

Refinery Wastewater Priority Pollutant Study-Sample Analysis and Evaluation of Data

API PUBLICATION 4346
ENVIRONMENTAL AFFAIRS DEPARTMENT
DECEMBER 1981

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



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STUDY-SAMPLE ANALYSIS AND EVALUATION
OF DATA

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December, 1981

ACKNOWLEDGEMENT

This report is dedicated to the memory of Mr. Frank Hochgesang, Mobil Research and Development Corporation, who passed away in August 1980. As Chairman of the Analytical Systems Task Force until his death, Mr. Hochgesang provided invaluable technical expertise and direction to the work of the task force. He is remembered with the greatest respect and affection by his friends and colleagues.

Support and direction for this project was provided by members of the Analytical Systems Task Force of API's Department of Environmental Affairs.

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Special acknowledgement is extended to personnel of the two refineries involved for their cooperation and assistance and to the Environmental Protection Agency for its assistance in providing wastewater samples for API analysis and EPA analytical data.

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EXECUTIVE SUMMARY

This report presents and discusses the priority pollutant and traditional parameter data obtained by the American Petroleum Institute (API) and the Environmental Protection Agency (EPA) during a wastewater study carried out at two petroleum refineries in the New Orleans area during the period July 10 to September 13, 1980. The report also includes a statistical evaluation of the analytical methods used by the API and EPA consultant laboratories and a qualitative assessment of the utility of traditional parameters to act as surrogates for priority pollutants.

The study was initiated by EPA as part of an overall program to develop refinery effluent guidelines for toxic pollutants reflecting the application of Best Available Technology Economically Achievable (BAT). API was invited to participate in the study by EPA and the two refineries involved. Although EPA collected and analyzed samples every other day during the two-month period, API obtained split samples for analysis on only 12 of the 30 sampling days; six days at the beginning of the study and six at the end. It was believed that API's additional sampling would provide sufficient data to allow an independent evaluation of the results of the EPA study.

Wastewater samples were collected from the influent to the refineries' treatment systems (API separator effluent) and at the final discharge point after treatment (final effluent). These samples were analyzed by API and EPA laboratories for trace organic and elemental priority pollutants, as well as for traditional parameters present in refinery wastewaters.

The concentrations of organic priority pollutants were determined using two GC-MS quantification techniques; the

recently developed "isotope dilution" procedure (EPA Methods 1624 and 1625) and the more generally known "internal standard" technique (EPA Methods 624 and 625) which has been previously used to analyze refinery samples. Elemental priority pollutants were analyzed by atomic absorption and/or inductively coupled argon plasma spectroscopy (ICAP) procedures. EPA-approved standard methods were used for the traditional pollutants.

The analytical methods were evaluated in terms of bias (systematic differences between a measured concentration and the true concentration or designated-reference concentration) and within-laboratory precision (variability in concentrations resulting from random measurement errors within a laboratory). This evaluation was used as a baseline to assess both the magnitude of pollutant concentrations in the refinery wastewaters and the day-to-day variation in raw waste load and treatment system performance.

Method Evaluation Results

The recovery bias of the internal standard quantification procedure was estimated using the percent recovery of the 28 isotopically labeled analogs of priority pollutants spiked into each refinery sample. (An assumption of the isotope dilution technique is that the percent recovery of labeled compounds is equal to the percent recovery of their unlabeled analogs.) Substantial bias (average recovery significantly different than 100 percent) was found for 14 of the 28 compounds. Even where no bias was found, the large recovery standard deviations indicate that recoveries substantially different than 100 percent were obtained for individual samples. For many of the compounds, observed recoveries much greater than 100 percent were often found, indicating that reported concentrations of priority pollutants may at times be greater than the concentration actually present in the wastewater.

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The observed recovery bias and large recovery standard deviations indicate that the internal standard technique provides a variable and somewhat inaccurate measurement of actual priority pollutant concentrations. The recovery bias of the isotope dilution procedure could not be determined since known amounts of individual priority pollutants were not spiked in wastewater samples. However, as discussed below, the two laboratories obtained substantially different priority pollutant concentrations using this procedure on split samples.

The between-laboratory bias of both the internal standard and the isotope dilution quantification procedures was determined from the data obtained by API and EPA on 44 split samples. A qualitative assessment found that the two laboratories frequently disagreed on whether or not a priority pollutant was present. The percent disagreement ranged from five to thirty-five percent, depending on the priority pollutant class (volatiles, acids, polynuclear aromatics, or phthalates). Agreement was considerably improved by classifying detected concentrations (by either laboratory) which were less than 10 ug/l as "not detected."

A quantitative assessment of between-laboratory bias was performed using regression analysis. Substantial bias was found for some compounds. The amount of bias varied depending on the compound and the quantification procedure and, for a few compounds, on the concentration level.

For compounds where no significant bias was found, substantially different pollutant concentrations were often reported by the two laboratories for the split samples. The differences in pollutant concentrations obtained by API and EPA laboratories were attributed to a combination of between-laboratory bias and within-laboratory precision. By correcting for any

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observed between-laboratory bias, an estimate of the pooled within-laboratory precision (variation) of the two laboratories was obtained. An analysis of this estimate indicates that the precision is poor, especially for the volatile compounds. No significant differences in precision were observed between the two GC-MS quantification procedures (i.e., internal standard and isotope dilution).

Wastewater Characterization Results

A total of 24 organic and 7 elemental priority pollutants were found by API during the study. Twenty-eight of the thirty-one pollutants detected were found at both refineries. Priority pollutants found at average concentrations exceeding 100 ug/l in the influent samples were benzene, ethylbenzene, toluene, chloroform, phenol, 2,4-dimethyl phenol, anthracene/phenanthrene, naphthalene, chromium, and zinc. Chromium and zinc were detected in the final effluent samples at concentration levels ranging from 30 to 240 ug/l (Atomic Absorption data). The remainder of the priority pollutants were either not detected, or detected at very low concentrations (< 20 ug/l), in the final effluent samples (Internal Standard data).

Analysis of field and laboratory blank samples revealed that sample contamination from methylene chloride, benzene, toluene, chloroform, and several phthalates was a possibility. The amount of contamination was sufficient to invalidate all methylene chloride data obtained on refinery samples and to throw suspicion on the validity of the phthalates and chloroform data.

Substantial variability in daily concentrations of priority and traditional pollutants occurred in refinery influent samples and, to a lesser extent, in effluent samples. This variability is due to both analytical variability and variability

in refinery raw waste loads and treatment system performance. For all pollutants analyzed, the analytical variability made a significant contribution to the observed day-to-day variation in concentrations. In most cases, the magnitude of the analytical variability was similar to raw waste load or treatment system variability.

Surrogate Analysis Results

Since much of the final effluent data consisted of "not detected" or low concentrations, a quantitative analysis of surrogate relationships between concentrations of priority pollutants and traditional parameters could not be conducted. A qualitative comparison of concentrations of potential surrogates (TOC, BOD, TSS, COD, Oil and Grease and 4AAP phenolics) and priority pollutants in effluent waters was performed. The results of this comparison indicated that a possible relationship was present between chromium and total suspended solids (TSS).

Conclusions

- Refinery treatment systems can reduce priority pollutants present in raw wastewater to very low levels. Much of the variability of final effluent concentrations is due to variability associated with the analytical methods currently available to measure effluent concentrations at the part-per-billion level.
- The two refineries were remarkably similar with respect to the pollutants present in the influent and effluent samples and the concentrations of these pollutants.
- Continued evidence of the possibility of sample contamination with such priority pollutants as methylene chloride, benzene, toluene, chloroform, and phthalates indicates that analytical data for low levels of these pollutants is subject to question.

