

Analysis Of Refinery Wastewaters For The EPA Priority Pollutants

Interim Report

API PUBLICATION 4296
MAY 1978

American Petroleum Institute
2101 L Street, Northwest
Washington, D.C. 20037



DCN 78-200-192-01

ANALYSIS OF REFINERY WASTEWATERS
FOR THE EPA PRIORITY POLLUTANTS

INTERIM REPORT

Prepared for
American Petroleum Institute
Analytical Systems Task Force (W-22)
Washington, D. C.

May 1978

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766



ACKNOWLEDGEMENT

This report was made possible through the combined efforts of the American Petroleum Institute who sponsored and coordinated the study, and the individual member companies who provided substantial support to the study by supplying samples and analytical data and participating in the API analytical Systems Task Force (W-22). The Task Force members and advisors who directed this study are listed below. Additionally, the support of the API contractors, Exxon Research and Engineering Company for analytical services and Radian Corporation for analytical services and data evaluation, is acknowledged. Special acknowledgement is extended to Ron Oldham and Lloyd Provost of Radian for their participation. Special acknowledgement is also extended to the respective refinery representatives for their cooperation and assistance to the API contractors.

Members: J. D. Hallett (Chairman) - Shell Oil Company
S. C. Blum - Exxon Research and Engineering Company
R. A. Brown* - Exxon Research and Engineering Company
L. J. Duffy - Standard Oil (Indiana)
W. O. Fitzgibbons* - Standard Oil Company of Ohio
U. V. Henderson - Texaco Incorporated
F. P. Hochgesang - Mobil Research and Development Corporation
D. S. Rulison - Standard Oil Company of Ohio
G. H. Stanko - Shell Development Company
F. T. Weiss* - Shell Development Company

* Former members

Statistical

Advisors: N. R. Crawford - Texaco Incorporated
J. W. Gorman - Amoco Oil Company

API Staff: J. G. Thatcher
W. M. Ollison

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT.	ii
LIST OF FIGURES	iv
LIST OF TABLES	vi
EXECUTIVE SUMMARY	xi
CONCLUSIONS AND RECOMMENDATIONS	xiii
1.0 INTRODUCTION	1
2.0 WASTEWATER SAMPLING.	6
3.0 SAMPLE ANALYSES	9
4.0 ANALYTICAL RESULTS	11
4.1 Refinery Wastewater	12
4.2 Special Analytical Studies	25
5.0 DISCUSSION OF ANALYTICAL DATA	27
5.1 Interference and Contamination of the Samples.	27
5.2 Recoveries - Spiked Samples	28
5.3 Repeatability of Analytical Methods - Duplicate Analyses	28
5.4 Reproducibility of Sampling and Analytical Methods	29
5.5 PNA Comparisons	30
5.6 Trace Element Data	32
BIBLIOGRAPHY	34
GLOSSARY	35
APPENDIX A	
APPENDIX B	

LIST OF FIGURES

		<u>Page</u>
A-1	Element Analysis Protocol	A-15
B-1	Comparison of Volatile Organics Analysis, Refinery 2, Radian vs. EPA Results	B-22
B-2	Comparison of Volatile Organics Analysis, Refineries 2, 7, 9, Radian vs. Company Results	B-23
B-3	Comparison of Volatile Organics Analysis, Refinery 2, EPA vs. Company Results	B-24
B-4	Comparison of Liquid/Liquid Extractable Organics Analysis, Refinery 2, Radian vs. EPA Results	B-25
B-5	Comparison of Liquid/Liquid Extractable Organics Analysis, Refineries 2, 7, 9, Radian vs. Company Results	B-26
B-6	Comparison of Liquid/Liquid Extractable Organics Analysis, Refineries 2, 6, EPA vs. Company Results	B-27
B-7	Comparison of Liquid/Liquid Extractable Organics Analysis, Refinery 7, Company vs. Other Results	B-28
B-8	Comparison of Trace Element Analysis, Refineries 2, 7, 9, Radian vs. EPA Results .	B-29

B-9	Comparison of Trace Element Analysis, Refineries 7 and 9, Radian vs. Company Results	B-30
B-10	Comparison of Trace Element Analysis, Refineries 7, 8, 9, 11, 16, EPA vs. Company Results	B-31

LIST OF TABLES

		<u>Page</u>
1-1	Appendix A Priority Pollutants	2
2-1	Initial Refinery Sampling	7
3-1	Petroleum Refining Screening Survey	10
4-1	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Intake Waters - API Data	13
4-2	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Wastewater Feeds to Biotreatment - API Data	14
4-3	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Final Effluents - API Data	15
4-4	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Intake Waters - EPA Data	16
4-5	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Wastewater Feeds to Biotreatment - EPA Data	17
4-6	Frequency and Concentration Range of Organic Priority Pollutants in Refinery Final Effluents - EPA Data	18
4-7	Frequency and Concentration Range of Trace Elements in Refinery Intake Waters - API Data	19
4-8	Frequency and Concentration Range of Trace Elements in Refinery Wastewater Feeds to Biotreatment - API Data	20
4-9	Frequency and Concentration Range of Trace Elements in Refinery Final Effluents - API Data	21
4-10	Frequency and Concentration Range of Trace Elements in Refinery Intake Waters - EPA Data	22

4-11	Frequency and Concentration Range of Trace Elements in Refinery Wastewater Feeds to Biotreatment - EPA Data	23
4-12	Frequency and Concentration Range of Trace Elements in Refinery Final Effluents - EPA Data	24
5-1	Comparison of Polynuclear Aromatic Hydrocarbon Data from Refinery 7	31
A-1	Organic Priority Pollutants	A-3
A-2	Summary of Methods Utilized for the Analysis of Organic Priority Pollutants . . .	A-5
A-3	Comparison of Extraction Procedures Employed for the Analysis of the Liquid/Liquid Extractable Organics	A-8
A-4	Recovery of Liquid/Liquid Extractable Organics from Refinery Final Effluent	A-11
A-5	Interlaboratory Analysis	A-12
A-6	Summary of Methods Utilized for the Analysis of Trace Elements	A-14
A-7	Comparison of Radian and EPA Digestion Procedures in the Analysis of a Petroleum Refinery Final Effluent	A-18
A-8	Spiking Studies - Elemental Analysis	A-19
A-9	Summary of Analyses for the Volatile Organic Priority Pollutants for the Petroleum Refining Industry - EPA and API Data	A-21
A-10	Summary of Analyses for the Liquid/Liquid Extractable Organic Priority Pollutants for the Petroleum Industry - EPA and API Data	A-22
A-11	Summary of Analyses for the Trace Element Priority Pollutants for the Petroleum Refining Industry - EPA and API Data	A-23

A-12	Concentration of Priority Volatile Organics at Refinery 1	A-24
A-13	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 1	A-25
A-14	Concentration of Trace Elements at Refinery 1	A-26
A-15	Concentration of Priority Volatile Organics at Refinery 2	A-28
A-16	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 2	A-30
A-17	Concentration of Trace Elements at Refinery 2	A-32
A-18	Concentration of Priority Volatile Organics at Refinery 3	A-34
A-19	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 3	A-34
A-20	Concentration of Trace Elements at Refinery 3	A-35
A-21	Concentration of Priority Volatile Organics at Refinery 4	A-36
A-22	Concentration of Priority Liquid/Liquid Organic at Refinery 4	A-36
A-23	Concentration of Trace Elements at Refinery 4	A-37
A-24	Concentration of Priority Volatile Organics at Refinery 5	A-38
A-25	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 5	A-39
A-26	Concentration of Trace Elements at Refinery 5	A-40
A-27	Concentration of Priority Volatile Organics at Refinery 6	A-41
A-28	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 6	A-42

