E-05	-5.99E-05	-5.99E-05
Avg. Flux (g/m2/sec)		-1.38E-05	-1.38E-04	-1.38E-04	-1.38E-04
Std. Deviation		2.01E-05	2.01E-04	2.01E-04	2.01E-04
Analytical Detection Limit (ug/sample)		1.0	10	10	10

NOTE - NEGATIVE VALUES FOR ANALYTE MASS, AMBIENT CONCENTRATION AND FLUX INDICATE THAT THE INDICATED VALUE IS BASED ON THE METHOD DETECTION LIMIT

The emission flux is expressed as grams of pollutant emitted per second of stored, treated wood on a plan-view basis (such as would be seen in an aerial photograph of the storage yard). The "area" that emits the pollutants is therefore the plan-view area of the storage pallets (each of which is roughly 40 feet by 40 feet), and not the total surface area of the logs (circumference times length) stored on the pallets.

6.4.3 Semi-Volatile Compounds Emission Flux

The emission fluxes for semi-volatile organic compounds from the treated wood storage area north of the processing area that were measured between October 19 and October 21, 1988 are listed in Tables 6-10, 6-11 and 6-12, respectively. Compounds not listed in those tables were never detected in the ambient air at concentrations above the detection limits listed in Table 6-8. The emission fluxes were measured using the procedures described in Section 5.7.

As described in Section 6.4.1, the wind speeds during the sampling periods in October, 1988 were lower than the annual average at the site, and the ambient temperature was warmer than the annual average at the site. It is therefore expected that the annual-average fluxes will differ from those measured during the sampling period, because the evaporative emissions theoretically depend on the wind speed and the temperature. The emission fluxes measured on each of the three sampling days were therefore scaled to approximate the annual-average values, using the known wind speeds and temperatures during each sampling period. The method used to scale the emission fluxes is described below.

TABLE 6-11
PAH EMISSIONS FROM WOOD STORAGE PILE (10/20/88)

Date - 10/20/88

Weather Data

Avg. Wind Speed (mps) 1.98
Avg. Temperature (deg C) 30

Sampling Data

F/AAPAH-9
1.08E-01
0.544
J/AAPAH-15
2.70E+00
0.871
K/AAPAH-17
1.89E+00
0.864

Polynuclear Aromatic Hydrocarbons

	NAPTH	ACENPHTHYLEN	ACENAPHTHENE	FLUORENE	PHENANTHREN	FLRANTHENE	PYRENE	B(b)FLRTH	B(a)P
Location/Sample									
X/F (g/m3)/(g/m2/sec)	1.08E-01	1.08E-01	1.08E-01	1.08E-01	1.08E-01	1.08E-01	1.08E-01	1.08E-01	1.08E-01
Air Vol (m3)	0.544	0.544	0.544	0.544	0.544	0.544	0.544	0.544	0.544
Analyte Mass (ug)	6.4	0	3.3	1.8	1	0	0	0	0
Ambient Conc. (ug/m3)	11.76	0.00	6.07	3.31	1.84	0.00	0.00	0.00	0.00
Calc. Flux (g/m2/sec)	1.09E-04	0.00E+00	5.62E-05	3.06E-05	1.70E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Location/Sample									
X/F (g/m3)/(g/m2/sec)	2.70E+00	2.70E+00	2.70E+00	2.70E+00	2.70E+00	2.70E+00	2.70E+00	2.70E+00	2.70E+00
Air Vol (m3)	0.871	0.871	0.871	0.871	0.871	0.871	0.871	0.871	0.871
Analyte Mass (ug)	12	0	3	8.3	6.7	2.4	1.3	0	0
Ambient Conc. (ug/m3)	13.78	0.00	3.44	9.53	7.69	2.76	1.49	0.00	0.00
Calc. Flux (g/m2/sec)	5.10E-06	0.00E+00	1.28E-06	3.53E-06	2.85E-06	1.02E-06	5.53E-07	0.00E+00	0.00E+00
Location/Sample									
X/F (g/m3)/(g/m2/sec)	1.89E+00	1.89E+00	1.89E+00	1.89E+00	1.89E+00	1.89E+00	1.89E+00	1.89E+00	1.89E+00
Air Vol (m3)	0.864	0.864	0.864	0.864	0.864	0.864	0.864	0.864	0.864
Analyte Mass (ug)	24	0.6	32	19	13	2.2	1.2	0	0
Ambient Conc. (ug/m3)	27.78	0.69	37.04	21.99	15.05	2.55	1.39	0.00	0.00
Calc. Flux (g/m2/sec)	1.47E-05	3.67E-07	1.96E-05	1.16E-05	7.96E-06	1.35E-06	7.35E-07	0.00E+00	0.00E+00
Avg. Flux (g/m2/sec)	4.29E-05	1.22E-07	2.57E-05	1.53E-05	9.28E-06	7.89E-07	4.29E-07	0.00E+00	0.00E+00
Std. Deviation	4.68E-05	1.73E-07	2.28E-05	1.14E-05	5.86E-06	5.74E-07	3.12E-07	0.00E+00	0.00E+00
Analytical Detection Limit (ug/sample)	1.0	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0

The evaporative vapor flux from landfills is estimated as follows (Thibodeaux, 1981):

$$\text{Flux} = 0.0292 V_x^{0.78} Sc^{-0.67} P_i \quad (6-2)$$

where V_x is the wind speed, Sc is the Schmidt number, and P_i is the vapor pressure.

The Schmidt number is independent of either temperature or wind speed. The vapor pressure of the emitted contaminant is roughly proportional to the exponent of the absolute temperature (Bird et al, 1960). The evaporative flux is therefore proportional to the wind speed and ambient temperature as follows:

$$\text{Flux} = V_x^{0.78} \exp(T) \quad (6-3)$$

Using the above relationship, an "annual average scale factor" was calculated for each of the three ambient sampling days:

$$\text{Scale Factor} = \frac{V_a}{V_s}^{0.78} \exp(T_a - T_s) \quad (6-4)$$

Where V_s and T_s are the wind speed and absolute temperature ($^{\circ}K$) that were measured during each of the sampling periods, and V_a and T_a are annual-average wind speed and temperature.

The scale factor was applied to the daily-average emission rates measured during each of the three sampling periods to calculate the equivalent annual-average emission rate:

$$\text{Annual Average Flux} = \text{Daily Average Flux} * \text{Scale Factor}$$

The calculated annual-average fluxes for each of the sampling days are listed in Table 6-13. Theoretically, the annual-average flux calculated from the daily-average fluxes on each sampling day should be equal, if the flux from every pallet was identical and the dispersion patterns could be perfectly predicted by the ISCST computer model. However, because of routine uncertainties in the measurement methods the annual-average fluxes differed slightly for each of the three sampling days. A "Grand Average Annual Flux" was therefore calculated for each contaminant by averaging the annual-average fluxes from each of the three sampling days. The "Grand Average Annual Flux" for each contaminant is listed in Table 6-13.

TABLE 6-13
ANNUAL-AVERAGE PAH EMISSION RATES FROM TREATED WOOD STORAGE

Annual Average Weather Conditions		10/19/88		10/20/88		10/21/88		Final Stack Gas Conc. (mg/m3)	Grand Avg. Annual Flux (g/m2/sec)
Wind Speed, mps	Temperature, C	Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)	Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)	Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)		
2.2	17.6								
Sample Date		10/19/88		10/20/88		10/21/88			
Wind Speed, mps		1.95		1.98		1.7			
Temp, C		27		30		25			
Annual Scale Factor		1.06		1.04		1.19			
Compound		Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)	Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)	Daily Flux (g/m2/sec)	Scaled Annual Flux (g/m2/sec)		
Naphthalene		3.9E-05	4.1E-05	4.3E-05	4.5E-05	2.0E-05	3.3E-05	105	4.0E-05
Acenaphthylene		1.4E-07	1.5E-07	1.2E-07	1.2E-07	5.9E-08	7.1E-08	--	1.1E-07
Acenaphthene		2.6E-05	2.8E-05	2.6E-05	2.7E-05	1.8E-05	2.2E-05	--	2.5E-05
Fluorene		1.4E-05	1.5E-05	1.5E-05	1.6E-05	9.9E-06	1.2E-05	--	1.4E-05
Phenanthrene		9.7E-06	1.0E-05	9.3E-06	9.7E-06	6.3E-06	7.5E-06	--	9.1E-06
Fluoranthene		3.2E-07	3.4E-07	7.9E-07	8.2E-07	4.9E-07	5.8E-07	--	5.8E-07
Pyrene		0.0E+00	0.0E+00	4.3E-07	4.5E-07	2.1E-07	2.5E-07	--	2.3E-07
B(b)Flrth		7.3E-07	7.7E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00	--	2.6E-07
B(a)Pyrene		0.0E+00	0.0E+00	0.0E+00	0.0E+00	2.9E-06	3.4E-06	--	1.1E-06
Benzene		0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	--	0.0E+00
Toluene		0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	--	0.0E+00
Pyridine		0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	--	0.0E+00
Cresol(**)								967	3.65E-04
Phenol(**)								-2.2	-8.31E-07
Dibenzofuran(**)								-2.2	-8.31E-07

(**) - Calculated from Equation 6-5

The ambient concentrations of phenol, cresol, and dibenzofuran were not measured for this project. The annual-average fluxes for those compounds were therefore calculated from the measured naphthalene flux and the measured stack gas concentrations from the treatment cylinder vacuum exhaust at the end of the final vacuum cycle (just before the wood was removed from the cylinder). The following equation was used:

$$F_i = F_{\text{naphthalene}} \times \frac{C_i}{C_{\text{naphthalene}}} \quad (6-5)$$

F_i = calculated flux of component i

$F_{\text{naphthalene}}$ = annual average naphthalene flux (Table 6-13)

C_i = measured stack gas concentration from final vacuum exhaust treatment cycle, mg/m^3

$C_{\text{naphthalene}}$ = naphthalene stack gas concentration, mg/m^3

6.5 ESTIMATED EMISSIONS FROM PROCESS PIPING

The estimated emissions from the process piping are listed in Table 6-14. The listed emission rates are annual-average values, that account for the total number of hours per year that process chemicals are pumped through the piping.

The fugitive emissions from the process piping were estimated using the procedures that were described in Section 5.6. The spreadsheets that were used to calculate the emission rates are given in Appendix B. The results of the in-plant inventory of the process piping is given in Table 5-2. The measured

TABLE 6-14

CALCULATED EMISSIONS FROM PROCESS PIPING
(Emission Rates in kg/yr)

	CYLINDER NO. 3 PIPING (FS-9)		CYLINDER NO. 4 PIPING (FS-10)		CYLINDER NO. 3 & 4 COMMON PIPING (FS-11)		TOTAL EMISSION RATE
	FILL & DRAIN	PRESSURE CYCLE	FILL & DRAIN	PRESSURE CYCLE	DILUENT	CREOSOTE	
Benzene	0.05	2.31	8.44	17.50	0.00	0.76	29.07
Toluene	0.11	2.17	7.94	16.40	0.00	0.72	27.34
Pyridine	222.00	120.00	438.00	906.00	6.67	39.50	1732.17
Cresols	19.10	10.30	376.00	77.80	5.72	3.39	492.31
Napthalene	7.44	5.94	47.90	99.20	0.22	4.32	165.02
2-Methylnapthalene	6.75	5.39	54.90	114.00	0.20	4.95	186.19
Acenaphthene	0.99	0.79	7.23	15.00	0.00	0.65	24.66
Acenaphthalene	0.55	4.35	0.12	0.24	0.00	0.10	5.36
Fluorene	0.28	2.23	1.77	3.66	0.01	0.16	8.11
Phenanthrene	0.20	0.16	1.62	3.35	0.01	0.15	5.49
Other Detected PAHs	0.01	0.01	0.22	0.15	0.00	0.15	0.54
PAHs Below Detection Limits in Gas Stream	0.01	0.01	0.03	0.07	0.00	0.00	0.12

chemical compositions of the process chemicals are given in Table 5-1. Analytical reports for the process chemical samples are given in Appendix E.

6.6 ESTIMATED EMISSIONS FROM PROCESS CHEMICAL LOADING OPERATIONS

The estimated fugitive emissions rates during process chemical unloading are listed in Table 6-15. The emission rates were calculated using the procedures described in Section 5.2. The spreadsheets used to calculate the emission rates are given in Appendix B. The chemical compositions of the process chemicals are given in Table 5-1. Analytical reports for the process chemicals are given in Appendix E.

6.7 ESTIMATED EMISSIONS FROM TREATMENT CYLINDER UNLOADING

The estimated emission rates during unloading of the Treatment Cylinders 2, 3 and 4 are listed in Table 6-16. The emission rates were calculated using the procedures described in Section 5.3. The spreadsheets that were used to calculate the emission rates are given in Appendix B. The emission rates listed in Table 6-16 are annual-average values, that account for the number of times per year that each treatment cylinder is unloaded.

6.8 ESTIMATED EMISSIONS FROM WASTEWATER TREATMENT OPERATIONS

The estimated contaminant emission rates from the wastewater treatment operations are listed in Table 6-17. The emission rates were calculated using the procedures described in Section 5.4. Spreadsheets that were used to calculate the

TABLE 6-15

CALCULATED EMISSIONS FROM PROCESS CHEMICAL UNLOADING

COMPOUND	RAIL CAR UNLOADING DILUENT (kg/yr)	RAIL CAR UNLOADING CREOSOTE (kg/yr)	TOTAL ESTIMATED EMISSIONS (kg/yr)
Benzene	0.00	0.61	0.61
Toluene	0.00	0.68	0.68
Pyridine	4.28	32.00	36.28
Cresols	0.50	3.76	4.26
Napthalene	0.23	5.68	5.91
Methylnapthalene	0.23	7.22	7.45
Acenaphthene	0.04	1.03	1.07
Fluorene	0.01	0.27	0.28
Phenanthrene	0.09	0.27	0.36
Other Detected PAHs	0.00	0.06	0.07
PAHs Below Detection Limits in Gas Stream	0.01	0.01	0.02

TABLE 6-16

CALCULATED EMISSIONS FROM TREATMENT CYLINDER UNLOADING

COMPOUND	CYLINDER		TOTAL ESTIMATED EMISSIONS (kg/yr)
	CYLINDER No. 3 UNLOADING DILUENT (kg/yr)	CYLINDER No. 4 UNLOADING CREOSOTE (kg/yr)	
Benzene	0.02	0.17	0.19
Toluene	0.00	0.17	0.17
Pyridine	0.60	0.90	1.50
Cresols	0.07	0.10	0.17
Napthalene	0.51	2.37	2.88
Methylnapthalene	3.69	2.17	5.86
Acenaphthene	0.04	0.02	0.06
Fluorene	0.01	0.05	0.06
Phenanthrene	0.01	0.06	0.06
Other Detected PAHs	0.01	0.07	0.08
PAHs Below Detection Limits in Gas Stream	0.01	0.05	0.06

TABLE 6-17

CALCULATED EMISSIONS FROM WASTEWATER TREATMENT

COMPOUND	OIL/ WATER SEPARATOR	CYLINDER No. 3 DOOR PIT	CYLINDER No. 4 DOOR PIT	TOTAL ESTIMATED EMISSIONS (kg/yr)
	(kg/yr)	(kg/yr)	(kg/yr)	
Benzene	0.022	0.639	0.015	0.676
Toluene	0.001	0.133	0.028	0.162
Pyridine	0.036	0.011	4.830	4.877
Cresols	0.003	0.000	0.008	0.011
Napthalene	0.012	0.001	0.409	0.422
Methylnapthalene	0.001	0.000	0.294	0.295
Acenaphthene	0.000	0.000	0.009	0.009
Fluorene	0.000	0.000	0.001	0.001
Phenanthrene	0.000	0.000	0.000	0.000
Other Detected PAHs	0.001	0.000	0.000	0.001
PAHs Below Detection Limits in Gas Stream	0.001	0.000	0.010	0.011

emission rates are given in Appendix B. The measured wastewater composition is given in Table 5-1. Analytical reports for the wastewater analyses are given in Appendix E.

6.9 AMBIENT PARTICLE CONCENTRATION

The ambient particle concentration and size distribution that were measured on 10/21/88 are given in Table 6-18. The methods that were used to collect and analyze the particle samples are described in Section 5.7.2.

6.10 RESULTS SUMMARY

The estimated annual emission rates (combining both predicted and measured) from all sources for organic chemicals is presented in Table 6-19. The different sources were combined according to cylinder operations in order to examine individual operations. It was assumed that Cylinder No. 3 would be used for only diluent operations and Cylinder No. 4 would be used for only creosote operations. The Total General Fugitive emissions column combines the wastewater treatment, the sumps, chemical unloading, and the fugitive piping emissions of piping common to both cylinders.

The pyridine emissions were not included in this table because the pyridine was analyzed as part of the semi-volatile fraction which as previously described was diluted to bring the major components on scale. Pyridine was not detected in the air samples. As a result of this dilution, the detection limit of pyridine was elevated. These high detection limits then caused unrealistic estimates of pyridine emissions.

TABLE 6-18

AMBIENT PARTICLE CONCENTRATION AND SIZE DISTRIBUTION

Particle Concentration

<u>Sample Number</u>	<u>Measured Concentration (ug/m³)</u>
AATSP-1	204
AATSP-2	244

Particle Concentration

<u>Size Class (microns)</u>	<u>Percent of Particles Counted in Size Class</u>	
	<u>AASEM-1</u>	<u>AASEM-2</u>
1-2	17	43
2-4	37	28
4-8	25	20
8-16	15	8
16-32	5	0
32-64	<u>1</u>	<u>1</u>
	100	100

TABLE 6-19
SUMMARY OF EMISSION SOURCES
(Emission Rates in kg/year)

Organic Compound	Cylinder No. 3		Cylinder No. 4		Total General Fugitive Emissions	Wood Storage Yard	Total Emission Rates	Maximum Possible Emissions
	Total Stacks	Total Fugitive Emissions	Total Stacks	Total Fugitive Emissions				
Benzene	1.3 P	2.4 P	66.1 P	26.1 P	2.7 P	**	99	130
Toluene	3.2 P	2.3 P	73.6 P	24.5 P	2.2 P	**	106	362
Pyridine	**	**	**	**	**	**	0	<24000
Cresols	208.9 <P	29.5 <M	48.6 <P	453.9 <M	17.6 <P	194.0 <M	953	<24000
Napthalene	264.5 P	13.9 M	867.9 P	149.5 M	16.8 P	9500.0 M	10813	106000
2-Methylnapthalene	194.5 P	15.8 M	1023.2 P	171.1 M	20.4 P	86000.0 M	87425	320000
Acenaphthene	33.4 P	1.8 M	263.3 P	22.3 M	2.8 P	5900.0 M	6223	144000
Fluorene	11.9 P	4.9 M	72.2 P	5.4 M	0.7 P	3300.0 M	3395	84000
Phenanthrene	15.9 P	2.5 <M	47.2 P	5.5 M	0.9 P	2100.0 M	2172	384000
Other Detected PAHs Below Detection Limits in Gas Stream	18.4 <P	0.0 <M	25.9 <P	5.0 M	0.3 P	454.0 M	460	1060900
				0.2 <M	0.0 P	400.0 <M	445	

1/ "P" Means that the listed value was predicted.

2/ "M" Means that the listed value was based on stack measurements.

3/ "<" Prefix indicates that the listed value is partially based on the Method Detection Limit.

4/ "****" Means that the compound predictions based on MDL were out of reasonable range.

5/ Total emission rates are the sum of all values based on detected concentrations and the method detection limit for samples where compounds are not detected.

This is out of range for the maximum possible emissions as given in Table 6-1 and inconsistent with other predictions and therefore estimated emission rates were used based upon a comparison of the relative concentration of pyridine in process chemical and then compared with the measured emission rates of other compounds.

The total stack emissions for the PAH compounds was 3,003 kg/yr and the total fugitive emissions were 467 kg/yr. The total PAH emissions were then 3,470 kg/yr not counting the wood storage emissions. This can be compared with the potential total maximum emission of 1,779,000 kg/yr of PAHs from Table 6-1.

If the predicted PAH emissions (28,247 kg/yr) from the storage pile were considered also, the total PAH emissions would be 31,700 kg/yr. This is approximately 2% of the total material consumed at the facility.

Since the stack emission levels of benzene and toluene exceeded the sampling equipment detection capabilities, these emission results were calculated based upon the measured emissions of other compounds and the relative concentration of benzene and toluene in process chemicals.

The total predicted benzene and toluene emissions were 99 and 106 kg/yr respectively. This can be compared with the maximum possible VOC emissions of 130 and 362 kg/yr respectively. The major bulk of these VOC emissions occurs during the steam cycle of creosote operations where 55 kg/yr of benzene and 61 kg/yr of toluene are predicted to be emitted. This is also the same cycle where the major portions of naphthalene is also emitted.

6.11 ACCURACY OF THE EMISSION ESTIMATES

The emission rates listed in this report were estimated using a variety of techniques. The calculated emission rates are subject to the following limitations:

- o As shown in Table 6-19, the treated wood storage pile is the major source of semi-volatile organic emissions and the assumptions relating to the magnitude of flux (i.e., number of storage piles, age of storage piles and weather conditions). The main uncertainty in the storage pile emission calculations was the use of the ISCST computer dispersion model. Computer dispersion models such as ISCST are generally believed to be accurate within no better than a factor of two. This level of accuracy is recognized in the scientific community as the best that atmospheric dispersion models can do under well controlled conditions. The best that the model can be expected for this study is that the predicted value is within a factor range between two to ten of the actual values.

- o Emissions of semi-volatile organic compounds from Stack SS-1 (Working Tank Vent), listed in Tables 1-1 and 6-4, are another major source of contaminants. The emission rates from the creosote process emitted through that stack were measured directly, and are considered to be reasonably accurate given that the operating conditions remain the same. The emissions from the diluent process were estimated by comparison with the emission rates from the creosote process (see Section 4.5). There is no way of assessing the accuracy of the Diluent Process emission estimates.

- o The emission rates of benzene, toluene, and pyridine from the stacks were estimated by comparison with the measured emission rates of other compounds (see Section 4.2.2). Because of the many assumptions required to justify that method, the listed emission rates for benzene, toluene, and pyridine are probably accurate to within only an order of magnitude. However, the maximum emission rates for benzene, toluene, and pyridine measured or estimated for this project cannot exceed the Maximum Quantifiable Emission Rates listed in Table 6-1.

- o The emission factor equations that were used to predict the fugitive emissions from the process piping and the wastewater systems are reported to be accurate to within about an order of magnitude (EPA 1987b).

7.0 QUALITY CONTROL SAMPLE RESULTS

Quality control samples taken for this project confirmed that the stack samples, ambient air samples and liquid samples were measured with satisfactory precision and accuracy. Quality control samples consisted of duplicate or collocated samples, trip blanks, and field blanks. Analytical accuracy was confirmed by analyses of surrogate spikes, in accordance with EPA Methods 0010 (Semi-VOST) and 0030 (VOST). The results of the specific quality control sampling and analyses are described in the following sections.

7.1 AMBIENT MONITORING

7.1.1 Collocated Samplers

The results of collocated sampling during the ambient air monitoring that was conducted on October 21, 1988 are summarized in Table 7-1. The collocated sample results generally were in very good agreement. Collocated samples were taken to measure PAHs, VOCs, total suspended particulate and the ambient particle size distribution. There are no EPA requirements for the precision of low-volume ambient air samplers. As shown in Table 7-1, the concentrations measured by the collocated PAH samplers agreed to within 15 percent. There were no VOCs detected by either of the collocated VOC samplers. The total suspended particulate concentrations measured by the two collocated samplers agreed to within 20 percent. The ambient particle size distributions measured by the collocated samplers were in reasonable agreement.

TABLE 7-1
RESULTS OF COLLOCATED SAMPLES DURING AMBIENT AIR SAMPLING

<u>PAH Sampling (10/21/88)</u>		
<u>Analyte</u>	<u>Sample AAPAH-23 (ug/m3)</u>	<u>Sample AAPAH-27 (ug/m3)</u>
Napthalene	30.1	28.0
Acenapthalene	ND ^{1/}	ND
Acenapthene	28.8	30.5
Fluorene	15.7	17.8
Phenanthrene	11.8	12.5
Fluoranthene	2.0	2.0
Pyrene	1.05	1.02
Benzo(b)Fluoranthene	ND	ND
Benzo(a)Pyrene	ND	ND

<u>Volatile Organic Compounds</u>		
<u>Analyte</u>	<u>Sample AAV-14 (ug/m3)</u>	<u>Sample AAV-16 (ug/m3)</u>
Benzene	ND	ND
Toluene	ND	ND
Pyridine	ND	ND

<u>Total Suspended Particulates</u>		
<u>Analyte</u>	<u>Sample AATSP-1 (ug/m3)</u>	<u>Sample AATSP-2 (ug/m3)</u>
TSP	204	244

<u>Particle Size Distribution</u>		
<u>Percent of Particles Counted</u>		
<u>Size Class (microns)</u>	<u>Sample AASEM-1</u>	<u>Sample AASEM-2</u>
1-2	17	43
2-4	37	28
4-8	25	20
8-16	15	8
16-32	5	0
32-64	1	1

^{1/} ND - Not detected above Method Detection Limits (Table 6-7).

7.1.2 Trip Blanks and Field Blanks

Trip blanks were sorbent tubes that were quickly opened then resealed, then shipped to the laboratory along with the actual field samples. Field blanks were sorbent tubes that were kept open during the sampling period, but through which no air was pumped. There were no PAHs or VOCs detected above the analytical limits listed in Table 6-7 on any of the sample sorbent tubes that were prepared for use as either trip blanks or field blanks:

Trip Blanks

AAV - 10
AAV - 11
AAV - 17
AAPYR - 10
AAPYR - 11
AAPYR - 17

Field Blanks

AAPAH - 29
AAV - 18
AAPYR - 18

7.2 STACK TESTING

No collocated stack samples were planned because of the difficulty of the sampling and the specialized equipment that was needed to obtain the stack samples.

The trip blank and field blank VOST tubes were found to contain benzene and toluene concentrations above the Method Detection Limit, but less than one percent of the analyte collected in the actual stack sample tubes. No analytes were detected in either the trip blank or field blank semi-VOST tubes. Roughly

half of the concentrations of chromium and copper detected in the metals stack samples from the CCA Treatment Cylinder No. 2 were also detected in the impinger field blanks. However, in all cases, the copper and chromium concentrations were only slightly above the detection limits. No arsenic or hexavalent chrome were detected in any of the stack samples or quality control samples.

The accuracy of the stack samples was assessed by analysis of surrogate spikes in accordance with EPA Methods 0010 and 0030. The results of the surrogate spike analyses are given in Table 7-2. In most cases the percent recoveries were within the desired limits specified in the SAP.

7.3 WASTEWATER SAMPLING

Analyses of duplicate samples and a trip blank demonstrated good precision for the wastewater sampling. The results of the collocated samples that were taken at the oil/water separator (samples LSP-4 and LSP-8) are shown in Table 7-3. The concentrations measured in the liquid sample trip blank (LSP-9) are also listed in that table.

7.4 RESULTS OF EPA DATA VALIDATION

EPA performed the data validation on the sample packages. A comparison of the validated data to the unvalidated data revealed negligible quantitative and minimal qualitative discrepancies with the exception of Air Chromium (VI) sample being rejected by validation due to the holding time being exceeded. The most significant emissions of Chromium (VI) were from the working tank vent (see Table 1-2). These emissions were calculated from the analysis of liquid samples which were

properly handled, tested and validated. Overall the qualified data for sample data obtained in February 1989 was only marginally in excess of validation criteria. There were no quantitative differences of concern with the exception of detection limit adjustments and detections just above the limits of detection. Unvalidated calculations were rechecked using the validated data which verified the original calculations as usable.

TABLE 7-2

RESULTS OF SURROGATE SPIKES FOR
VOST AND SEMI-VOST ANALYSES

Compound	Percent Recovery
VOST TUBE ANALYSES	
Deuterated Toluene	78-170
Bromofluorobenzene	110-130
SEMI-VOST ANALYSES	
2-Fluorophenol	101-388
Deuterated Phenol	129-197
Deuterated Nitrobenzene	79-105
2-Fluorobiphenyl	81-99

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TABLE 7-3
 DUPLICATE SAMPLES DURING WASTEWATER SAMPLING
 (mg/l)

Analyte	Duplicate Samples		Trip Blank LSP-9
	LSP-4	LSP-8	
Benzene	0.061	0.19	<0.001
Toluene	0.094	0.32	<0.001
Pyridine	2.3	2.5	<0.02
Phenol	18.0	18.0	NA ^{1/}
Cresols	9.3	8.7	"
Napthalene	8.8	7.6	"
Acenapthene	2.3	2.4	"
Fluorene	1.2	1.1	"
Phenanthrene	4.1	3.4	"
Fluoranthene	1.6	1.3	"
Pyrene	1.2	1.1	"
Dibenzofuran	1.1	1.0	"

1/ NA - Not Applicable. Trip blank was analyzed for only volatile compounds.

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8.0 REFERENCES

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