- The use of the isotope dilution procedure offered no advantage over the internal standard procedure in terms of eliminating between-laboratory bias or improving within-laboratory precision. The magnitude of the between-laboratory bias and the within-laboratory precision of either procedure remains a limitation of the methods' utility for regulatory purposes.
- The ICAP and AA methods of elemental analysis are essentially equivalent for measuring chromium and zinc in refinery wastewaters.
- The concentrations of priority pollutants in the refinery effluents studied are too low to allow a valid assessment of the utility of using traditional parameters as surrogates for priority pollutants. Although a qualitative relationship between total chromium and total suspended solids was found, this is insufficient to show that a valid surrogate relationship exists.

1.0 INTRODUCTION

During the period of July 16 to September 30, 1980, EPA carried out a sampling and analysis study of priority pollutants in wastewaters from two refineries in the New Orleans area. At the invitation of EPA and personnel representing the two refineries, API agreed to participate in the study. API obtained replicate and split samples for analysis concurrently with EPA during the initial and final two weeks of the study. The objective of API's limited study was to obtain sufficient data to conduct an independent evaluation of the results of the EPA study.

This report presents and discusses the priority pollutant and traditional parameter data obtained by API and EPA on the split samples obtained during the study. The report also includes a statistical evaluation of the analytical methods used by the API and EPA consultant laboratories and a qualitative assessment of the utility of traditional parameters to act as surrogates (indicators) for priority pollutants. The statistical evaluation of the analytical methods was used as a baseline to assess both the magnitude of pollutant concentrations in refinery wastewaters and the day-to-day variation in raw wasteload and treatment system performance.

Background

The New Orleans study was conducted as part of an overall program initiated by EPA in the fall of 1976 to develop refinery effluent guidelines reflecting the application of Best Available Technology Economically Achievable (BAT) for toxic and nonconventional pollutants and Best Conventional Pollutant Control Technology (BCT) for conventional pollutants. The stated purpose of EPA's New Orleans study "was to (1) determine if there

is a surrogate relationship between the priority pollutants and one or more of the traditional pollutant parameters (e.g., TOC, COD); (2) confirm the presence or absence of specific priority pollutants; and (3) evaluate stable isotope spiking techniques (stable label) as a monitoring tool in this industry."¹ The isotope dilution techniques referred to above are Methods 1624 and 1625 recently developed by EPA's Effluent Guidelines Division.²

Previous three-day wastewater sampling and analyses studies carried out by EPA and API at 17 refineries during the spring of 1977 showed that those priority pollutants detected were removed to low, or in most cases, non-detectable levels in refinery effluents.^{3,4} These studies, however, did not provide any long-term data to evaluate the day-to-day variability of priority pollutants in refinery influent and effluent wastewaters. Additionally, statistical analyses of data obtained during the 1977 studies showed that the gas chromatography-mass spectrometry (GC-MS) method used to quantify the organic priority pollutants needed substantial improvement. Recovery of compounds was extremely variable and agreement (precision) between laboratories on replicate samples and within laboratories on replicate spiked samples was poor.³ EPA proposed the study reported here in order to develop a more definitive long-term characterization of priority pollutants in refinery effluents and to evaluate the recently developed GC-MS techniques.

Finally, the Agency stated in its preamble to the 21 December 1979 proposed refinery guidelines that it was considering the possibility of establishing numerical effluent limitations for the following specific toxic pollutants: benzene, toluene, ethylbenzene, naphthalene, and 2,4-dimethyl phenol.⁴ The use of GC-MS methods in measuring organic priority pollutants, however, is both costly and time-consuming. For this

reason, EPA has sought to use traditional pollutants as surrogates or indicators for the priority pollutants where appropriate. That is, by establishing effluent limitations for the surrogate or indicators, toxic pollutants would be indirectly controlled. The two-refinery New Orleans study was designed to provide data for further investigation of the surrogate/indicator-toxic pollutant relationship.

2.0 WASTEWATER SAMPLING

Sampling was conducted at the two refineries in the New Orleans area from July 16 to September 13, 1980 by Burns and Roe Industrial Services Corporation, under contract to EPA (EPA Contract No. 68-01-5163). The API sampling and analysis program was designed to duplicate the EPA program during the first two and last two weeks of the EPA effort. Although most API samples were analyzed by Radian, two sets of samples obtained during the first two weeks at Refinery B were analyzed at the company's research center.

2.1 Sampling Plan

Samples of the influent to wastewater treatment (API separator effluent) and treated effluent were collected by EPA, every other day at both refineries over a 60-day period. Twelve of these samples from each refinery were split with API during six sampling days at the start and at the end of the EPA effort. These two six-day periods are referred to as Phase I and Phase II. Also, samples of each refinery's intake (river) water were collected twice by API during the sampling period. Grab samples of the river water were likewise obtained by EPA on three occasions during the program. Table 2-1 summarizes the API sampling effort. All samples were assigned EPA sample identification numbers provided by the EPA sampling team to facilitate subsequent data comparison.

2.2 Sampling Protocol

Grab, blank, and composite samples were collected during each sample period, utilizing specific containers and preservation techniques as summarized in Table 2-2. All grab samples were collected at the start and end of each sampling period.

Table 2-1

SUMMARY OF API SAMPLING

Sample Day	Calendar Day	Refinery A		Refinery B	
		Influent	Effluent	Influent	Effluent
02	7-18/7-19	X	X	X ¹	X ¹
04	7-22/7-23	X	X	X	X
05	7-24/7-25	X	X	X ²	X ²
06	7-26/7-27	X	X	X	X
07	7-28/7-29	X	X		
08	7-30/7-31	X	X	X	X
25	9-2/9-3	X	X	X	X
26	9-4/9-5	X ³	X ³	X ³	X ³
27	9-6/9-7	X	X	X	X
28	9-8/9-9	X	X	X	X
29	9-10/9-11	X ³	X ³	X ³	X ³
30	9-12/9-13	X	X	X	X

¹Sample split with company research laboratory.

²Sample analyzed by company research laboratory only.

³Sample collected in duplicate.

NOTE: Unless noted, all samples were analyzed by Radian.

Table 2-2
SUMMARY OF SAMPLING INFORMATION

<u>Parameter</u>	<u>Type</u>	<u>Container</u>	<u>On-Site Preservation</u>	<u>Comment</u>
Extractable Organics	Composite	Gallon Glass ¹	Cool, 4°C	24-hour sampling period
Volatile Organics	Grab	40 ml vial ²	Cool, 4°C	Duplicate vials collected at beginning and end of 24-hour sampling period ³
Phenolics	Grab	1 Qt. Glass ¹	H ₂ SO ₄ to pH<2; cool, 4°C	Collected 1/2 of sample at beginning and end of 24-hour sampling period
Metals	Composite	1 l-Plastic	HNO ₃ to pH<4; cool, 4°C	
Oil and Grease I	Grab	1 Pt. Glass ¹	H ₂ SO ₄ to pH<2; cool, 4°C	Collected at beginning of 24-hour sampling period
Oil and Grease II	Grab	1 Pt. Glass ¹	H ₂ SO ₄ to pH<2; cool, 4°C	Collected at end of 24-hour sampling period
BOD, TSS	Composite	1 l-Plastic	Cool, 4°C	
Volatile Trip Blank	Blank	40 ml vial ²	Cool, 4°C	1 blank per plant per day
COD, TOC	Composite	1 Qt. Glass ¹	H ₂ SO ₄ to pH<2; cool, 4°C	

¹Teflon®-lined metal caps.

² Silicone septa with teflon liner.

³Samples from each of the sample points were tested for residual chlorine with ortho toluidine, but none was found.