A-29	Concentration of Trace Elements at Refinery 6	A- 43
A-30	Concentration of Priority Volatile Organics at Refinery 7	A- 44
A-31	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 7	A- 45
A-32	Concentration of Trace Elements at Refinery 7	A- 4
A-33	Concentration of Trace Elements at Refinery 8	A-47
A-34	Concentration of Priority Volatile Organics at Refinery 9	A-48
A-35	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 9	A-49
A-36	Concentration of Trace Elements at Refinery 9	A-50
A-37	Concentration of Trace Elements at Refinery 10	A-51
A-38	Concentration of Priority Volatile Organics at Refinery 11	A-52
A-39	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 11	A-52
A-40	Concentration of Trace Elements at Refinery 11	A-53
A-41	Concentration of Trace Elements at Refinery 12	A-54
A-42	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 13	A-55
A-43	Concentration of Trace Elements at Refinery 13	A-56
A-44	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 14	A-58
A-45	Concentration of Trace Elements at Refinery 14	A-59

A-46	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 15	A-61
A-47	Concentration of Trace Elements at Refinery 15	A-62
A-48	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 16	A-63
A-49	Concentration of Trace Elements at Refinery 16	A-66
A-50	Concentration of Priority Liquid/Liquid Extractable Organics at Refinery 17	A-69
A-51	Concentration of Trace Elements at Refinery 17	A-70
B-1	Analyses of Field Blank Samples - Volatile Organics	B-3
B-2	Summary of Recovery Studies	B-5
B-3	Duplicate Sample Analysis Studies	B-7
B-4	Volatile Organics - Laboratory Comparisons .	B-15
B-5	Liquid/Liquid Extractable Organics - Laboratory Comparisons	B-16
B-6	Trace Elements - Laboratory Comparisons . . .	B-17

EXECUTIVE SUMMARY

Intake waters, wastewater feed to biotreatment units, and final effluent streams from 17 petroleum refineries were sampled by the EPA within the past year to screen for the presence or absence of the 129 substances on the EPA Priority Pollutant list. Concurrently, an API contractor and/or various individual petroleum companies sampled nine of the 17 refineries. Analytical results, except for trace elements, are not available at this time for all 17 refineries sampled either from EPA or the petroleum industry.

The following table summarizes analytical results from this study:

ORGANICS

<u>Total No. Identified</u>	<u>Refinery Intake Waters</u>	<u>Wastewater Feed to Biotreatment</u>	<u>Refinery Final Effluents</u>
API	40	45	36
EPA	24	33	18
Combined	44	49	38
<u>Range (ppb)</u>			
API	<1-150	<1-44,000	<1-60
EPA	<1-160*	<1-16,000	<1-35*
Combined	<1-160*	<1-44,000	<1-60*

TRACE ELEMENTS

<u>Total No. Identified</u>			
API	13	13	13
EPA	11	12	12
Combined	13	13	13
<u>Range (ppb)</u>			
API	<1-1,300	<1-9,600	<1-1,100
EPA	<1-210	<1-4,900	<1-1,000
Combined	<1-1,300	<1-9,600	<1-1,100

*The EPA reported values from 190 to 2,000 ppb for bis(2-ethylhexyl) phthalate among five refineries. These values are extremely suspect. EPA also reported a value of 750 ppb for methylene chloride at one refinery. This value is suspect because of EPA-acknowledged contamination. Therefore these values have been excluded from this table.

In no case were all of the identified pollutants detected in any of the samples from any one refinery. Pollutants detected in samples of feeds to refinery biotreatment systems were significantly reduced, or removed, within the treatment system. Numerous cases occurred where levels of particular pollutants were found to be higher in the refinery's intake than effluent waters.

In addition special analytical studies were conducted by API on refinery final effluents. The studies included spiking experiments, inter-laboratory comparisons and analysis of sample blanks. Results from these investigations indicated that clarification recoveries and precision were extremely variable. Differences in the inter-laboratory data ranged from 0 to 200 percent. Analysis of samples for the PNAs by an alternate technique demonstrated that the EPA analytical protocol was unable to differentiate between certain isomeric species. Many of the samples analyzed were found or were suspected to be contaminated with substances such as methylene chloride and bis(2-ethylhexyl)phthalate. Therefore, the currently applied EPA analytical and sampling protocol was found to be inadequate for the quantification and, in some cases, identification of priority pollutants at the low ppb level.

Although the combined EPA-API data base is limited both in scope and accuracy, it does indicate that many (approximately 65%) of the Priority Pollutants are not present in refinery effluents. In addition, most of the pollutants detected are generally found at extremely low levels and are not uniformly present among refineries sampled nor in replicate samples taken within a single refinery.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Best Practicable Control Technology Currently Available, as utilized by refineries in this study, provides effective removal of Priority Pollutants from refinery wastewaters.
- The Priority Pollutants not detected by any laboratory in any of the samples taken during this study can be eliminated from further consideration in developing BATEA limitations for Priority Pollutants for the refining industry. Numerous other pollutants detected in occasional samples or at low levels in samples may also be eliminated as additional data are obtained.
- The current data base is inadequate to derive specific numerical effluent limitations for individual Priority Pollutants. Only limited data are available to assess analytical and effluent variability. The analytical procedures used to derive the data have not been validated and adequate accuracy and precision data are not available.
- The sampling methodology is inadequate to insure that contamination of samples with substances on the Priority Pollutant list will not occur.
- The variability of the results obtained by two or more laboratories for individual pollutants in replicate samples verifies that individual data points should be viewed in terms of ranges rather than specific values. (Specific values have been used in this report only to give the reader a basis for comparison.)

Recommendations

- Validation of analytical and sampling methods must be carried out. Any effluent limitations proposed for specific Priority Pollutants must be derived from data obtained using validated methods.
- Prior to proposing effluent limitations for any of the Priority Pollutants a more thorough study of refinery wastewaters is necessary. This study should be designed to afford meaningful statistical evaluation and should consider factors presumed to affect effluent quality and variability such as refinery geographic location, crude supply sources, size, complexity, and other appropriate factors to obtain representative sampling.
- Unless appropriate validation programs are completed, Priority Pollutant data must be viewed in terms of ranges rather than as specific values.

1.0 INTRODUCTION

In late 1976, the United States Environmental Protection Agency (EPA) commenced a two-phase program designed to determine the concentrations of 129 inorganic and organic Priority Pollutants (Table 1-1) in the wastewaters from industrial facilities contained in 21 broad categories. Phase I of the program consisted of a screening study aimed at defining the approximate concentrations of the Priority Pollutants in effluents. Under Phase II, the EPA intended to conduct a verification study designed to confirm the concentrations of the Priority Pollutants in effluents. Under Phase II, the EPA proposes to use the information derived from this screening study to provide a data base necessary for the development of Priority Pollutant limitations. No verification study has been announced.

The petroleum refining industry was included in the EPA Priority Pollutants study. Therefore, the American Petroleum Institute (API) formed an Analytical Systems Task Force (W-22) to conduct an independent program that would parallel the EPA screening study. In Phase I, the R.S. Kerr Laboratories (RSKERL) of the EPA collected samples from 12 refineries. An additional five refineries were later included and were sampled by Ryckman, Edgerly, Tomlinson and Associates (RETA) and Burns and Roe personnel. The objectives of the API program included the development of an independent Priority Pollutants data base and the evaluation of sampling and analytical procedures employed by the EPA. In order to provide the needed support for the study, the API contracted with Radian Corporation and Exxon Research and Engineering Company (Exxon R & E). The sampling effort was conducted by Exxon R & E and API member companies, while the analytical support was provided by Radian, Exxon R & E and various API member companies and independent contractors.