Radian and EPA each provided two ISCO samplers for the collection of composite samples at each refinery. All extractable organic samples (API and EPA) were taken from the EPA sampler in order to minimize differences between duplicates. The API sampler was employed for the trace metal and traditional pollutant samples. The Radian and EPA samplers were operated side by side in the time proportional mode. Each sampler collected 40 ml every 15 minutes for a total of 9.5 liters (2.5 gal.) during each 24-hour cycle.

At the end of each sampling period, the composite sample was capped and shaken to ensure uniform mixing. The sample was then split by pouring aliquots into the API and EPA sample bottles. The samples were then preserved, placed in ice chests, and shipped by air freight on the day of collection.

3.0 ANALYTICAL METHODOLOGY

Radian Corporation, the API contractor, analyzed wastewater samples for volatile organics, liquid-liquid extractable (acid and base-neutral) organics, elements, and traditional parameters. Neither Radian nor TRW, the EPA contract laboratory, analyzed for pesticides/PCB's since they would not be expected in refinery effluents. The methods used for preparation and analysis of the samples are described below.

Analyses for organic priority pollutants were conducted by GC-MS. Both Radian and TRW used EPA Methods 1624 and 1625.² These methods are reproduced in Appendices B and C; any known deviations from these methods are detailed in Appendix A, Sections 2.0, 3.0, and 4.0.

Methods 1624 and 1625 are the recently developed stable label alternatives to the EPA proposed Methods 624 and 625.⁵ The major difference between Methods 1624 and 1625 and the EPA proposed methods is the spiking of isotopically labeled analogs of the organic priority pollutants (labels). The labels are added to the sample before extraction for subsequent use in quantification. The quantification of each organic priority pollutant is based on its labeled analog. This technique is designated "isotope dilution." Methods 624 and 625 utilize an "internal standard" technique for quantification. During this study, the addition of internal standards together with labeled analogs to the sample allowed quantification by both the isotope dilution and internal standard techniques from a single analysis. At Radian, the internal standard calculation technique was also employed to measure the concentration of the isotopically labeled compounds. This permitted calculation of the recoveries of the labeled compounds which are presumed equal to the recoveries of the corresponding priority pollutants.

In Section 5.0 a comparison is made of the concentrations determined by the two methods of quantification: isotope dilution and internal standard. Results and conclusions discussed in Sections 6.0 and 7.0, however, are based on measurements quantified by the internal standard procedure (Methods 624 and 625), since this is the procedure which has been widely used to generate effluent data for EPA effluent guidelines development and for National Pollutant Discharge Elimination System (NPDES) permit applications.

The GC-MS methods subdivide the organic species into three groups for analytical purposes. The three groups and the method for each group are:

- Volatile organics - purge and trap, GC-MS (Methods 624 and 1624);
- Base-neutral extractable organics - liquid-liquid extraction with methylene chloride at pH 12, GC-MS (Methods 625 and 1625); and
- Acid extractable organics - liquid-liquid extraction with methylene chloride at pH 2, GC-MS (Methods 625 and 1625).

Detailed discussions of the analytical methods and calculations are in Appendix A. These are briefly summarized below.

3.1 Volatile Organics Procedure

Methods 624 and 1624 utilize a similar procedure based on removing the volatile compounds by purging with an inert gas and trapping the purged species on a suitable sorbent. Five ml of a water sample are purged with helium for 12 minutes. The purged organics are trapped on a Tenax®-silica gel trap at room temperature. The species are then desorbed by rapidly heating the trap to 180°C. Analysis of the desorbed organics is then

performed by GC-MS utilizing a Carbowax[®]-Carbowax chromatographic column. Analysis for the volatile species is accomplished by the measurement of characteristic parent or fragment ion intensities which maximize at known retention times. The volatile priority pollutants which are determined by Methods 624 and 1624 are listed in Table 3-1.

Labeled analogs of the 10 compounds indicated in Table 3-1 were added to the sample before purging. Each labeled analog was spiked at a concentration level of 20 ug/l with the exception of acrylonitrile-d₃ which was added at 100 ug/l. Details of this spiking procedure are described in Appendix A, Section 2.0.

3.2 Liquid-Liquid Extractable Organics Procedure

Methods 625 and 1625 employ a liquid-liquid extraction procedure to separate the extractable priority pollutants into two fractions, acid and base-neutral, as shown in Table 3-2. These extracts are obtained by first adjusting the pH of two liters of the sample to pH 12. The basic and neutral compounds are then removed by extraction with methylene chloride. After adjusting the sample to pH 2, acidic compounds are removed from the remaining sample by a second methylene chloride extraction. After concentration, the extracts are individually analyzed by GC-MS for the appropriate priority pollutants. Quantitative analyses are performed by the measurement of the ion intensities of selected parent or fragment ions of both the priority pollutant and its isotopic analog or internal standard.

Labeled analogs of the 20 compounds indicated in Table 3-2 were added to the sample before extraction. Each labeled analog was spiked at a concentration level of 100 ug/l. Details of this spiking procedure are described in Appendix A, Section 2.0.

Table 3-1

VOLATILE COMPOUNDS AMENABLE TO ANALYSES BY METHODS 624 AND 1624

Acrolein
*Acrylonitrile
*Benzene
Bromoform
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
2-Chloroethylvinyl ether
*Chloroform
Dichlorobromomethane
Dichlorodifluoromethane
1,1-Dichloroethane
*1,2-Dichloroethane
1,1-Dichloroethene
1,2-Dichloropropane
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
*Ethylbenzene
Methyl bromide
Methyl chloride
*Methylene chloride
*1,1,2,2-Tetrachloroethane
Tetrachloroethene
*Toluene
1,2-trans-Dichloroethylene
*1,1,1-Trichloroethane
*1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
Vinyl chloride

*Compounds for which a labeled analog was spiked into the sample.

Table 3-2

COMPOUNDS AMENABLE TO ANALYSES BY METHODS 625 AND 1625

Base/Neutral Compounds

Acenaphthene
 Acenaphthylene
 *Anthracene
 Benzidine
 *Benzo(a)anthracene
 Benzo(a)pyrene
 3,4-Benzofluoranthene
 Benzo(g,h,i)perylene
 Benzo(k)fluoranthene
 bis(2-Ethylhexyl)phthalate
 4-Bromophenyl phenylether
 bis(2-Chloroethoxy)methane
 bis(2-Chloroethyl)ether
 bis(2-Chloroisopropyl)ether
 Butyl benzyl phthalate
 2-Chloronaphthalene
 4-Chlorophenyl phenyl ether
 *Chrysene
 Dibenzo(a,h)anthracene
 *1,2-Dichlorobenzene
 1,3-Dichlorobenzene
 *1,4-Dichlorobenzene
 3,3'-Dichlorobenzidine
 Diethyl phthalate
 Dimethyl phthalate
 *Di-N-butyl phthalate
 2,4-Dinitrotoluene
 2,6-Dinitrotoluene
 *Di-N-octyl phthalate
 1,2-Diphenyl hydrazine
 (as Azobenzene)
 Fluoranthene
 *Fluorene
 Hexachlorobenzene
 Hexachlorobutadiene

Base/Neutral Compounds

Hexachlorocyclopentadiene
 Hexachloroethane
 Indeno(1,2,3-c,d)pyrene
 Isophorone
 *Naphthalene
 *Nitrobenzene
 N-Nitrosodimethylamine
 N-Nitrosodi-N-propylamine
 *N-Nitrosodiphenylamine
 (detected as diphenylamine)
 *Phenanthrene
 *Pyrene
 1,2,4-Trichlorobenzene

Acid Compounds

*2-Chlorophenol
 *2,4-Dichlorophenol
 2,4-Dimethylphenol
 2,6-Dinitro-o-cresol
 *2,4-Dinitrophenol
 2-Nitrophenol
 4-Nitrophenol
 p-Chloro-m-cresol
 *Pentachlorophenol
 *Phenol
 *2,4,6-Trichlorophenol

*Compounds for which a labeled analog was spiked into the sample.

3.3 Quantification Techniques for Organics

As discussed in Section 3.0, the major difference between Methods 624, 625 and Methods 1624, 1625 lies in the quantification procedure. By spiking the samples with internal standards (used in Methods 624 and 625) and isotopically labeled compounds (used in Methods 1624 and 1625), results could be obtained for each procedure. A brief description of the internal standard and the isotope dilution quantification procedures is given below. Additional details and any known deviations from the published methods are given in Appendix A.

3.3.1 Internal Standard Technique

The concentrations of priority pollutants referred to as "internal standard" values were calculated as prescribed by EPA Methods 624 (Volatiles) and 625 (Acids and Base-Neutrals).⁴ Using these methods, a known amount of an internal standard compound is added to the sample before the GC-MS analysis. (In Method 624, the internal standard is added just before the purge step; in Method 625, it is added after extraction.) It is assumed that any subsequent losses of sample and changes of instrument response equally affect the analyte (priority pollutant) and the internal standard. The instrument response (the peak area of a selected fragment ion) is measured for each analyte (A_x) and for the internal standard (A_{IS}). The concentration of the analyte (C_x) can then be calculated as follows:

$$C_x = \frac{A_x}{A_{IS}} \cdot C_{IS} \cdot \frac{1}{RF}$$

where C_{IS} is the known concentration of added internal standard, and RF is a response factor which must be experimentally determined for each analyte by analysis of prepared standards.

Method 624 (Volatiles) automatically corrects results for recoveries found in reagent water during calibration, but not for any different recovery caused by other components in the sample matrix or by instrument variation. Method 625 (acid and base-neutral extractables) makes no recovery corrections.

Analyses indicated that the spiking solution of labeled analogs added to samples for quantification by the isotope dilution technique (described below) contained small amounts of some of the (unlabeled) priority pollutants as impurities. The concentrations calculated as described above, therefore, were corrected for these impurities and for any mass spectral interference arising from the presence of the labeled analogs.

3.3.2 Isotope Dilution Technique

The concentrations of priority pollutants referred to as "isotope dilution" values were calculated as prescribed by Methods 1624 (Volatiles) and 1625 (Acids and Base-Neutrals). A detailed discussion of the calculation technique, including the appropriate equations, is given in Appendix A. The principles of quantification by this technique are similar to those of the internal standard technique except that for each compound analyzed, the internal standard chosen is an analog of that compound labeled with a stable isotope to make it distinguishable by the mass spectrometer.

The labeled analogs generally differ from their corresponding priority pollutant in that they contain deuterium (a hydrogen isotope) rather than ordinary hydrogen. Since the labeled analogs differ remarkably little in chemical and physical properties from their corresponding priority pollutants, they should exhibit similar properties during purging or extraction and in subsequent handling of samples.

In addition, unlike the internal standards used in Method 625, the labeled analogs in Method 1625 are added to the sample before extraction. Thus, the isotope dilution method makes corrections for recovery losses during extraction. Higher and more accurate concentrations than those calculated by the internal standard technique might therefore be expected.

For convenience in the laboratory, all of the labeled analogs were combined into one spiking solution (cocktail) for each fraction (volatiles, acids, and base-neutrals). These three cocktails were prepared by Radian as described in Appendix A and were used by both Radian and TRW.

Some priority pollutants did not have labeled analogs that could be spiked as an internal standard. In those instances, a surrogate labeled compound had to be chosen as the reference standard for the isotope dilution calculation. These surrogate labeled compounds were chosen on the basis of the "nearest neighbor" principle, i.e., the labeled compound that was judged to be closest to the unlabeled analyte in terms of chemical class, volatility and/or polarity. The "nearest neighbor" stable label standards were jointly chosen by Radian and TRW and are indicated in appendix Tables A-4.6 and A.4-7. For example, fluoranthene (Quantifying Ion #202 in Table A-4.6) has pyrene-d₁₀ as its "nearest neighbor." Pyrene-d₁₀ is, of course, the stable labeled analog of pyrene. The use of "nearest neighbor" labeled compounds is not strictly part of the isotope dilution method; therefore, results calculated in this manner are noted in Appendix D.

3.4 Analysis of Elements and Traditional Parameters

Methods employed by Radian and TRW for the analysis of elements and traditional parameters are described in Appendix A, Sections A-5.0 and 6.0. Analyses for 38 elements, including all of the priority pollutant elements with the exception of mercury, were performed by inductively coupled argon plasma emission spectrometry (ICAP). Four elements--chromium, lead, zinc and arsenic--were also determined by atomic absorption spectrophotometry. EPA-approved methods were used for the analysis of the other water quality parameters--total suspended solids, BOD, COD, TOC, oil and grease, and 4-AAP phenols.⁵

4.0 REFINERY DESCRIPTIONS

Refinery A and Refinery B selected for this study are proximally located such that the EPA team could collect samples from both refineries and then transport the samples to the airport in a single day. Both refineries have moderately complex process configurations and manufacture a mixed slate of petroleum products. Both refineries draw their intake water from the Mississippi River and operate wastewater treatment systems which utilize dissolved air flotation, oil-water separators, and biological treatment units.

4.1 Refinery A

The 255,000 barrels per stream day Refinery A is ranked by EPA as a Class B* refinery on the basis of process complexity factors. Foreign crudes are the main feedstocks to the complex. During the 1980 sampling program, the crude slate was chiefly comprised of Arabian and Mexican stocks. In the course of the EPA study all major distillation and downstream process units were operating with the exception of the alkylation and isomerization units, which were on-line for only one to two weeks during the 60-day study. The units which operated on a regular schedule during the study, as well as those cited above, are listed in Table 4-1. The 1980 stream day capacities reported to EPA and the actual average stream day throughput recorded during the sampling program are also listed there. The component units and flow pattern of the Refinery A wastewater treatment system are shown in Figure 4-1. The two EPA sample points are marked for easy reference.

*EPA has defined five subcategories of the petroleum industry which reflect differences in wastewater characteristics. The subcategories are: A-topping, B-cracking, C-petrochemical, D-lube, and E-integrated. The basic operations of category B refineries include topping and cracking.

Table 4-1

REFINERY A PROCESS UNIT CAPACITIES

Process	Stream Day ¹ Capacity (1,000 BBL/Day)	Actual Stream Day ² Throughput (1,000 BBL/Day)
Atmospheric Crude Distillation	255.0	166.6
Crude Desalting	255.0	166.6
Vacuum Crude Distillation	94.24	92.2
Desulfurization	86.5	67.4
Catalytic Reforming	37.5	29.5
Asphalt Production	10.0	37.5 ³
Caustic Treating	54.1	20.5
Mercox Treating	97.0	53.7
Sulfur Recovery (Long Tons/Day)	461.0	102.6
Reformer Feed Prep	40.0	31.5
Fluid Catalytic Cracking	70.0	52.0
HF Alkylation	20.5	14.6 ⁴
Isomerization	15.1	10.8 ⁴

20

¹Capacities reported in 1980 on the "Additional Information Table for the U.S. EPA Surrogate Sampling Program."

²Average actual throughput reported for operating days during 60-day sampling program.

³Asphalt produced in batch operation during third week only of program.

⁴Unit in service during final two weeks only.