TABLE 1-1. PRIORITY POLLUTANTS

<u>Compound Name</u>	
1.	*Acenaphthene
2.	*Acrolein
3.	*Acrylonitrile
4.	*Benzene
5.	*Benzidene
6.	*Carbon tetrachloride (Tetrachloromethane)
	<u>*Chlorinated benzenes</u> (other than
	dichlorobenzenes)
7.	Chlorobenzene
8.	1,2,4-Trichlorobenzene
9.	Hexachlorobenzene
	<u>*Chlorinated ethanes</u> (including 1,2-Dichloroethane,
	1,1,1-Trichloroethane and Hexachloroethane)
10.	1,2-Dichloroethane
11.	1,1,1-Trichloroethane
12.	Hexachloroethane
13.	1,1-Dichloroethane
14.	1,1,2-Trichloroethane
15.	1,1,2,2-Tetrachloroethane
16.	Chloroethane
	<u>*Chloroalkyl ethers</u> (chloromethyl, chloroethyl
	and mixed ethers)
17.	bis(Chloromethyl) ether
18.	bis(2-Chloroethyl) ether
19.	2-Chloroethyl vinyl ether (mixed)
	<u>*Chlorinated naphthalene</u>
20.	2-Chloronaphthalene
	<u>*Chlorinated phenols</u> (other than those listed
	elsewhere; includes trichlorophenols and
	chlorinated cresols)
21.	2,4,6-Trichlorophenol
22.	Parachlorometa cresol
23.	*Chloroform (Trichloromethane)
24.	*2-Chlorophenol
	<u>*Dichlorobenzenes</u>
25.	1,2-Dichlorobenzene
26.	1,3-Dichlorobenzene
27.	1,4-Dichlorobenzene
	<u>*Dichlorobenzidine</u>
28.	3,3'-Dichlorobenzidine
	<u>*Dichloroethylenes</u> (1,1-Dichloroethylene and
	1,2-Dichloroethylene)
29.	1,1-Dichloroethylene
30.	1,2-trans-Dichloroethylene

Table 1-1 continued

- 31. *2,4-Dichlorophenol
- *Dichloropropane and Dichloropropene
- 32. 1,2-Dichloropropane
- 33. 1,2-Dichloropropylene (1,3-Dichloropropene)
- 34. *2,4-Dimethylphenol
- *Dinitrotoluenes
- 35. 2,4-Dinitrotoluene
- 36. 2,6-Dinitrotoluene
- 37. *1,2-Diphenylhydrazine
- 38. *Ethylbenzene
- 39. *Fluoranthene
- *Haloethers (other than those listed elsewhere)
- 40. 4-Chlorophenyl phenyl ether
- 41. 4-Bromophenyl phenyl ether
- 42. bis(2-Chloroisopropyl) ether
- 43. bis(2-Chloroethoxy) methane
- *Halomethanes (other than those listed elsewhere)
- 44. Methylene chloride (Dichloromethane)
- 45. Methyl chloride (Chloromethane)
- 46. Methyl bromide (Bromomethane)
- 47. Bromoform (Tribromomethane)
- 48. Dichlorobromomethane
- 49. Trichlorofluoromethane
- 50. Dichlorodifluoromethane
- 51. Chlorodibromomethane
- 52. *Hexachlorobutadiene
- 53. *Hexachlorocyclopentadiene
- 54. *Isophorone
- 55. *Naphthalene
- 56. *Nitrobenzene
- *Nitrophenols (including 2,4-Dinitrophenol and
 Dinitrocresol)
- 57. 2-Nitrophenol
- 58. 4-Nitrophenol
- 59. *2,4-Dinitrophenol
- 60. 4,6-Dinitro-o-cresol
- *Nitrosoamines
- 61. N-Nitrosodimethylamine
- 62. N-Nitrosodiphenylamine
- 63. N-Nitrosodi-n-propylamine
- 64. *Pentachlorophenol
- 65. *Phenol
- *Phthalate esters
- 66. bis(2-Ethylhexyl) phthalate
- 67. Butyl benzyl phthalate
- 68. Di-n-butyl phthalate
- 69. Di-n-octyl phthalate¹
- 70. Diethyl phthalate
- 71. Dimethyl phthalate

Table 1-1 continued

	<u>*Polynuclear aromatic hydrocarbons</u>
72.	Benzo(a)anthracene (1,2-Benzanthracene)
73.	Benzo(a)pyrene (3,4-Benzopyrene)
74.	Benzo(b)fluoranthene (3,4-Benzofluoranthene)
75.	Benzo(k)fluoranthene (11,12-Benzofluoranthene)
76.	Chrysene
77.	Acenaphthylene
78.	Anthracene
79.	Benzo(g,h,i)perylene (1,12-Benzoperylene)
80.	Fluorene
81.	Phenanthrene
82.	Dibenzo(a,h)anthracene (1,2,5,6-Dibenzanthracene)
83.	Indeno(1,2,3-c,d)pyrene (2,3-o-phenylpyrene)
84.	Pyrene
85.	*Tetrachloroethylene (1,1,2,2-Tetrachloroethene)
86.	*Toluene
87.	*Trichloroethylene
88.	*Vinyl chloride (Chloroethylene)
	<u>Pesticides and Metabolites</u>
89.	*Aldrin ³
90.	*Dieldrin ³
91.	*Chlordane (technical mixture and metabolites)
	<u>*DDT and Metabolites</u>
92.	4,4'-DDT ³
93.	4,4'-DDE (p,p'DDX) ³
94.	4,4'-DDD (p,p'TDE) ³
	<u>*Endosulfan and Metabolites</u>
95.	α -Endosulfan-Alpha ³
96.	β -Endosulfan-Beta ³
97.	Endosulfan sulfate ³
	<u>*Endrin and Metabolites</u>
98.	Endrin ³
99.	Endrin aldehyde ³
	<u>*Heptachlor and Metabolites</u>
100.	Heptachlor ³
101.	Heptachlor epoxide ³
	<u>*Hexachlorocyclohexane (all isomers)</u>
102.	α -BHC-Alpha ³
103.	β -BHC-Beta ³
104.	γ -BHC (Lindane)-Gamma ³
105.	Δ -BHC-Delta ³
	<u>*Polychlorinated biphenyls (PCB's)</u>
106.	PCB-1242 (Arochlor 1242) ^{1,3}
107.	PCB-1254 (Arochlor 1254) ^{1,3}
108.	PCB-1221 (Arochlor 1221) ^{1,3}
109.	PCB-1232 (Arochlor 1232) ^{1,3}
110.	PCB-1248 (Arochlor 1248) ^{1,3}
111.	PCB-1260 (Arochlor 1260) ^{1,3}
112.	PCB-1016 (Arochlor 1016) ^{1,3}

Table 1-1 continued

113.	*Toxaphene
114.	*Antimony (Total)
115.	*Arsenic (Total)
116.	*Asbestos (Fibrous) ²
117.	*Beryllium (Total)
118.	*Cadmium (Total)
119.	*Chromium (Total)
120.	*Copper (Total)
121.	*Cyanide (Total) ²
122.	*Lead (Total)
123.	*Mercury (Total)
124.	*Nickel (Total)
125.	*Selenium (Total)
126.	*Silver (Total)
127.	*Thallium (Total)
128.	*Zinc (Total)
129.	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

*Specific compounds and chemical classes as listed in the Consent Decree (8ERC 2120).

¹Not included in the list at the start of the refining screening study.

²Not included in this report. Cyanide data will be included in a future report. Asbestos analyses were not conducted due to limitations in the available analytical procedures.

³API analyses conducted by GC/MS the base/neutral organic extractable fraction.

**RADIAN
CORPORATION**2.0 WASTEWATER SAMPLING

The initial EPA refinery sampling effort was directed toward a screening survey of 12 refineries during March-July, 1977. An additional five refineries were sampled during April-June, 1977. At certain sites, Exxon R & E and individual company personnel obtained duplicate samples in parallel with EPA sampling teams for subsequent analysis by API contractors. The EPA provided duplicate samples to refineries where requested. Some selected EPA duplicate samples, were subsequently analyzed by some refinery personnel and/or API contractors. The various groups involved in the sampling are identified in Table 2-1. Both API and Burns and Roe (EPA contractor) site designations are included in this table.