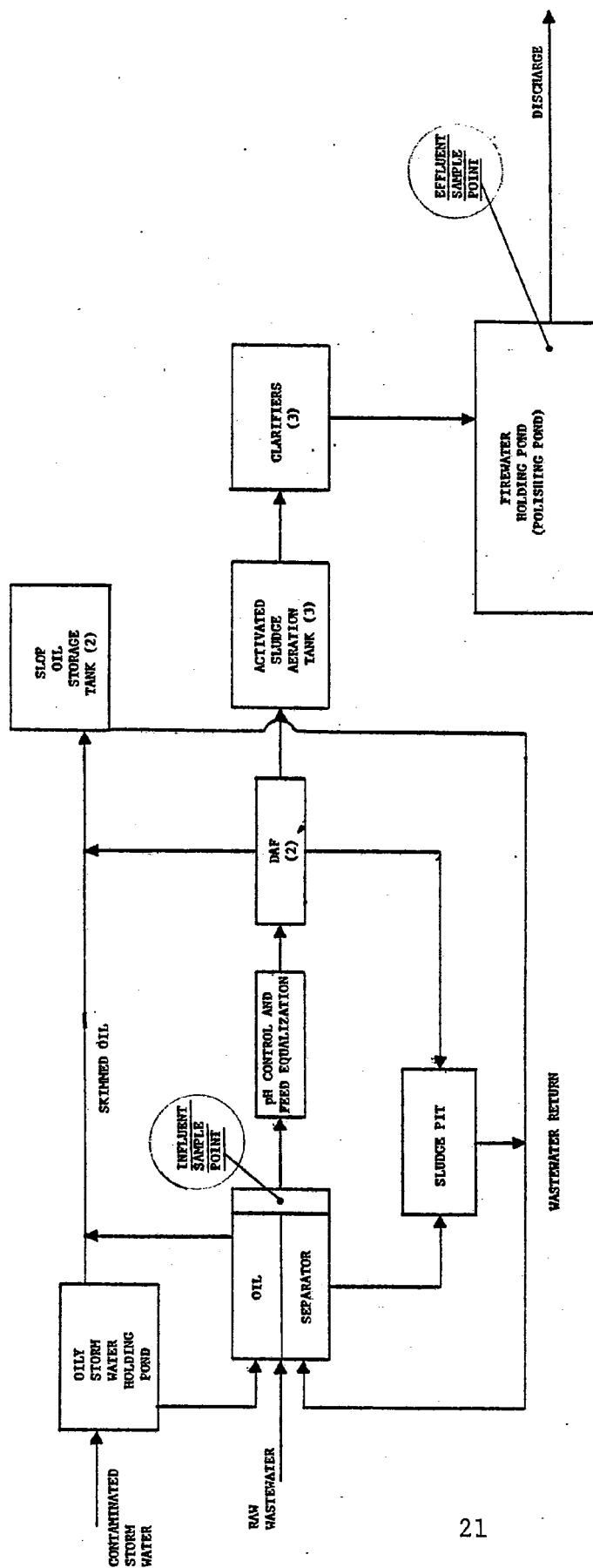


Figure 4-1
REFINERY A FLOW DIAGRAM TREATMENT PLANT

4.2 Refinery B

Refinery B is a 202,000 barrels per stream day Class B* refinery which processes primarily Gulf Coast crudes. During the first six weeks of the EPA study, several units were out of service for a scheduled maintenance turn-around. Those units included: hydroprocessing, catalytic reforming, aromatic extraction, reformer feed separation, and hydrodemethylation. Table 4-2 gives stream day capacities for all process units as reported in the refinery's NPDES permit application, as well as the average stream day throughput reported for operating days during the 60-day program. The Refinery B wastewater treatment facility and the two EPA sample points are shown in Figure 4-2.

*EPA has defined five subcategories of the petroleum industry which reflect differences in wastewater characteristics. The subcategories are: A-topping, B-cracking, C-petrochemical, D-lube, and E-integrated. The basic operations of category B refineries include topping and cracking.

Table 4-2

REFINERY B PROCESS UNIT CAPACITIES

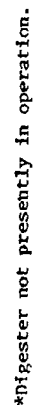
Process	Stream Day ¹ Capacity (1,000 BBL/Day)	Actual Stream Day ² Throughput (1,000 BBL/Day)
Atmospheric Crude Distillation	202.0	173.2
Crude Desalting	202.0	173.2
Vacuum Crude Distillation	73.5	65.5
Fluid Catalytic Cracking	89.0	79.6
HF Alkylation	37.5	37.2
Hydroprocessing	22.0	20.9 ³
Catalytic Reforming	37.5	32.4 ³
Aromatic Extraction	22.5	19.9 ³
Delayed Coking	16.0	15.9
Caustic or KOH Treating	64.0	NA
Sulfur Recovery (Long tons/day)	50.0	27.5
Reformer Feed Prep	42.0	35.9 ³
Hydrodemethylation	6.3	5.4 ³
Hydroprocessing	16.0	17.6

¹Capacities reported in response to EPA's 1977 Petroleum Refining Survey, Portfolio A, Section II.

²Average actual throughput reported for operating days during 60-day sampling program.

³Unit in service during final two weeks only of program.

NA - Not Available



1 - Partitioned area of pond. Flow into sampling area by underflow from main pond. Storm water segregated from pond waters prior to sampling and pumping from this area.

2 - Separate concrete sump receiving storm water only.

Figure 4-2

REFINERY B FLOW DIAGRAM WASTEWATER TREATMENT FACILITY

5.0 EVALUATION OF ANALYTICAL PROCEDURES

To aid in the interpretation of data obtained during this study, an evaluation of the analytical procedures used to determine the priority pollutant concentrations was conducted. The results of this evaluation are presented in this section to put the data from refinery influent and effluent samples in proper perspective.

The analytical procedures are evaluated in two stages. The first stage addresses the problem of estimating bias. Bias is a measure of the systematic displacement of a measured concentration from the true concentration or designated reference. In this study bias estimates are used to interpret the average concentrations of priority pollutants found in the refinery waste streams. Three types of bias were evaluated in this study:

- Recovery Bias (Internal Standard Procedure) - Systematic differences between the measured and spiked concentrations of labeled compounds. The bias determined for a labeled compound should represent the bias expected for its corresponding unlabeled analog (i.e., the priority pollutants), since the compounds exhibit little difference with respect to physical and chemical properties. (The isotope dilution technique assumes that the recovery of labeled compounds is equal to the recovery of the corresponding priority pollutant.)
- Between-Laboratory Bias - Systematic differences in concentrations reported by different laboratories analyzing the same samples (e.g., one laboratory reporting concentrations consistently greater than a second laboratory). In this analysis, the Radian result was arbitrarily designated as the reference and the bias of the TRW results relative to the Radian results was estimated.

- Between Quantification Procedure Bias - Systematic differences between reported concentrations made using two different quantification procedures on the same sample. In the analysis, the internal standard procedure was designated as the reference and the bias of the isotope dilution procedure relative to the internal standard procedure was estimated.

The second stage of this evaluation addresses the problem of estimating analytical variation (precision). The amount of analytical variation found in the New Orleans study provides the baseline required to assess variation in treatment system performance.

This section also contains a summary of contamination data for priority pollutants which were detected in blank samples. These data are used to assess the effect of contamination on the concentration values reported for priority pollutants detected in the refinery samples.

Other technical terms used in this and subsequent sections are defined as follows:

- Percent Recovery - The measured concentration of a spiked parameter expressed as a percent of the spike level and given by the formula

$$\text{PERCENT RECOVERY} = \frac{\text{MEASURED CONCENTRATION}}{\text{SPIKE CONCENTRATION}} \times 100$$

- Within-Laboratory Precision - The variability in concentrations resulting from random measurement errors within a laboratory.
- Geometric Mean - A summary statistic often used in place of the arithmetic mean when data are skewed towards high concentrations. For the type of data contained in this report, the geometric mean can be thought of as a median. The geometric mean is calculated by exponentiating the arithmetic average of the logarithms of the measurements.