Sample collection points at the 17 refineries included intake water, wastewater feed to biotreatment, and final effluent. For the first 12 refineries, EPA obtained composite samples for trace elements and liquid/liquid extractable organics by taking approximately 450-ml aliquots every three hours over a 24-hour period. EPA sampling at the last five refineries employed automatic sampling device that delivered 3.6 liters of sample over a 24-hour period. Grab samples for volatile organics were obtained during the last compositing period of each 24-hour sampling period. Sample sets were obtained for volatile organics, non-volatile organics, and trace elements over three consecutive 24-hour periods. In selected cases 72-hour composites were prepared from the individual 24-hour samples. Grab samples for asbestos analysis were also taken by EPA.

The EPA sampling effort, conducted by RSKERL and Burns and Roe personnel, used the EPA sampling and preservation procedure as outlined in the March, 1977, protocol. However, several notable exceptions occurred. These included: the addition of

TABLE 2-1. SAMPLING PARTICIPANTS IN THE
PETROLEUM REFINING SCREENING SURVEY

<u>API Site Designation</u>	<u>Burns & Roe Site Designation</u>	<u>API Sampling</u>	<u>EPA Sampling</u>
1	L	--	RSKERL ¹ /Burns & Roe
2	N	Exxon R & E	RSKERL/Burns & Roe
3	A	--	RSKERL/Burns & Roe
4	D	--	RSKERL/Burns & Roe
5	E	--	RSKERL/Burns & Roe
6	F	--	RSKERL/Burns & Roe
7	P	Exxon R & E	RSKERL/Burns & Roe
8	O	--	RSKERL/Burns & Roe
9	B	Exxon R & E	RSKERL/Burns & Roe
10	H	--	RSKERL/Burns & Roe
11	K	--	RSKERL/Burns & Roe
12	M	--	RSKERL/Burns & Roe
13	C	--	RETA ² /Burns & Roe
14	G	--	RETA/Burns & Roe
15	I	--	RETA/Burns & Roe
16	J	--	RETA/Burns & Roe
17	Q	--	RETA/Burns & Roe

¹R.S. Kerr Environmental Research Laboratory.¹¹

²Ryckman, Edgerly, Tomlinson and Associates.¹¹

trace element samples to bottles previously charged with nitric acid preservative; the collection of volatile organic samples and blanks with head space volumes; the collection of trace element samples in containers that were not previously acid-washed; and the collection of samples by manual grab and composite techniques rather than with an automatic sampler. Sampling at the last five refineries followed the revised April, 1977, protocol utilizing automatic sampling techniques.

3.0 SAMPLE ANALYSES

Samples obtained by Exxon R & E, other companies and EPA were analyzed during the API study for the inorganic and organic Priority Pollutants. A summary of the API and EPA participants who conducted analyses is presented in Table 3-1.

In general all participants employed the EPA analytical protocol dated March, 1977, for the analyses. Analytical deviations from the EPA protocol are listed in the following table.

<u>Participant</u>	<u>Parameter</u>	<u>Method</u>
Radian Corp.	Trace Elements	AA, Digestion for Total Elements
Radian Corp.	PCBs & Pesticides	GC/MS
Exxon R & E	Volatile Organohalides	Bellar-GC/microcoulometric (1)
Exxon R & E	Volatile Aromatic Hydrocarbons	Grob - GC/FID (4, 5, and 6)
Exxon R & E	PNAs	GC/UV (2, 3, 7, and 9)
Exxon R & E	Selected Organics	Column Chromatography followed by GC, MS, or IR (10)

Specificity and/or lower limits of detection for each of the deviating methods are equivalent to or better than those for the methods outlined in the EPA protocol. A detailed description of all analytical techniques employed is provided in Appendix A.

In addition to the analyses of collected wastewater samples, the API study included special analyses to define the reliability of the EPA protocol. These included duplicate and spiked samples. A description of this work is included in Appendix A.

TABLE 3-1. ANALYTICAL PARTICIPANTS IN THE PETROLEUM REFINING SCREENING SURVEY

EPA FUNDED				
Laboratory	Refineries	Volatile Organics	Liquid/Liquid Extractable Organics	Trace Elements
RSKERL	1-12			X
RETA	13-17	X	X	X
MRI	1-6	X	X	
NUS	7-12	X	X	
API OR COMPANY FUNDED				
Exxon R & E	2,7,9	X	X	X
Radian	2,7,9,11	X	X	X
Environmental Analysis, Inc. Company	4			X
Spectrix Company	5	X	X	X
Company	5	X	X	
Company	6	X	X	X
Company	7	X	X	X
Edna Wood Laboratories Company	8			X
Company	11			X
Company	16			X

4.0 ANALYTICAL RESULTS

The reliability and ultimate usefulness of analytical data depend on several field and laboratory factors. They include: the measures taken to avoid field and laboratory sample contamination, the methods utilized for the preservation and transportation of samples, the adequacy of the methods applied for the isolation and concentration of the species and the accuracy of the techniques applied for the final analytical measurements. Therefore, unless these factors are fully defined for a given sampling and analytical protocol all analytical results must be viewed with discretion.

The adequacy of the EPA sampling and analytical protocol, which was employed, with the exception of the deviations outlined in Section 3.0, in the API study has not been fully defined. Therefore, all numerical analytical data presented must be viewed as being approximate rather than absolute values.

The analytical results obtained from the API analyses of refinery wastewater samples and the data gathered from the special analytical studies are summarized in the following subsections. EPA data are provided as a comparison.

The elemental Priority Pollutants were also determined by API participants and the EPA in the intake waters, wastewater feeds to biotreatment and final effluents. Nine petroleum refining facilities were included in the API study, while EPA data are available from 17 facilities¹¹. The API and EPA data are summarized in Tables 4-7 through 4-12.

A detailed listing of all organic and elemental Priority Pollutant data generated is given in Appendix A. The volatile

organic pollutant data found in Appendix A represent sample concentrations that are uncorrected with respect to the field sample blanks. The certain instances it was judged highly probable that the field blanks had been contaminated; therefore, correction of the sample concentration was not possible. For example, blank water from Refinery 9 was found to contain methylene chloride at 63 ppb, a value five times greater than that found at any sampling point. Methylene chloride contamination of field blanks was also suspected for samples obtained from Refineries 2, 7, and 11. Examination of the analytical data for the liquid/liquid extractables from the 17 refineries also indicates that contamination with bis(2-ethylhexyl)phthalate was experienced at refineries 13-17.

4.1 Refinery Wastewater

Analyses of wastewater samples for the inorganic and organic priority pollutants were conducted by the API contractors and individual company personnel. Priority Pollutants were determined by API participants in the intake waters, wastewater feeds to biotreatment, and final effluents.

A total of 36 organics and 13 elemental Priority Pollutants were identified by the API study of six refinery effluent streams. Concentrations ranged from <1 to 60 ppb for organics and <1 to 1100 ppb for trace elements. In no case were all identified pollutants found at each refinery.

In the wastewater feed streams to the biological treatment facilities, 45 organics ranging from <1 to 44,000 ppb and 13 trace elements ranging from <1 to 9,600 ppb were found.

Corresponding refinery intake water samples were found to contain 40 organics ranging from <1 to 150 ppb and 13 trace

TABLE 4-1. FREQUENCY AND CONCENTRATION RANGE OF
ORGANIC PRIORITY POLLUTANTS IN REFINERY INTAKE WATERS¹
API DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
Chloromethane ⁴	1	D(<.5)	D(<.5)	1
Methylene chloride ⁴	6	0.4	80	18
1,1-Dichloroethane ⁴	1	4	7.6	3
Trans-1,2,-dichloroethylene	1	1	4	3
Chloroform ⁴	4	D(<.5)	37	8
1,2-Dichloroethane ⁴	2	D(<.5)	3.5	4
1,1,1-Trichloroethane ⁴	5	1	58	10
Carbon Tetrachloride ⁴	1	0.5	2	3
Bromodichloromethane ⁴	1	3	15	3
1,2-Dichloropropane ⁴	1	D(<1)	1	2
Trichloroethylene	3	D(<1)	1	5
Benzene ⁴	6	D(<1)	40	13
1,1,2,2-Tetrachloroethene	1	1	1	1
Toluene ⁴	6	D(<1)	15	13
Ethylbenzene ⁴	6	D(<.5)	D(<20)	14
Naphthalene ⁴	3	D(<2)	D(<5)	3
Acenaphthylene ⁴	2	D(<2)	D(<40)	2
Acenaphthene ⁴	3	D(<2)	D(<40)	3
Phenanthrene/Anthracene ⁵	2	3	146	2
Diethyl phthalate	4	2.9	20	4
Fluoranthene	1	3.4	3.4	1
Pyrene	3	0.2	65	3
Di-n-butyl phthalate	4	1	20	4
Butyl benzyl phthalate	1	2	2	1
Chrysene/Benz(a)anthracene ⁵	1	76	76	1
Chrysene	1	0.3	0.3	1
Bis(2-ethylhexyl)phthalate	5	D(<1)	16	5
Benz(a)Anthracene	1	0.1	0.1	1
1-Benzo(b)/(k)fluoranthene ⁵	1	3.2	3.2	1
Benzo(a)pyrene ⁴	4	0.03	8	4
Indeno(1,2,3-c,d)pyrene	1	0.4	0.4	1
Benzo(g,h,i)perylene	1	2.5	2.5	1
Phenol	2	D(<1)	4	2
2,4-Dimethylphenol	1	5	5	1
2-Nitrophenol	2	D(<1)	D(<1)	2
2,4-Dichlorophenol	1	D(<1)	D(<1)	1
4-Nitrophenol	1	4	4	1
4,6-Dinitro-o-cresol	2	D(<1)	D(<1)	2
Pentachlorophenol	1	D(<1)	D(<1)	1

NOTES:

D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

¹Organic Priority Pollutant data from six refineries only as summarized below:

Company	5, 6, 7
Radian	2, 7, 9, .11
Exxon R&E	2, 7, 9
Other	5

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Does not include duplicate determinations.

⁴Some values for this compound were obtained by a method other than the EPA Protocol.

⁵Combined value for these unresolved isomers.

TABLE 4-2. FREQUENCY AND CONCENTRATION RANGE OF ORGANIC PRIORITY POLLUTANTS IN REFINERY WASTEWATER FEEDS TO BIOTREATMENT¹
API DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
✓ Chloromethane ⁴	1	17000	17000	1
✓ Methylene chloride ⁴	5	D(<.5)	300	23
1,1-Dichloroethane ⁴	1	D(<1)	D(<1)	3
✓ 1,1-Dichloroethylene	1	10	10	1
✓ trans-1,2-Dichloroethylene	1	1	1	1
✓ Chloroform ⁴	4	0.9	30	18
✓ 1,2-Dichloroethane ⁴	3	D(<.5)	51	9
1,1,1-Trichloroethane ⁴	3	D(<1)	15	8
Carbon tetrachloride ⁴	1	D(<1)	2	4
✓ Bromodichloromethane	1	D(<1)	D(<1)	3
1,2-Dichloropropane	1	D(<1)	40	2
trans-1,3-Dichloropropene	2	2	3	2
✓ Trichloroethylene	4	D(<1)	5	8
cis-1,3-Dichloropropene	1	20	20	1
✓ Benzene ⁴	5	D(<10)	31000	19
Bromoform	1	D(<1)	D(<1)	2
1,1,2,2-Tetrachloroethene ⁴	2	D(<.5)	6	7
✓ 1,1,2,2-Tetrachloroethane	1	2	2	2
✓ Toluene ⁴	5	40	44000	19
✓ Ethylbenzene ⁴	4	1	460	17
✓ Naphthalene ⁴	4	22	5200	9
Acenaphthylene ⁴	2	D(<40)	200	3
Acenaphthene ⁴	2	9	200	4
✓ Fluorene ⁴	4	2.9	62	6
Phenanthrene/Anthracene ⁵	5	2	110	6
✓ Phenanthrene ⁴	3	2.7	32	3
✓ Anthracene ⁴	1	0.1	0.1	1
✓ Diethyl phthalate	4	2	60	4
✓ Fluoranthene ⁴	5	0.04	23	10
✓ Pyrene ⁴	6	0.06	6.9	12
Di-n-butyl phthalate	3	D(<1)	45	4
Chrysene/Benz(a)anthracene ⁵	4	0.3	16	4
✓ Chrysene ⁴	3	0.3	9	4
✓ Benz(a)anthracene ⁴	3	0.1	1.4	3
Butyl benzyl phthalate	1	6	6	1
✓ bis(2-Ethylhexyl) phthalate	4	1.8	6	4
Benzo(b)/(k)fluoranthene ⁵	1	0.9	0.9	1
Benzo(b)fluoranthene ⁴	1	0.3	0.3	1
Benzo(k)fluoranthene ⁴	1	0.3	0.3	1
✓ Benzo(a)pyrene ⁴	4	0.02	7.8	6
Indeno(1,2,3-c,d)pyrene ⁴	2	0.02	0.5	2
✓ Dibenzo(a,h)anthracene ⁴	2	0.07	0.4	2
✓ Benzo(g,h,i)perylene ⁴	4	0.2	1.2	4
✓ Phenol ⁴	6	6	26000	10
✓ 2,4-Dimethylphenol	5	8	3000	7
2-Chlorophenol	1	1	1	1
2,4-Dichlorophenol	1	D(<1)	D(<1)	1
✓ p-Chloro-m-cresol	1	D(<1)	D(<1)	1
Pentachlorophenol	1	D(<1)	D(<1)	1

NOTES:

D(X) - Compound was detected as some concentration less than X, but the concentration could not be quantified.

¹Organic Priority Pollutant data from six refineries only as summarized below:

Company	5, 6, 7
Radian	2, 7, 9, 11
Exxon R&E	2, 7, 9
Other	5

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Does not include duplicate determinations.

⁴Some values for this compound were obtained by a method other than the EPA Protocol.

⁵Combined value for these unresolved isomers.