Standard Deviation - A statistical measure of variability. The more variable a set of data, the larger the standard deviation.

- Relative Standard Deviation (RSD) - A measure of variation (also called the coefficient of variation) which expresses the magnitude of variation in concentrations as a percent of the average concentration and is given by the formula

$$RSD = \frac{\text{STANDARD DEVIATION}}{\text{ARITHMETIC MEAN}} \times 100$$

This measure is useful when the variability of concentrations increases as the average concentration increases.

- Confidence Interval - An interval placed around parameter estimates such as mean concentration or standard deviation to indicate the uncertainty of the estimate. The more uncertain the estimate of the parameter, the wider the confidence interval.

Since an exhaustive statistical evaluation of the analytical methods was not the primary purpose of this study, the data available for method evaluations were somewhat limited. The uses and limitations of the available data are:

- Recovery Data - Thirty deuterated compounds were spiked into each refinery sample. The measured concentrations of these compounds were used to estimate the recovery bias of the internal standard procedure. Since all compounds were spiked at the same concentration (100 ug/l for extractable organics and 20 ug/l for volatiles), the relationship between concentration and bias could not be evaluated. A second limitation of this data is that only one laboratory (Radian) provided analytical recovery data. Thus, no data were available to estimate the recovery bias of the TRW laboratory.
- Duplicate Data - Eight samples (four influent and four effluent) were separated into two portions in the field, and both portions were analyzed for the organic priority pollutants by Radian on the same day. These data were used to evaluate within-laboratory precision of the Radian GC-MS analyses.

Since many of the pollutants of interest in this study were not detected in the four effluent samples which were analyzed in duplicate, the within-laboratory precision could not be estimated for many of the priority pollutants.

- Split Sample Data - Forty-four samples were split and analyzed by Radian for API and by TRW for EPA. These data were used to evaluate the bias between Radian and TRW for the internal standard and isotope dilution procedures. Since only two laboratories participated in this study, between-laboratory precision was not estimated.

Given these limitations, the evaluation of the analytical procedures is still useful as a baseline for evaluating the magnitude of pollutant concentrations in the New Orleans refinery samples and day-to-day variation in treatment system performance.

The analytical data used to evaluate the bias and precision of the analytical methods are presented in Appendix D. Detailed notes concerning the assumptions and statistical procedures used in this section and subsequent evaluations are provided in Appendix E.

5.1 Bias

Three types of bias are evaluated in this section: recovery bias, relative biases between quantification procedures, and relative biases between laboratories. These estimates can be used to explain differences in average concentrations of priority pollutants calculated from different sets of data. For example, if one laboratory had a positive 30 percent bias with respect to a second laboratory, average effluent concentrations estimated from the data provided by the first laboratory would be approximately 30 percent higher than those estimated from the data provided by the second laboratory.

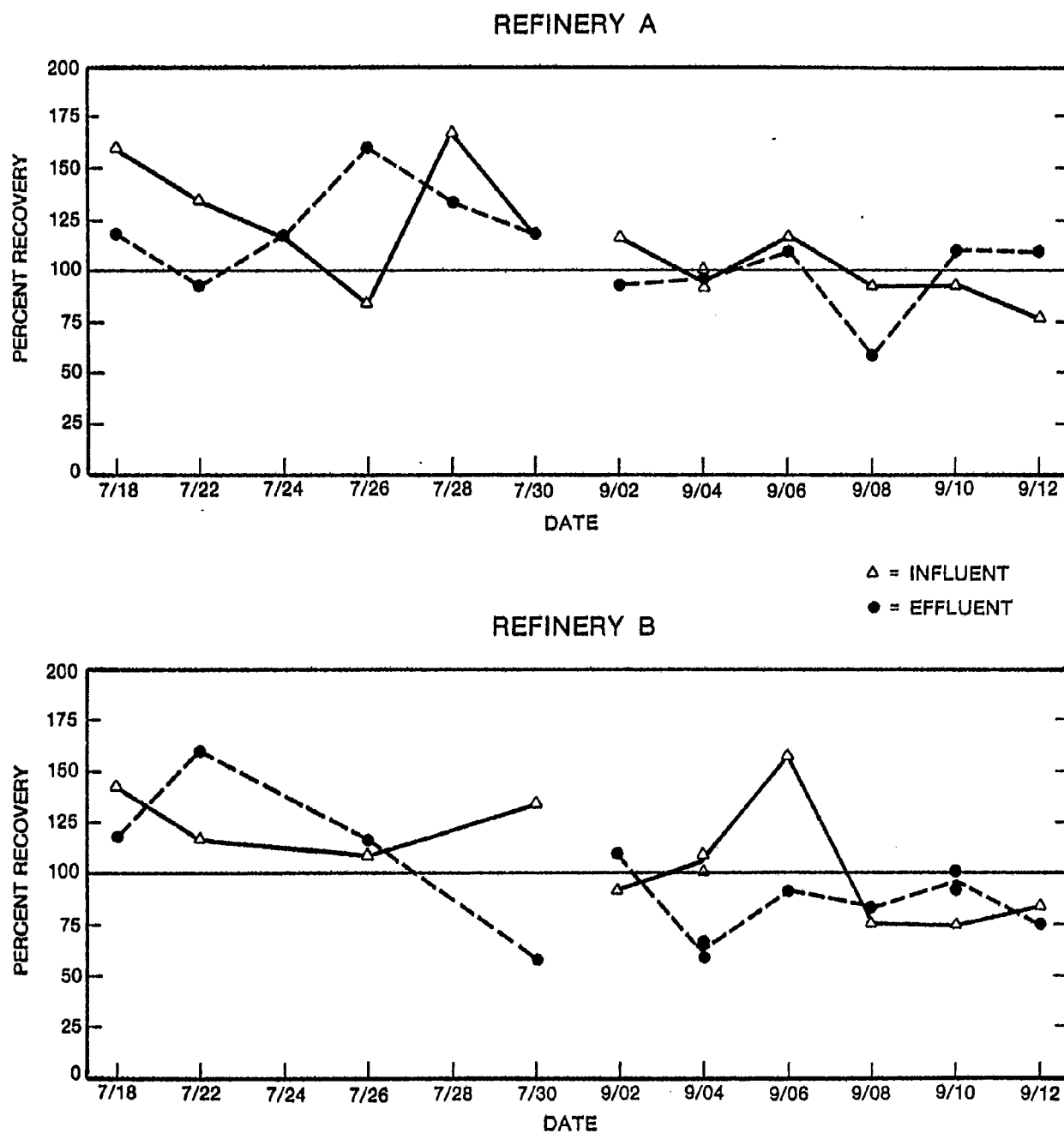
5.1.1 Recovery Bias

Ideally, bias of a measurement method is determined relative to a reference method or other standard, but this was not possible for this study. Recovery bias of the Internal Standard Method is defined relative to the spiked concentration of labeled compounds and estimated using the percent recovery of the labeled compounds in this study. If the average recovery is 100 percent, no recovery bias is present.

Thirty labeled compounds were spiked into each refinery sample. Extractable organics and acrylonitrile were spiked at 100 ug/l. All other labeled compounds were spiked at 20 ug/l. Recoveries of the labeled compounds were calculated for each sample analyzed using the internal standard quantification procedure. The recovery data are contained in Appendix D.