TABLE 4-3. FREQUENCY AND CONCENTRATION RANGE OF ORGANIC
PRIORITY POLLUTANTS IN REFINERY FINAL EFFLUENTS¹
API DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
Chloromethane ⁴	1	D(<.5)	D(<.5)	1
Methylene chloride ⁴	5	D(<.5)	55	16
1,1-Dichloroethylene ⁴	1	D(<1)	10	3
1,1-Dichloroethane	1	D(<1)	D(<1)	3
Chloroform ⁴	4	D(<.5)	16	12
1,2-Dichloroethane ⁴	3	D(<.5)	D(<1)	7
1,1,1-Trichloroethane ⁴	2	D(<1)	3	6
Carbon tetrachloride ⁴	1	D(<1)	D(<1)	3
Bromodichloromethane	1	D(<1)	D(<1)	3
1,2-Dichloropropane ⁴	1	D(<1)	5	2
trans-1,3-Dichloropropene ⁴	1	1	1	1
Trichloroethylene	4	D(<1)	3	7
Benzene ⁴	5	D(<1)	30	12
Toluene ⁴	5	D(<1)	60	13
Ethylbenzene ⁴	4	D(<1)	D(<40)	12
Naphthalene ⁴	3	0.1	50	3
Acenaphthylene ⁴	2	D(<10)	D(<10)	2
Acenaphthene ⁴	2	D(<10)	40	2
Fluorene	1	0.6	0.6	1
Phenanthrene/Anthracene ⁵	1	0.4	0.4	1
Diethyl phthalate	3	4.3	7	3
Fluoranthene ⁴	3	0.1	0.3	3
Pyrene ⁴	4	D(<.1)	1.9	7
Di-n-butyl phthalate	4	D(<1)	32	4
Chrysene/Benz(a)anthracene ⁵	3	0.1	1.4	3
Chrysene ⁴	1	0.2	0.2	1
Benz(a)anthracene ⁴	2	0.01	0.08	2
bis(2-Ethylhexyl) phthalate	4	2	15	4
Benzo(b)/(k)fluoranthene ⁵	1	0.2	0.2	1
Benzo(a)pyrene ⁴	3	0.08	0.9	5
Benzo(g,h,i)perylene	1	0.2	0.2	1
Phenol	2	1.9	59	2
2,4-Dimethylphenol	3	2.2	8	3
p-Chloro-m-cresol	1	0.2	0.2	1
4,6-Dinitro-o-cresol	1	D(<1)	D(<1)	1

NOTES:

D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

¹Organic Priority Pollutant data from six refineries only as summarized below:

Company	5, 6, 7
Radian	2, 7, 9, 11
Exxon R&E	2, 7, 9
Other	5

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Does not include duplicate determinations.

⁴Some values for this compound were obtained by a method other than the EPA Protocol.

⁵Combined value for these unresolved isomers.

TABLE 4-4. FREQUENCY AND CONCENTRATION RANGE OF ORGANIC
PRIORITY POLLUTANTS IN REFINERY INTAKE WATERS¹
EPA DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values
		Minimum Value	Maximum Value	
Methylene chloride	5	D(<10)	G(100)	5
Chloroform	1	70	70	1
1,1,1-Trichloroethane	2	D(<10)	G(50)	2
Carbon tetrachloride	1	G(50)	G(50)	1
Trichloroethylene	1	20	20	1
1,1,2,2-Tetrachloroethene	1	50	50	1
1,4-Dichlorobenzene	1	D(<.5)	D(<.5)	1
1,2-Dichlorobenzene	1	D(<.5)	D(<.5)	1
Naphthalene	2	1	1.8	2
Acenaphthylene	1	0.2	0.2	1
Acenaphthene	2	1.8	29	2
Fluorene	1	1	1	1
Phenanthrene/Anthracene ³	5	D(<.1)	160	5
Dimethylphthalate	1	20	20	1
Diethylphthalate	1	D(<10)	D(<10)	1
Fluoranthene	3	D(<.2)	29	3
Pyrene	3	D(<.1)	143	3
Di-n-butyl phthalate	4	0.2	30	4
Chrysene/Benz(a)anthracene ³	1	49	49	1
bis(2-Ethylhexyl)phthalate	5	110	1100	5
Benzo(a)pyrene	1	33	33	1
Phenol	2	10	10	2

NOTES:

D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

¹Results from Refineries 1, 2, 3, 4, 5, 6, 13, 14, 15, 16, and 17, except volatile organics from Refineries 1, 2, 3, 4, 5, and 6 only.

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Combined value for these unresolved isomers.

TABLE 4-5. FREQUENCY AND CONCENTRATION RANGE OF ORGANIC PRIORITY POLLUTANTS IN REFINERY WASTEWATER FEEDS TO BIOTREATMENT¹
EPA DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values
		Minimum Value	Maximum Value	
Chloromethane	1	G(100)	G(100)	1
Bromomethane	1	D(<10)	D(<10)	1
Methylene chloride	5	10	G(100)	7
trans-1,2-Dichloroethylene	1	20	20	1
Chloroform	3	D(<5)	15	6
1,2-Dichloroethane	1	D(<10)	D(<10)	1
Bromodichloromethane	3	D(<10)	D(<10)	3
1,2-Dichloropropane	2	D(<10)	D(<10)	2
Chlorodibromomethane	1	107	107	1
Benzene	5	90	G(100)	7
1,1,2,2-Tetrachloroethene	1	G(50)	G(50)	1
Toluene	5	G(100)	G(100)	7
Ethylbenzene	5	20	G(100)	7
Acrolein	1	D(<10)	D(<10)	1
Naphthalene	8	27	1100	11
Acenaphthylene	2	4	87	2
Acenaphthene	5	37	3000	5
Fluorene	3	80	304	4
N-Nitroso diphenylamine	1	D(<10)	D(<10)	1
Phenanthrene/Anthracene ³	9	0.6	1100	13
Diethyl phthalate	1	12	12	1
Fluoranthene/Pyrene	2	20	40	3
Fluoranthene	3	2.5	8.5	3
Pyrene	6	0.7	20	7
Di-n-butyl phthalate	1	1.3	1.3	1
Chrysene/Benz(a)anthracene ³	3	6.5	50	6
Chrysene	4	0.1	20	6
bis(2-Ethylhexyl)phthalate	5	50	1100	11
Benzo(a)pyrene	1	9.5	9.5	1
Phenol	9	13	16000	15
2,4-Dimethylphenol	4	71	750	7
p-Chloro-m-cresol	1	10	10	1
Pentachlorophenol	1	850	850	1

NOTES:

D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

¹Results from Refineries 1, 2, 3, 4, 5, 6, 13, 14, 15, 16, and 17, except volatile organics from Refineries 1, 2, 3, 4, 5, and 6 only.

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Combined value for these unresolved isomers.

TABLE 4-6. FREQUENCY AND CONCENTRATION RANGE OF ORGANIC
PRIORITY POLLUTANTS IN REFINERY FINAL EFFLUENTS¹
EPA DATA

Compound	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values
		Minimum Value	Maximum Value	
Methylene chloride	4	D(<10)	60	4
Chloroform	1	D(<5)	D(<5)	1
Benzene	1	6	6	1
1,1,2,2-Tetrachloroethene	1	D(<10)	D(<10)	1
Toluene	1	35	35	1
Naphthalene	1	0.1	0.1	1
Acenaphthene	1	6	6	1
Phenanthrene/Anthracene ³	2	0.8	D(<10)	2
Dimethylphthalate	1	3	3	1
Diethylphthalate	2	D(<10)	30	2
Fluoranthene	1	D(<.1)	D(<.1)	1
Pyrene	3	D(<.1)	7	3
Chrysene/Benz(a)anthracene ³	1	0.8	0.8	1
Chrysene	3	D(<.1)	1.4	3
bis(2-Ethylhexyl) phthalate	5	190	2000	5
Benzo(a)pyrene	2	1.3	2.9	2

NOTES:

D(X) - Compound was detected at some concentration less than X, but the concentration could not be quantified.

G(X) - Greater than the value X.

¹Results from Refineries 1, 2, 3, 4, 5, 6, 13, 14, 15, 16, and 17, except volatile organics from Refineries 1, 2, 3, 4, 5, and 6 only.

²Number of refineries where the compound was detected by one or more of the reporting laboratories.

³Combined value for these unresolved isomers.

TABLE 4-7. FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY INTAKE WATERS¹
API DATA

Element	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
Zinc	7	10	230	14
Chromium	6	2	1,300	14
Copper	6	20	290	11
Lead	7	1.2	30	12
Beryllium	2	.4	1.1	4
Antimony	5	.3	30	9
Thallium	1	15	15	1
Nickel	6	1	70	10
Arsenic	4	10	22	6
Selenium	5	3	19	9
Silver	4	0.1	9	5
Cadmium	4	.2	4	6
Mercury	5	.13	.4	5

¹Data from nine refineries only; reporting laboratories summarized below:

Company: 2*, 4*, 5, 6, 7, 8, 9, 11, 16* (*Chromium only)

Radian : 2, 7, 9

²Number of refineries where the element was detected by one or more of the laboratories.

³Does not include duplicate determinations.

TABLE 4-8. FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY WASTEWATER FEEDS TO BIOTREATMENT¹
API DATA

Element	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
Zinc	7	12	9,600	15
Chromium	9	23	1,300	28
Copper	6	5	460	13
Lead	7	4	75	15
Beryllium	3	.3	2.2	7
Antimony	5	.4	240	11
Thallium	4	1	190	9
Nickel	6	1.5	120	12
Arsenic	6	6	50	10
Selenium	5	8	35	11
Silver	4	0.2	160	6
Cadmium	4	0.6	13	7
Mercury	5	0.9	0.8	6

¹Data from nine refineries only; reporting laboratories summarized below:

Company: 2*, 4*, 5, 6, 7, 8, 9, 11, 16* (*Chromium only)

Radian: 2, 7, 9

²Number of refineries where the element was detected by one or more of the reporting laboratories.

³Does not include duplicate determinations.

TABLE 4-9. FREQUENCY AND CONCENTRATION RANGE
OF TRACE ELEMENTS IN REFINERY FINAL EFFLUENTS¹
API DATA

Element	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values ³
		Minimum Value	Maximum Value	
Zinc	7	10	190	14
Chromium	9	11	1,100	21
Copper	6	3	130	12
Lead	7	2	46	11
Beryllium	3	0.2	2.1	6
Antimony	5	5.3	190	10
Thallium	3	4.8	9.5	4
Nickel	6	0.9	82	12
Arsenic	5	2	70	8
Selenium	5	9	74	9
Silver	4	0.8	170	5
Cadmium	4	0.8	16	6
Mercury	5	0.7	0.8	5

¹Data from nine refineries only; reporting laboratories summarized below:

Company: 2*, 4*, 5, 6, 7, 8, 9, 11, 16* (*Chromium only)
Radian: 2, 7, 9

²Number of refineries where the element was detected by one or more of the reporting laboratories.

³Does not include duplicate determinations.

TABLE 4-10. FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY INTAKE WATERS¹
EPA DATA

Element	Frequency of Detection ²	Concentration Range, ppb		Number of Reported Values
		Minimum Value	Maximum Value	
Zinc	15	15	120	15
Chromium	13	1	60	13
Copper	10	1	210	10
Lead	8	1	40	8
Antimony	1	1	1	1
Thallium	1	3	3	1
Nickel	5	1	58	5
Arsenic	5	3	27	5
Selenium	6	2	13	11
Cadmium	1	2	2	1
Mercury	5	0.1	6	13

¹RSKERL and RETA data from all seventeen refineries.

²Number of refineries where the element was detected by one or more of the reporting laboratories.

TABLE 4-11. FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY WASTEWATER FEEDS TO BIOTREATMENT¹
EPA DATA

Element	Frequency of Detection ²	Concentration, ppb		Number of Reported Values
		Minimum Value	Maximum Value	
Zinc	17	24	4,800	58
Chromium	15	1	4,900	53
Copper	14	2	500	30
Lead	10	2	2,000	27
Antimony	4	1	360	4
Thallium	1	3	6	4
Nickel	10	1	77	15
Arsenic	7	3	480	16
Selenium	5	4	31	44
Silver	1	1	2	2
Cadmium	3	3	16	6
Mercury	5	0.1	9	25

¹RSKERL and RETA data from all seventeen refineries.

²Number of refineries where the element was detected by one or more of the reporting laboratories.

TABLE 4-12. FREQUENCY AND CONCENTRATION RANGE OF
TRACE ELEMENTS IN REFINERY FINAL EFFLUENTS¹
EPA DATA

Element	Frequency of Detection ²	Concentration, ppb		Number Reported Results
		Minimum Value	Maximum Value	
Zinc	16	25	700	22
Chromium	15	1	1,000	18
Copper	10	3	180	10
Lead	5	2	58	8
Antimony	3	1	370	3
Thallium	2	3	12	5
Nickel	5	3	58	8
Arsenic	4	5	900	7
Selenium	7	3	32	21
Silver	1	15	15	1
Cadmium	2	1	5	2
Mercury	5	0.5	6	10

¹RSKERL and RETA data from all seventeen refineries.

²Number of refineries where the element was detected by one or more of the reporting laboratories.

metals ranging from <1 to 1300 ppb. The organics in the intake waters occurred infrequently among the refineries and may not be representative of waters in all geographic areas where refineries are located.

Eighteen organics and 12 elemental Priority Pollutants were identified in 17 refinery effluents by EPA. Concentrations ranged from <1 to 2000 ppb for organics and from <1 to 1000 ppb for trace elements. EPA found 33 organics and 12 trace elements in the wastewater feeds to biotreatment. In these streams, organics ranged from <1 to 16,000 ppb, while trace elements ranged from <1 to 4900 ppb. Intake water analyses by EPA gave concentrations of 24 organics ranging from <1 to 1100 ppb and 10 trace elements ranging from <1 to 210 ppb.

4.2 Special Analytical Studies

Previously analyzed final effluent samples from Refineries 7 and 9 were spiked with PNAs, phthalate esters, and phenols to determine the recoveries of these classes of materials. The spiked samples were solvent extracted and analyzed according to the EPA Protocol by Radian and data from these studies are summarized below.

<u>Species</u>	<u>Concentration Range</u>	<u>Range of Recovery</u>
PNAs	5 - 7 ppb	46 - 70%
PNAs	18 - 33 ppb	67 - 84%
PNAs	54 - 220 ppb	19 - 112%
Phthalate Esters	6 - 25 ppb	4 - 7%
Phthalate Esters	140 - 610 ppb	41 - 420%
Phenols	4 - 9 ppb	68 - 92%
Phenols	14 - 29 ppb	55 - 93%
Phenols	84 - 330 ppb	25 - 89%

In addition, previously analyzed final effluent samples from Refineries 2, 7, and 9 were spiked with the elemental Priority Pollutants at levels from approximately 0.05 ppb to 500 ppb and reanalyzed. Average recovery ranged from 72% to 139%.

A single interlaboratory study was conducted on a spiked final effluent from Refinery 7. Midwest Research Institute (MRI) analyzed the same spiked effluent extract according to the EPA Protocol after an elapsed time of approximately three months. Analytical data from this study are summarized below.

<u>Compound</u>	<u>Calculated* Concentration (ppb)</u>	<u>Radian (ppb)</u>	<u>MRI (ppb)</u>
Naphthalene	74	19	N.D.
Fluorene	54	51	66
Phenanthrene/Anthracene**	78	88	40
Pyrene	33	24	4
Di-n-butyl phthalate	140	420	194
bis(2-ethylhexyl) phthalate	220	190	69

(N.D. = Not detected.)

*Concentration in sample based on the first analysis by Radian plus the concentration of the spike

**Sample spiked with phenanthrene.

Complete analytical data obtained from the studies are presented in Appendix A.

5.0 DISCUSSION OF ANALYTICAL DATA

In a data base of this type and importance, it is essential to evaluate the quality of the data developed. Analyses of parallel samples at several refineries make it possible to compare the data from different laboratories to obtain an indication of the reproducibility of the sampling and analytical methods employed. The special studies discussed in Section 4.2 can also be used to evaluate the quality of the data base.

However, these limited studies do not fully define the adequacy of the sampling and analytical protocol. Therefore, the analytical data must be viewed as approximate instead of exact and interpretations must be made with discretion. Factors that were used to judge the reliability of the data are discussed in detail in the Subsections below.