As a first step in analyzing the recovery data, the percent recovery was plotted versus the sample collection date. (The order of sample analysis dates closely follows the sample collection dates.) These plots are contained in Appendix E. Two typical examples for deuterated ethylbenzene and pyrene are given in Figures 5-1 and 5-2, respectively. The plot for deuterated ethylbenzene shows similar recoveries in influent samples (solid lines) and effluent samples (dashed lines). The data at both refineries show a positive bias among the Phase I samples. This means that the measured concentration of the labeled compound was greater than the amount spiked. The plot of labeled pyrene shows a negative bias in recovery for most samples. The bias appears to be greater in Phase I than in Phase II.

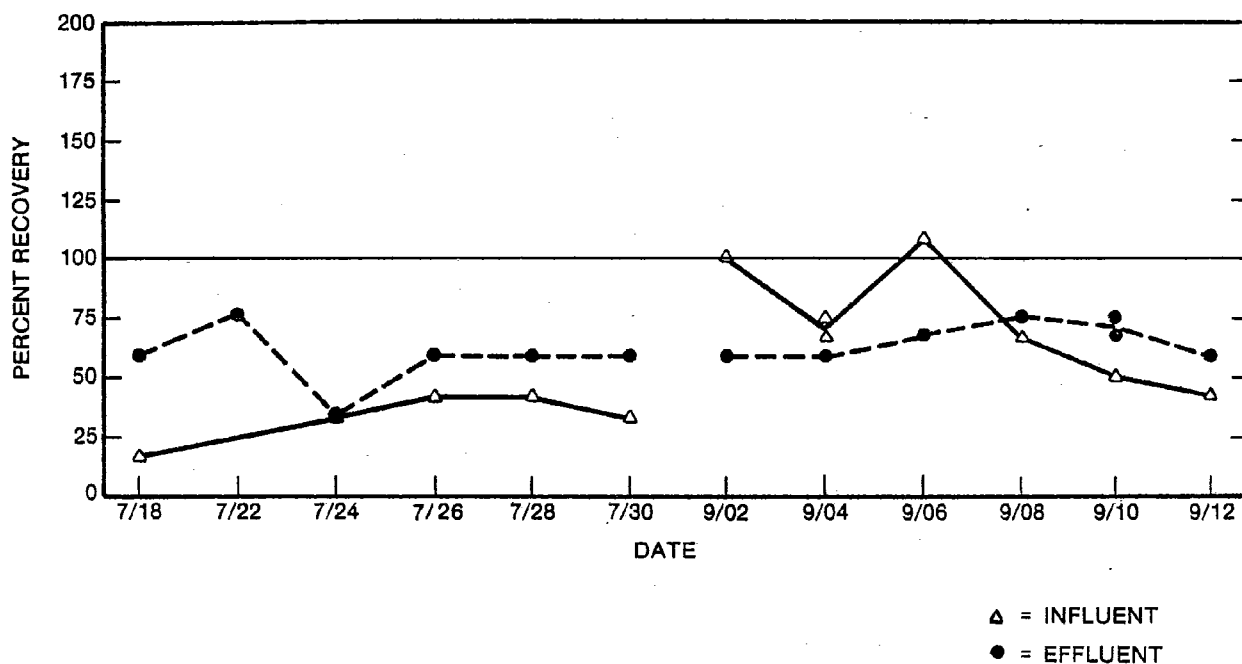
Although there were cases where recoveries for a specific compound differed between refineries or sampling points, these differences were usually small relative to the change in



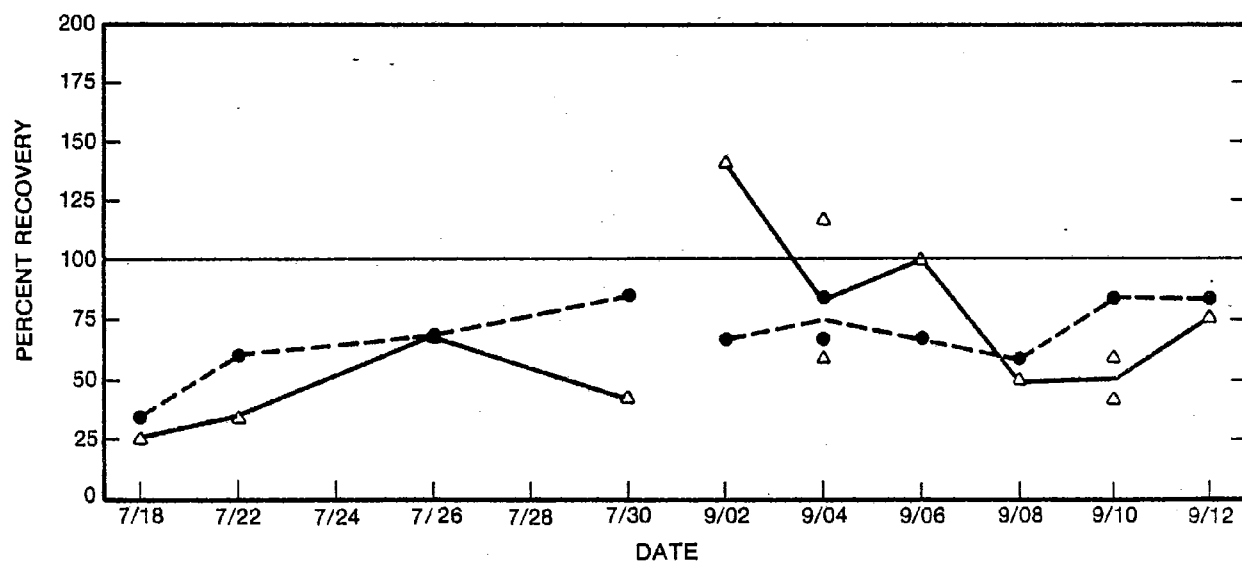
Solid lines connect Influent recoveries. Dashed lines connect effluent recoveries. Duplicate recoveries are plotted on 9/04 and 9/10. When duplicate results do not coincide, the lines connect the average of the duplicate values.

Figure 5-1
PERCENT RECOVERY OF DEUTERATED ETHYLBENZENE

REFINERY A



REFINERY B



Solid lines connect influent recoveries. Dashed lines connect effluent recoveries. Duplicate recoveries are plotted on 9/04 and 9/10. When duplicate results do not coincide, the lines connect the average of the duplicate values.

Figure 5-2

PERCENT RECOVERY OF DEUTERATED PYRENE

recovery with time. Based on the time plots for each compound, it was decided to summarize recoveries separately by phase. A check was made for systematic differences in laboratory procedures which could account for the differences observed between Phase I and Phase II recoveries. Since no systematic differences in laboratory procedures were found, the differences in laboratory performance over time probably resulted from laboratory instrumentation settings or response factors.

Table 5-1 gives the mean and the standard deviation of the percent recovery for each deuterated compound. Recoveries are summarized separately for Phase I and Phase II samples and for all samples combined. The mean percent recovery indicates whether or not bias was present. Means which are significantly greater than 100 percent indicate positive bias, and means which are significantly less than 100 percent indicate negative bias. (Analytical uncertainties in the GC-MS procedures can result in observed recoveries which are greater than 100 percent.) Statistical tests were performed to determine which means were significantly different from 100 percent. Compounds with significant recovery bias are noted in Table 5-1 with an asterisk. These tests are presented in Appendix E.

The recovery bias gives an indication of the adjustment to concentration level obtained through the isotope dilution equation. When positive recovery bias is present, the average isotope dilution concentrations will tend to be lower than the average concentrations obtained by internal standard. For negative recovery bias, the opposite is true.

The standard deviation of percent recovery is also given in the table. The larger the standard deviation, the more variable the recoveries. It is important to note that even for compounds with no significant recovery bias, the large recovery

Table 5-1
PERCENT RECOVERY OF DEUTERATED COMPOUNDS
(BASED ON METHODS 624/625 TYPE QUANTIFICATIONS)

	PHASE I			PHASE II			ALL SAMPLES				
	N	MEAN	STD	N	MEAN	STD	N	MEAN	STD	MIN	MAX
VOLATILES											
Acrylonitrile	20	140*	38	24	109	68	44	123	58	55	340
Benzene	20	118*	26	24	116	38	44	117*	33	60	260
Chloroform	20	158*	29	24	108	38	44	131*	42	70	215
Ethylbenzene	20	122*	26	24	94	20	44	107	27	60	165
Methylene chloride	20	117	33	24	82*	27	44	98	35	45	180
Toluene	20	111	23	23	105(83)*	107(23)	44	107(96)	80(27)	45	600(160)
1,1,1-Trichloroethane	20	141*	33	24	106	47	44	122*	44	65	265
1,1,2-Trichloroethane	20	135*	25	24	91	27	44	111	34	41	190
1,2-Dichloroethane	20	148*	31	24	97	33	44	120*	41	55	230
ACIDS											
Pentachlorophenol	20	69*	28	24	184*	84	44	132	87	39	420
Phenol	20	42*	12	24	52*	20	44	47*	17	13	98
2-Chlorophenol	20	93	23	24	97	44	44	95	35	34	260
2-Nitrophenol	20	100	30	24	151*	65	44	128*	57	64	410
2,4-Dichlorophenol	20	79*	17	24	122*	33	44	102	35	47	220
2,4,6-Trichlorophenol	20	67*	23	24	118	50	44	95	48	38	320
POLYNUCLEAR AROMATIC HYDROCARBONS											
Anthracene/Phenanthrene	19	59*	16	24	60*	18	43	60*	17	28	95
Benzo(a)anthracene/Chrysene	19	45*	20	24	63*	20	43	55*	22	1	135
Fluorene	19	64*	21	24	65*	14	43	64*	17	26	98
Naphthalene	19	94	20	24	104	33	43	99	28	49	200
Pyrene	19	48*	17	24	73*	22	43	62*	23	17	140
PHTHALATES											
Di-n-butyl phthalate	19	71*	22	24	82*	22	43	77*	23	36	140
Di-n-Octyl phthalate	19	73*	31	24	104*	30	43	90	34	33	190
OTHER BASE/NEUTRALS											
N-Nitrosodiphenylamine	19	75*	22	24	93	22	43	85*	24	36	150
Nitrobenzene	19	102	37	24	99	40	43	100	39	1	220
1,2-Dichlorobenzene	19	97	36	24	111	37	43	105	37	46	200
1,4-Dichlorobenzene	19	99	35	24	113	41	43	107	39	55	219

NOTES: Extractable organics and acrylonitrile were spiked at 100 ug/l. All other deuterated compounds were spiked at 20 ug/l. Recovery data are not available for 2,4-Dinitrophenol and 1,1,2,2-tetrachloroethane because in most samples the amount spiked was less than the detection limit. Summary statistics for toluene were recalculated with the maximum value of 600% deleted. These statistics are given in parentheses. Means are arithmetic averages. One less sample was available for calculating the base/neutral means because recovery was not quantified. Mean percent recoveries which are different from 100 (significance level = .01) are indicated by an asterisk.

standard deviations indicate that recoveries substantially different from 100 percent can occur for individual samples.

5.1.2 Relative Biases Between Quantification Procedures

As discussed in Section 3.0, concentrations for organic priority pollutants reported in this study were calculated by two different quantification procedures: internal standard and isotope dilution. The internal standard procedure utilizes designated non-priority pollutant compounds as internal standards for identification and quantification of priority pollutants, whereas the isotope dilution procedure utilizes stable label compounds.

The data from refinery influent and effluent samples were used to determine the bias of the isotope dilution procedure relative to the internal standard procedure for individual organic priority pollutants. This bias will depend on the recovery of the deuterated compound and the difference between the calibration curves for the two procedures. Table 5-2 lists relative biases for organic priority pollutants which were detected in at least 10 of the samples analyzed.

For most compounds, the relative bias between procedures remained constant at all concentration levels. This was not the case for two compounds--pentachlorophenol and fluorene--which were found to have different relative biases at different concentration levels. The estimates provided in Table 5-2 for these compounds are based on an intermediate concentration of 100 ug/l. It should be noted that substantial differences in the concentrations measured by the two methods often occur in individual samples, even for pollutants which show no bias.

Table 5-2
RELATIVE BIASES BETWEEN QUANTIFICATION PROCEDURES

Compound	Deuterated ¹ Spike	Bias of Isotope ² Dilution Measurements Relative to Internal Standard Measurements (%)
<u>Acids:</u>		
Pentachlorophenol	analog	-77 @
Phenol	analog	+98
2,4-Dimethylphenol	Phenol	+108
<u>PNA's:</u>		
Anthracene/Phenanthrene	analog	*
Benzo(a)anthracene/Chrysene	analog	+138
Benzo(a)pyrene	Benzo(a)anthracene/chrysene	+86
Benzo(b/k)fluoranthene	Benzo(a)anthracene/chrysene	*
Fluoranthene	Pyrene	*
Fluorene	analog	+160 @
Naphthalene	analog	*
Pyrene	analog	+41
<u>Phthalates:</u>		
Bis(2-ethylhexyl)phthalate	Di-n-octyl phthalate	*
Diethyl phthalate	Di-n-butyl phthalate	*
Di-n-butyl phthalate	analog	+53
Di-n-octyl phthalate	analog	*
<u>Volatiles:</u>		
Benzene	analog	*
Ethylbenzene	analog	*
Toluene	analog	*

¹The deuterated compound used for quantification; e.g., the quantification of penta-chlorophenol was based on its deuterated analog; the quantification of 2,4-dimethyl-phenol was based on its nearest neighbor, deuterated phenol.

$$^2\text{Bias} = \frac{\left(\frac{\text{Average Isotope}}{\text{Dilution Concentration}} \right) - \left(\frac{\text{Average Internal}}{\text{Standard Concentration}} \right)}{\left(\frac{\text{Average Internal}}{\text{Standard Concentration}} \right)} \times 100$$

*Based on the analytical uncertainty, the bias was not statistically significant. (Significance Level = .01).

@The amount of bias depends on the concentration level. The bias given here is based on an internal standard concentration of 100 ug/l.

The stable label reference for each priority pollutant considered in this analysis is also provided in Table 5-2. The stable label reference indicates whether the deuterated analog of a priority pollutant or its "nearest neighbor" was used to quantify the concentration of the priority pollutant. Among the acid compounds, for example, pentachlorophenol and phenol were quantified using their deuterated analogs. However, 2,4-dimethyl phenol was quantified using deuterated phenol, its "nearest neighbor."

5.1.3 Comparison of Recovery Bias and Quantification Procedure Bias

Since the isotope dilution measurement is approximately equal to the internal standard measurement divided by the recovery of the labeled compound, the relative bias of the isotope dilution procedure given in Section 5.1.2 should be approximately equal to the reciprocal of the recovery bias which was presented in Section 5.1.1. Some discrepancies are to be expected, however, since a full set of 22 samples were available for calculating recovery bias, but only the detected data could be used to calculate the quantification procedure bias. For example, the bias of the isotope dilution procedure relative to the internal standard procedure for phenol is +98 percent (i.e., on the average, phenol concentrations based on the internal standard procedure were approximately half those based on the isotope dilution procedure). This corresponds to the fact that on the average, slightly less than half the labeled phenol was recovered. Therefore, if the basic assumption of the stable label procedure is satisfied (i.e., that the recovery of the compound behaves exactly like the recovery of its labeled analog), the procedure provides a means for eliminating bias due to low recoveries. Since no priority pollutant spikes were done as part of this study, this assumption could not be verified.