5.1 Interference and Contamination of the Samples

Field blanks were analyzed by the various laboratories as a check on potential contamination. A summary of the blank sample data is included in Appendix B. The analytical data indicate that many of the blanks were contaminated. Often there was a greater concentration of a component in the blank than in the samples associated with that blank. For example, blank water from Refinery 9 was found to contain methylene chloride at 63 ppb, a value five times greater than that found at any sampling point. This makes blank correction of sample concentrations impossible. The apparent case of contamination by the volatile compounds listed in Table B-2 forces one to question the concentrations of these compounds found in other samples at other sites.

5.2 Recoveries - Spiked Samples

The determination of recoveries from spiked samples provides an indication of the accuracy to be expected from the application of an analytical technique. As discussed in Section 4.2, five samples previously analyzed were spiked with various compounds in an attempt to determine the recoveries for samples analyzed. Data from Radian are reported in Section 4.2 and Appendix A. A statistical analysis of the trace element data is included in Appendix B, Table B-6.

The recoveries for PNAs are similar for all the compounds, ranging from 26% to 116% for spikes from 54 to 220 ppb, but declining significantly at concentrations below 30 ppb. For phenols the recoveries ranged from 41% to 90% for concentrations greater than 80 ppb. For the trace elements the recoveries ranged from 34% to 193% for the different species and were quite variable between samples. The EPA reported recovery studies for mercury show a range of 68% to 97% for samples spiked at 0.3 to 0.5 ppb. For phthalates, recoveries ranged from 4% to 300%.

A wide range of spiked sample recoveries indicates the possible inaccuracy of a given analytical protocol.

5.3 Repeatability of Analytical Methods - Duplicate Analyses

It is important to document the repeatability of the various test methods used to analyze the samples. The repeatability is a measure of the difference one might expect on a repeat analysis of the same sample by the same laboratory.

Appendix B, Table B-3, describes the results for duplicate analyses performed during this study for which some

quantitative data were reported. The percent difference between duplicates was quite variable, ranging from 0 to 105%. The median percent difference for the company data was 0% for the volatile organics and 14% for liquid/liquid extractable organics. The median percent difference for the volatile organics reported by Spectrix (Refinery 5) was 67%. The standard deviation of all API and company data averages about 30% for both the volatile organics and the liquid/liquid extractable organics.

Estimates of the analytical repeatability can also be derived from the spiked sample studies (Table A-4). An analysis of these data indicates that for the PNAs, the intralaboratory standard deviation is about 16% for concentrations greater than 40 ppb, while the standard deviation increases to 45% for samples at the one ppb level. For the phenols, the standard deviation is about 35% for samples greater than 20 ppb and increases to about 70% for samples at one ppb.

Estimates from the EPA reported quality control study of mercury show that the standard deviation is about 0.04 ppb (about 10%) for samples in the 0.3 to 0.5 ppb range.

5.4 Reproducibility of Sampling and Analytical Methods

Since analyses were conducted by different laboratories in some of the refineries studied, comparisons of the data from the laboratories gives an indication of the reproducibility of the analytical methods. The following laboratory comparisons are discussed and analyzed in Appendix B:

Comparisions Made	Refineries From Which Data Was Analyzed		
	Volatile Organics	Liquid/Liquid Extractable Organics	Trace Elements
EPA Labs vs. Radian	2	2	2, 7, 9
EPA Labs vs. Company Labs	2	2, 6	2, 7, 9, 11, 16
Radian vs. Company Labs	2, 7, 9	2, 7, 9	2, 7, 9
Radian vs. Other Contract Labs		7	

Since much of the data is reported as "not detected," "detected less than some value," or as "greater than some value," a quantitative comparison of the laboratories is not straight-gorward. In Appendix B, qualitative comparisons are made and a technique is developed to convert the qualitative data to quantitative data which allows comparisons to be made using scatter plots.

The comparisons show that laboratories frequently differ by greater than 75% when quantitative data is reported. There are examples where the differences are an order of magnitude. These extreme differences between laboratories are a composite of a number of effects including repeatability of the test method, interferences from the contamination of samples, and variability of recoveries, as well as the inherent variability between laboratories using the same test method.

5.5 PNA Comparisons

In four refineries, analyses for PNAs were conducted by two independent methods; the EPA GC/MS technique and the highly specific Exxon R & E GC/UV method. Selected comparative data for the two methods are summarized in Table 5-1.

TABLE 5-1. COMPARISON OF POLYNUCLEAR AROMATIC HYDROCARBON DATA FROM REFINERY 7¹

Compound	Intake Water		Wastewater Feed to Wastewater Treatment		Final Effluent	
	Radian	Company	ER & E ²	Radian	Company	ER & E ²
Naphthalene	ND (<0.1)	ND (<1.)	---	1100	5200	---
Fluorene	ND (<0.1)	ND (<1)	---	62	ND (<1)	5
Phenanthrene Anthracene	ND (<0.1) ⁴	ND (<1) ⁴	---	99 ⁴	ND (<1) ⁴	32 ND (<0.3)
Fluoranthene	ND (<0.1)	ND (<1)	ND (<0.03)	23.	ND (<1)	2.0
Pyrene	ND (<0.1)	ND (<1)	ND (<0.02)	6.9	ND (<1)	6.4
Chrysene Benzo(a)anthracene Triphenylene	ND (<0.1) ⁴	ND (<1) ⁴	ND (<0.01) ND (<0.01) ND (<0.01)	13. ⁴	ND (<1) ⁴	2.6 1.4 1.2
Benzo(a)pyrene Benzo(e)pyrene ⁵ Perylene ⁵	ND (<0.1) ⁴	ND (<1) ⁴	0.03 ND (<0.05) ND (<0.06)	4.4 ⁴	ND (<1) ⁴	1.1 1.3 0.3
Dibenzo(a,h)anthracene	ND (<0.3)	ND (<1)	---	ND (<0.3)	ND (<1)	0.4
Benzo(g,h,i)perylene	ND (<0.2)	ND (<1)	ND (<0.1)	ND (<0.2)	ND (<1)	0.6

¹All values in µg/l (ppb).²Analysis by GC-UV method.³Duplicate analyses were performed on this sample point; data presented is from analysis #1.⁴This is a combined value. The protocol procedure cannot distinguish between these structural isomers.⁵This compound is not on the list of Priority Pollutants.

NOTES: ND (<X): Compound was not detected; X equals the lowest limit of sensitivity of the method for that sample.

D (<X): Compound was detected at some concentration less than X, but the concentration could not be quantified.

PUBL 4296-78

0732290 0031163 1

The comparisons have shown that the EPA methodology is incapable of detecting and accurately quantifying individual isomeric PNAs. For example, at Refinery 7, analysis of the final effluent by the EPA GC/MS approach yielded concentrations for chrysene and benzo(a)pyrene of 9.1 and 0.4 ppb, while the values, as obtained by GC/UV, are less than 20% of those reported by GC/MS analysis.

Polynuclear aromatic hydrocarbon data obtained from the analysis of effluents conducted according to the EPA Protocol has been shown to be potentially inaccurate. This is due to the gas chromatographic conditions employed in the analytical methodology. Benzo(a)pyrene, benzo(e)pyrene and perylene and other isomeric PNA groups are not resolved under the chromatographic conditions. Therefore, all isomeric PNAs contained in a group are reported as a single compound. This leads to reported concentrations that are erroneously high.

Therefore, all PNA data obtained according to the EPA Protocol must be viewed with skepticism. Accurate PNA data can be only obtained from the utilization of techniques that differentiate between isomeric species.

5.6 Trace Element Data

Selected parallel samples for the element Priority Pollutants were analyzed by the EPA and API analytical participants. Considerable interlaboratory variation in the analytical data has been found. When quantitative comparisons could be made 42% of the interlaboratory differences exceeded 75%.

The variations can be attributed to several potential factors which include: