Preliminary Data Summary for the Petroleum Refining Category

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1. Introduction

1.1 Background

The purpose of this study is to provide information for determining whether the current effluent limitations guidelines and standards for the petroleum refining industry contained within Title 40 of the U.S. *Code of Federal Regulations* at Part 419 (cited as 40 CFR 419), should be revised or updated. This study was conducted to meet EPA's obligations under Section 304(m) of the Clean Water Act (CWA), in accordance with a consent decree in *Natural Resources Defense Council et al v. Reilly* (D.D.C. 89-2980, January 31, 1992).

This report is a compilation of data collected during 1992 and 1993, and includes comparisons with data collected in the late 1970's which formed the basis of the existing limitations. The industry has changed significantly since the 1970's and this report summarizes and evaluates these changes.

1.2 Status of Categorical Regulations

EPA's effluent limitations guidelines and standards program was initiated as one of the major provisions of the 1972 Federal Water Pollution Control Act Amendments (Clean Water Act Sections 301, 304, 306, 307 and 501). Under these provisions, EPA is required to establish Best Practicable Control Technology Currently Available (BPT), Best Available Technology Economically Available (BAT), New Source Performance Standards (NSPS) and Pretreatment Standards for Existing Sources and New Sources (PSES and PSNS respectively) regulations for major industrial categories.

In 1974, EPA promulgated BPT and BAT effluent limitations guidelines as well as NSPS and PSNS for the petroleum refining industry. (US EPA, 1974a). These regulations were based on the information presented in the 1974 Development Document for the Petroleum Refining Category (US EPA, 1974b). Data included in this report were gathered from a number of EPA and American Petroleum Institute (API) sources to identify facilities and unit processes employed in this industry, to characterize their wastewater discharges, and to review the performance of wastewater treatment systems within the U.S. petroleum refining industry.

When the 1974 regulations were developed, EPA found that the industry could be divided into five discrete subcategories:

- Topping Refineries (Subcategory A)
- Cracking Refineries (Subcategory B)
- Petrochemical Refineries (Subcategory C)
- Lube Refineries (Subcategory D)
- Integrated Refineries (Subcategory E).

These subcategories are defined as follows:

Subcategory	Basic Refinery Operations Included
Topping	Topping and catalytic reforming whether or not the facility includes any other process in addition to topping and catalytic reforming. This subcategory does not include facilities which include thermal processes (coking, visbreaking, etc.) or catalytic cracking.
Cracking	Topping and cracking, whether or not the facility includes any processes in addition to topping and cracking, unless specified in one of the subcategories listed below.
Petrochemical	Topping, cracking and petrochemical operations, whether or not the facility includes any process in addition to topping, cracking and petrochemical operations[1], except lube oil manufacturing operations.
Lube	Topping, cracking and lube oil manufacturing processes, whether or not the facility includes any process in addition to topping, cracking and lube oil manufacturing processes, except petrochemical operations[1].
Integrated	Topping, cracking, lube oil manufacturing processes, and petrochemical operations, whether or not the facility includes any processes in addition to topping, cracking, lube oil manufacturing processes and petrochemical operations[1].

From the data, a size and complexity factor were determined, and for each individual refinery these factors are calculated to account for additional variations within each subcategory.

The BPT limitations determined in 1974 are based on both in-plant and end-of-pipe technology. BPT in-plant technology consist of control practices widely used within the petroleum refining industry, and includes the following:

- Installation of sour water strippers to reduce the sulfide and ammonia concentrations entering the treatment plant.

- Elimination of once-through barometric condenser water by using surface condensers or recycle systems with oily water cooling towers.

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[1] The term "petrochemical operations" means the production of second generation petrochemicals (i.e., alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e., BTX, olefins, cyclohexane, etc.) when 15 percent or more of refinery production is as first generation petrochemicals and isomerization products.

- Segregation of sewers, so that unpolluted storm run-off and once through cooling waters are not treated normally with the process and other polluted waters.

- Elimination of polluted once-through cooling water, by monitoring and repair of surface condensers or by use of wet and dry recycle systems.

BPT end-of-pipe treatment technologies consist of equalization and storm water diversion; initial oil and solids removal (API separators or baffle plate separators); carbonaceous (biochemical and chemical oxygen demand, i.e., BOD and COD) waste removal using biological treatment (activated sludge, aerated lagoons, oxidation ponds, trickling filter, or combinations of these); and effluent polishing (polishing ponds or sand, dual-media, or multi-media filters) following biological treatment (US EPA, 1974b).

The BPT and BAT limitations, as well as NSPS were established in 1974. The BPT and BAT limitations, as well as NSPS, were challenged in the U.S. Court of Appeals for the Tenth Circuit. On August 11, 1976, the Court upheld the BPT limitations and NSPS, but remanded the BAT limitations, including limitations issued to control storm water discharges from refineries, to EPA for further consideration.

In 1977, EPA began restudying the BAT and storm water regulations. To update the information needed to establish BAT effluent limitations guidelines for the petroleum refining category, questionnaires were sent to all refineries in the United States and its territorial possessions. The information obtained described petroleum refining industry wastewater treatment practices for the year 1976 (US EPA, 1982a).

Information received as a result of this questionnaire was combined with existing information from the 1974 rulemaking in order to develop an industry profile. This profile included number of plants, their size, geographic location, manufacturing processes, and wastewater generation, treatment, and discharge methods. Information on number, size, and geographic location of refineries was later updated with 1980 data from the U.S. Department of Energy (DOE).

In 1982, EPA determined that BAT for the petroleum refining industry was equivalent to the 1976 (existing) level of control (US EPA, 1982b). However, as a result of litigation, BAT limitations were revised in 1985 to reflect additional flow reduction basis and lower attainable concentrations for phenol and chromium.

For BAT limitations covering phenol and chromium, the revised regulation is based on the following flow model:

$$\text{FLOW} = 0.0021C + 0.0127A + 0.0236K + 0.0549L + 0.0212R$$

Where:

FLOW = Net process wastewater in million gallons/day
C = Sum of crude process rates in 1000 bbl/day
A = Sum of asphalt process rates in 1000 bbl/day
K = Sum of cracking and coking process rates in 1000 bbl/day
L = Sum of lube process rates in 1000 bbl/day
R = Sum of reforming and alkylation process rates in 1000 bbl/day

PSES final regulations were promulgated on March 23, 1977 (US EPA, 1977), codifying the interim final rule published along with BPT in 1974. These regulations established a daily maximum limitations for oil and grease and ammonia of 100 mg/L each. There are no current pretreatment standards for toxic pollutants.

1.3 Software Disk Available

The calculations for determining permit limitations are simplified somewhat in that Mr. Ed McHam of EPA's Region 6 has developed a software program (spreadsheet) to complete the required calculation. The final spreadsheet is available in Lotus 1-2-3® format, with text in WordPerfect®. The program determines categorical limits and water quality limits after input of process through-put information. EPA Engineering and Analysis Division will provide a disk upon request.

2. Description of the Industry

2.1 Production Operations

Generally, a simple petroleum refinery includes catalytic reforming and treating processes in addition to crude oil distillation. A more complex refinery also includes catalytic cracking, polymerization, alkylation and asphalt oxidation as well as other selected unit processes. A very complex refinery may include high vacuum fractionation, solvent extraction, de-asphalting, de-waxing and treating processes, in addition to those found in simple and complex refineries.

Although many minor products can be produced from crude oil by simple physical separation processes, such as fractional distillation, the proportions of each product may not match the desired values, or the quality may not be adequate for the use intended. Therefore, many sophisticated chemical process operations also take place in a petroleum refinery, in order to produce the distribution, quality and quantity of products desired.

The following paragraphs describe the basic processes that are used in petroleum refineries.

2.1.1 Crude Oil and Product Storage

Petroleum refineries require storage facilities for both crude oil and individual final products. The amount of storage required is quite variable, depending on the type and reliability of crude supply and on the location and nature of markets. The crude oil storage area of a refinery serves to provide a working supply, equalize process flow and separate water and suspended solids from the crude oil.

During storage, water and suspended solids in crude oil and, in lesser quantities, in products tend to settle out to form a water layer at the tank bottom. This is typically in the form of a sludge which, in the case of crude oil, usually contains foul sulphur compounds and high dissolved solids concentrations.

2.1.2 Crude Distillation

Distillation is the basic refining process for the separation of crude petroleum into intermediate fractions of specified boiling point ranges. This separation or fractionation takes advantage of the differing boiling points and vapor pressures of the various components in the crude oil mixture.

In addition to the atmospheric distillation process it is normally necessary to subject the residual or bottoms from atmospheric distillation to a second and/or third stage distillation, conducted under vacuum.

The steam applied at the various stages to the process is in direct contact with hydrocarbons. It is eventually carried over with various fractions and is separated out by gravity when the fraction is condensed. These steam condensates are invariably foul, and constitute a foul or sour condensate waste stream, containing sulphides, ammonia, chlorides, mercaptans and phenols.

2.1.3 Cracking

In this process, heavy oil fractions are converted into lower molecular weight fractions including domestic heating oils, high octane gasoline stocks and furnace oils. The cracking process increases the yield of gasoline taken from the crude oil and improves its quality. By using cracking, refiners can double their gasoline output per unit volume of crude oil charged to their distillation towers or stills.

The cracking is usually the largest single source of sour and phenolic wastewater in a large refinery. The wastewater is derived from the steam condensate from the overhead accumulator and condensate from steam stripping of side streams. The major pollutants are oil, sulphides, phenols, ammonia and traces of cyanides.

2.1.4 Hydrocarbon Rebuilding

Higher octane products for use in gasoline are manufactured by alkylation. In this process, small hydrocarbon molecules are combined into large molecules: the reverse of cracking. The resulting products are valuable components of high quality motor fuel and aviation gasolines.

This operation produces sour water, high in sulphides, mercaptans, ammonia, suspended solids and oils.

2.1.5 Hydrocarbon Rearrangements

Isomerization and reforming are two process techniques for obtaining higher octane gasoline blending stock. Isomerization, a molecular rearrangement process rather than decomposition process, generates no major pollutant discharge. Catalytic reforming produces aromatics from naptha in the presence of a catalyst by molecular rearrangement. Dehydrogenation is the primary reaction.

2.1.6 Hydrotreating

Hydrotreating processes are used to purify and pretreat various feedstocks by reacting with hydrogen. Product contaminants, including sulphur and nitrogen compounds, odor, color and gum-forming materials, are removed in this process.

Many different hydrotreating processes are used, depending on the feedstock and intended use of the product. Common applications include:

- Pretreatment of reformer feedstock
- Naphtha de-sulphurization
- Lube oil polishing
- Pretreatment of cat-cracking feedstock
- Heavy gas oil and residual desulphurization
- Naphtha hydrogenation.

The strength and quantity of wastewaters generated by hydrotreating is largely dependent upon the specific process and feedstock used. Wastewaters are derived as condensates from fractionating the product hydrocarbons and are mainly contaminated by ammonia and sulphur compounds.

2.1.7 Solvent Refining

Various chemicals and solvents are used to improve the quality of a particular feedstock component. The compounds removed or isolated by this process may be highly objectionable in the specific product being prepared, but may be desirable in making other products or may be converted into desirable materials. The major pollutants from solvent refining are the solvents themselves, many of which can produce a high BOD. Under ideal conditions the solvents are continually recirculated, but in practice some solvent is always lost, usually through leaks at pump seals and flanges. Oil and solvent are major wastewater constituents.

2.1.8 Asphalt Production

The reduced crude fraction or residual taken from the bottom of the vacuum still may be blended into heavy fuel oil or may be made into asphalt by oxidation in an asphalt still.

Wastewater is derived from steam added to the reactor for stripping volatiles, as well as a small quantity of water produced for oxidation reactions with the asphalt. The water separated out is very oily, high in BOD and usually sour as a result of the normally high sulphur content of the residual.

2.1.9 Lubricating Oil Manufacture

Lubricating oils require closely controlled properties and are generally only manufactured from special high grade feedstocks. However, even with high grade feedstocks, lube oils must be treated to remove asphalt, wax and hydrocarbons whose viscosity is temperature sensitive (generally aromatic compounds).

This operation produces acidic rinse waters and acid sludges for disposal, which are high in dissolved and suspended solids, sulphates and sulphonates and which form stable oil emulsions.

2.1.10 Production of Petrochemicals

These operations are extremely varied, and include production of a wide range of products such as alcohols, ketones, cumene, styrene, benzene, toluene, xylene, olefins, cyclohexane, etc. Many petrochemicals are manufactured directly, while others are derivatives from intermediate products. Wastewaters from these processes are quite variable and dependent upon the specific operations employed.

2.2 Industry Trends

EPA identified 256 refineries in 1976. Total average production that year was 16,357,000 barrels per day. During the subsequent 14 years, 64 refineries closed, or approximately 25 percent of the facilities. However, the production capacity only dropped 1,000,000 barrels per day (bbl/day), or approximately six percent. This is because most of the facilities that closed were small inefficient refineries. Their capacity was replaced by increasing production at the larger existing refineries. Table 2.1 presents a summary of the number of refineries, and their associated production rates by state. This table indicates that the number of refineries decreased in 26 states; there was no changes in refinery count in nine states; and the number of refineries actually increased in five states (Alaska, Arizona, Nevada, New Jersey, and Tennessee). Figure 2.1 graphically presents the number of refineries by state.

Table 2.1 Capacity and Number of United States Refineries in 1991 vs. 1976

State	1976 Facilities	1976 Total Capacity Crude (b/cd)	1991 Facilities	1991 Total Capacity Crude (b/cd)	Difference in No. of Facilities	Difference in Total Capacity
Alabama	4	54,250	4	154,250	0	100,000
Alaska	3	73,000	5	224,500	2	151,500
Arizona	1	5,000	2	14,210	1	9,210
Arkansas	4	61,000	3	60,470	-1	-530
California	33	2,269,600	30	2,150,555	-3	-119,045
Colorado	3	65,000	3	91,200	0	26,200
Delaware	1	150,000	1	140,000	0	-10,000
Florida	1	4,000	0	0	-1	-4,000
Georgia	2	17,000	2	35,500	0	18,500

Hawaii	2	100,300	2	143,050	0	42,750
Illinois	12	1,272,000	7	948,500	-5	-323,500
Indiana	6	605,820	4	428,900	-2	-176,920
Kansas	10	410,011	8	353,225	-2	-56,786
Kentucky	4	171,200	2	218,900	-2	47,700
Louisiana	21	2,108,173	19	2,299,241	-2	191,068
Maryland	2	30,500	0	0	-2	-30,500
Michigan	6	155,920	4	125,200	-2	-30,720
Minnesota	3	223,900	2	285,600	-1	61,700
Mississippi	5	346,200	5	358,600	0	12,400
Missouri	1	107,000	0	0	-1	-107,000
Montana	6	116,500	4	138,900	-2	22,400
Nebraska	1	5,380	0	0	-1	-5,380
Nevada	0	0	1	4,500	1	4,500
New Hampshire	1	15,000	0	0	-1	-15,000
New Jersey	4	671,000	6	499,250	2	-171,750
New Mexico	7	92,620	4	76,650	-3	-15,970
New York	2	107,000	1	39,900	-1	-67,100
North Dakota	3	60,006	1	58,000	-2	-2,006
Ohio	7	602,000	4	454,150	-3	-147,850
Oklahoma	12	560,400	7	409,500	-5	-150,970
Oregon	1	14,000	1	0	0	-14,000
Pennsylvania	9	800,200	7	741,300	-2	-58,900
Tennessee	0	0	1	75,000	1	75,000
Texas	46	4,231,135	31	3,882,200	-15	-348,935
Utah	7	158,500	6	154,500	-1	-4,000
Virginia	1	55,000	1	53,000	0	-2,000
Washington	8	379,950	7	523,225	-1	143,275
West Virginia	3	22,700	2	29,680	-1	6,980
Wisconsin	1	42,000	1	32,000	0	-10,000
Wyoming	13	194,002	4	122,900	-9	-71,102
Totals	**256**	**16,357,267**	**192**	**15,326,556**	**-64**	**-1,030,711**

Source: Thrash, 1991

Figure 2.1. Number of Refineries per State

In 1976, there were 44 indirect dischargers. As of 1990, 22 remained in operation.

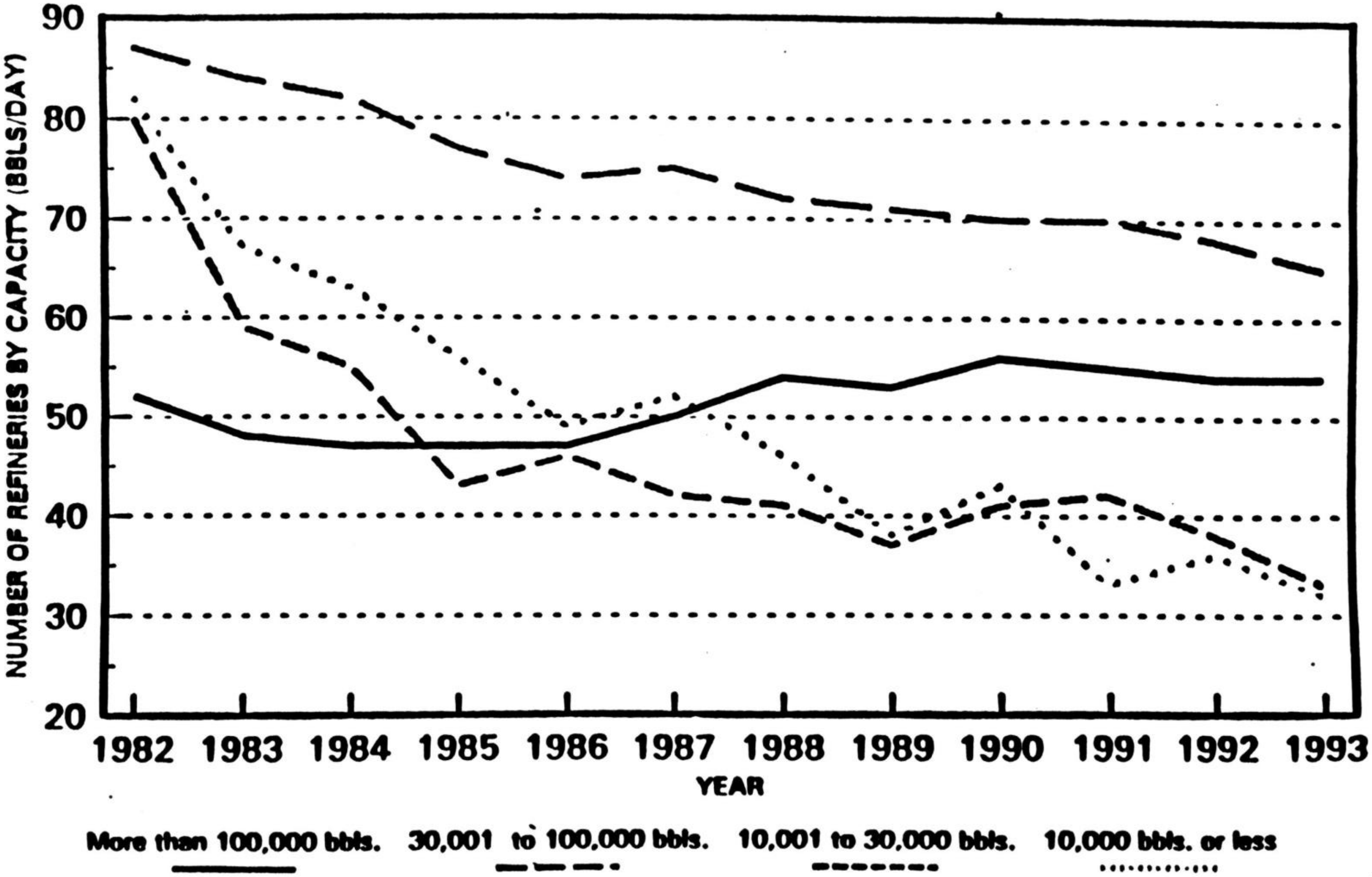
The data presented below indicate that the petroleum refining industry has been going through a consolidation, which has resulted in a large decrease in the number of refineries in the United States, but only a slight (six percent) decrease in production. Figure 2.2 graphically shows the number of refineries by capacity from 1982 through 1993. These data confirm that there has been a dramatic reduction in small refineries, and an increase in refineries with capacities over 100,000 bbl/day. It is expected that this trend will continue, with refineries continuing to close, but expansions occurring at others, keeping the total refinery capacity in line with demand for refinery products.

A factor affecting this industry is the addition and change of production operations. Although atmospheric and vacuum distillation, catalytic cracking, and their associated treating and reforming operations will remain the primary refinery operations, new production operations continue to be added. These include new innovative coking and desulphurization processes.

Many of these process changes occur as a result of the new gasoline reformulation rules designed to reduce the amount of volatile components in gasoline. These rules are causing refineries to make process modifications to their catalytic cracker units, as well as installing additional hydrotreaters and unit processes to manufacture additives. These improvements and changes may greatly effect the amount and quality of wastewaters generated by refineries.

Other process changes are being made to comply with 1990 Clean Air Act Amendments requirements, such as the lead phaseout rules, National Emissions Standards for Hazardous Air Pollutants (NESHAP) requirements covering benzene and hazardous organics and low sulfur diesel standards are in place or in the works.

Figure 2.2 Number of Refineries Since 1982
(Classified by Capacity)



Source: Energy Information Administration

3. Summary of Information Sources Used in This Study

The preponderance of information collected for use in this study was obtained from a number of readily available data sources. A description of these sources is contained below.

3.1 Oil And Gas Journal Survey

The *Oil and Gas Journal* publishes a list of all active U.S. and foreign refineries. For this study, the December 1991 report was used to provide an estimate of the number of refineries in use in the United States, their location and production capacity (Thrash, 1991). These data were used to show general industry trends since 1976.

3.2 EPA Office of Air and Radiation Questionnaire

EPA's Office of Air Quality Planning and Standards, in the Office of Air and Radiation (OAR), surveyed nine companies to obtain information on hazardous air pollutants (HAP) and volatile organic compounds (VOC) emissions from refineries. A total of 27 refineries were covered by the responses from these nine companies. For the purpose of this study, an additional data table was added to the survey form to request information on refinery production, process throughput, wastewater discharge rates, wastewater treatment systems and wastewater flow diagrams. The data from these 27 refineries (approximately 15 percent of the industry) have been used as a sample to represent the industry as a whole.

3.3 Plant Visits

EPA visited six refineries as part of this study. Four facilities in California were visited, which represent exemplary refineries in terms of water use and existing wastewater treatment technologies. One refinery in Texas and one in Pennsylvania were also visited to represent refineries that use greater amounts of process water or that did not have stringent water quality standards, but meet the existing effluent limitation guidelines. The data from these six sites have been used to obtain detailed data on site-specific water use practices and treatment system performance.

3.4 Permit Compliance System Data

EPA maintains a large computerized data base called the Permit Compliance System (PCS). This data base contains an inventory of National Pollutant Discharge Elimination System (NPDES) permittees, and discharge monitoring report (DMR) data supplied by industry permittees as part of their self monitoring program. (Generally DMR data are available on PCS only for certain facilities--major facilities as identified by their permit authorities). This data base contains DMR data on 137 refineries, and the data were used to estimate the levels of pollutants in refinery effluents for the reporting year of 1992.

3.5 Los Angeles County Sanitation Districts

Information from the Los Angeles County Sanitation Districts (LACSD) was provided for 14 refineries discharging into their municipal sewer system. These data were used to represent the status of refinery effluents to a sewer system with an exemplary pretreatment program.

3.6 Other Sewerage Authorities

Three additional sewerage authorities were contacted to obtain data on discharges from other indirect discharging refineries. These data were used to represent the pollutant levels of refinery discharges to smaller systems with less comprehensive pretreatment programs.

3.7 Province of Ontario, Canada Petroleum Study

Ontario's Ministry of Environment established the Municipal-Industrial Strategy for Abatement (MISA) Program in 1986 with an ultimate goal of achieving "virtual elimination" of the discharge of persistent toxic pollutants. As part of this program, the Ministry is setting sector (categorical) specific best available technology limitations. The petroleum refinery sector (industry) was identified as part of this program.

The data collected as part of this study (data on seven refineries) were used in this effort. The seven existing Ontario refineries collected extensive effluent quality data for a one year period on a full range of toxic pollutants. In addition, the refineries collected data on the presence of dioxins in the wastewaters from the regeneration of catalysts from their catalytic reformers. These data have been used to supplement the data collected on U.S. refineries.

3.8 Other Data Sources

Data from published literature, industry studies, previous effluent limitations guidelines studies and other EPA studies have been collected and also used in this study.

4. Treatment Technologies Used in The Industry

Historically (prior to the 1960's), process operations used large quantities of water, and often simple oil separation constituted end-of-pipe treatment. In fact, API separators were originally installed to economically recover oil rather than treat wastewater discharges. When EPA studied this industry in the early 1970's, secondary biological treatment was becoming common, and certain in-plant controls were becoming industry standards. These included sour water stripping and the replacement of barometric condensers with surface condensers.

As a result of the early 1970's studies, EPA promulgated the BPT and NSPS regulations in 1974 that were production-based mass limitations based upon the following technologies:

In-Plant Controls

- Installation of sour water strippers to reduce the sulfide and ammonia concentrations entering the treatment plant.
- Elimination of once through barometric condenser water by using surface condensers or recycle systems with oily water cooling tower.
- Segregation of sewers, so that unpolluted storm run-off and once through cooling waters are not treated normally with the process and other polluted waters.
- Elimination of polluted once through cooling water, by monitoring and repair of surface condensers or by use of wet and dry recycle systems.

End-of-Pipe Treatment

- Equalization
- Additional oil separation using dissolved air flotation (DAF)
- Biological treatment
- Polishing (polishing ponds, sand filtration).

EPA's 1982 BAT rulemaking confirmed the use of the above technologies as the framework for setting effluent limitations guidelines for priority pollutants. However, further water reduction had been experienced between 1972 and 1976, the years data had been collected by EPA. The new flow data was used to develop a revised (BAT) flow model, which formed the basis for more stringent chromium and phenolic production-based mass limitations.

The following subsections describe the technologies used by the petroleum refinery industry, the performance expected by them, and industry trends since the 1982 EPA rulemaking.

4.1 In-Plant Controls

In-plant technologies for refinery wastewater include steam stripping, neutralization, and source control. Table 4.1 summarizes the in-plant treatment technologies currently in use for treating wastewaters generated from specific refinery operations. A description of the technologies is contained below.

4.1.1 Steam Stripping

Sour waters generally result from water brought into direct contact with a hydrocarbon stream. This occurs when steam is used as a stripping or mixing medium or when water is used as a washing medium. Sour waters contain sulfides, ammonia, phenols and other organic chemical constituents of the crude oil.

The most common in-plant treatment for sour waters is steam stripping (i.e., sour water stripping). Sour water stripping is a gas-liquid separation process that uses steam or flue gas to extract the gases (sulfides and ammonia) from the wastewater. The stripper itself is a distillation-type column containing either trays or packing material. Columns range from simple one-pass systems to sophisticated reflux columns with reboilers.

In removing sulfides and ammonia, the efficiency of sour water treatment processes is greatly influenced by pH. In general, sour water strippers remove between 85 and 99 percent of the sulfides present. However, when the pH is lowered by means of acid treatment, stripping efficiency is increased. On the other hand, when caustic is utilized to maintain high pH, up to 95 percent ammonia removal can be achieved. By considering pH in the stripping process, one can either adjust the pH to optimize removal of one or another of sulfides or ammonia, or use a two stage sour water stripping process to obtain maximum removal of both pollutants.

Steam stripping can also be used to remove volatile organic compounds from selected refinery wastewater streams that have high concentrations of these pollutants. Stripping of the organic constituents of the wastewater stream occurs because the organic volatiles tend to vaporize into the steam until its concentration in the vapor and liquid phases (within the stripper) are in equilibrium. The height of the column and the amount of packing material and/or the number of metal trays along with steam pressure in the column generally determine the amounts of volatiles that can be removed and the effluent pollutant concentration levels that can be attained by the stripper.

Table 4.1 Demonstrated Wastewater Technologies for In-Plant Treatment of Refinery Process Streams

Refinery Operation	Technologies
Crude Desalting	Stripped sour water as makeup to the desalter
Atmospheric and Vacuum Distillation	Sour water stripping. Sour water can be recycled through crude desalters prior to processing in sour water strippers.
Thermal Cracking	Sour water stripping.
Catalytic Cracking	Sour water stripping.
Hydrocracking	Sour water stripping.
Polymerization	Neutralization
Alkylation	Acid recovery; neutralization.
Isomerization	Generally not pre-treated.
Catalytic Reforming	Granular activated carbon for removal of CDDs/CDFs.*
Solvent Refining	Generally not pre-treated.
Hydrotreating	Generally not pre-treated.
Grease Manufacturing	Generally not pre-treated.
Drying and Sweetening	Neutralization with acid or FCCU regenerator flue gas.
Lube Oil Finishing	Generally not pre-treated.
Blending and Packaging	Generally not pre-treated.
Equipment Cleaning; Spills; Miscellaneous	Segregation; slop oil tank.
Utilities	Equalization of ion exchange regeneration wastes; others generally not pre-treated.

* Presently, there is very limited capacity in the U.S. to regenerate carbon loaded with CDDs/CDFs.

4.1.2 Neutralization of Spent Acids and Caustics

Spent caustic solutions are generated by various finishing wet treatment processes aimed at neutralizing and extracting acidic materials occurring naturally in crude, acidic products from various chemical treatment steps, and acidic materials produced in cracking processes. Spent caustics generally contain sulfides, mercaptans, sulfates, sulphonates, phenols and naphthionic acids. The phenol concentrations, in particular, may be high enough to warrant processing of spent caustic for the recovery of phenols.

Spent acid is reclaimed on site or returned to the vendor for reclamation. if the bottoms are then sent to crude desalting, the high phenol content may be recovered within the process by extraction.

4.1.3 Source Control

Source control measures to minimize wastewater generation and contamination can significantly reduce the volume of effluent and the amount of pollutants discharged from refineries. Such measures include water use reduction, and wastewater reuse and recycle.

Along with several general measures to reduce water use, major wastewater discharge reduction techniques address segregation, boiler condensate recovery, and treated effluent reuse. A report entitled "Water Reuse Studies" (API, 1977) discusses the practicality (and costs) of specific wastewater reduction techniques. Another study, "Wastewater Reuse and Recycle in Petroleum Refineries" (Langer, 1983) also presents information on this topic. The Langer study investigated 15 U.S. refineries: three refineries were considered to be exemplary and the remaining 12 were candidates for further effluent discharge volume reduction programs. The report identifies specific wastewater reduction techniques with their anticipated effectiveness and associated costs. A summary of the findings from these studies is presented below.

4.1.4 Wastewater Segregation

Segregation of refinery wastewaters is important to allow for reuse of wastewaters with little or no treatment. Additionally, segregation of severely contaminated streams provides the opportunity for pretreatment, thus reducing the effects of dilution and contamination of the overall combined process wastewater stream. The API study recommended dividing streams into three groups, by level of contamination. The first stream is high quality and is suitable for reuse with only minimal treatment, if any. The second stream has low total dissolved solids (TDS) and requires some treatment prior to reuse, and the final stream, which has high TDS, is not suitable for reuse and requires complete treatment before discharge.

4.1.5 Boiler Condensate Recovery

Boiler steam condensate recovery and reuse can also significantly reduce the amount of boiler circuit wastewater requiring discharge. (Note: Many refineries are already recovering and reusing as much condensate as economically feasible.) Specific measures include the following:

- Increase condensate recovery by the installation or expansion of piping systems to collect steam lost by overheating, tracing, tank heating, traps, utility and leaks.

- Reduce vent losses by the elimination of vents at process units, turbines and steam traps.

4.1.6 Treated Effluent Reuse

For high quality wastestreams, the wastewater may be suitable for direct reuse in cooling systems or for steam generation without treatment. Other examples of reuse (with little or no treatment) include using sour water as make-up for desalters and acid gases for the neutralization of spent caustic solutions.

In the Langer report, several uses of treated effluent were identified. These included wastewater reuse for: exchanger and barometric condenser cooling, dampening of coke fines for dust control, firewater, service water and wash water, pump gland cooling, and other machine cooling processes. Once-through cooling water can be reused as make-up for desalters, cooling towers, or as process water, but may be unsuitable without prior treatment.

4.1.7 Other General Measures

Other general measures for the reduction of wastewater generation include:

- Conversion of barometric condensers to surface condensers.
- Improved management of firewater and wash water systems including the elimination of losses from overflowing sumps, freely running hoses, temporary exchange coolers, and underground leakage.

4.1.8 Cooling Water Systems

Historically, the primary factor considered in selecting cooling water systems was the availability of water and its associated cost. However, impacts of thermal discharges, water conservation, and compliance with discharge limitations have also become relevant considerations. The advantages and disadvantages of different cooling systems are presented in Table 4.2.

Table 4.2 Advantages and Disadvantages of Different Types of Cooling Systems

Factor	Once-Through Cooling Water	Cooling Tower	Air Cooling
Noise	None	low	high
Cold Weather Plumes	none	potential problem	none
Water Contamination Potential from Leaks	high	moderate	none
Soil Contamination Potential from Leaks	low	low	low
Air Contamination Potential	none	moderate	moderate
Cooling Efficiency	high	moderate to high	low to moderate
Energy Required	moderate	high	high
Maintenance and Labor	low	high	low
Potential for Impact for Thermal Shock to Fish	moderate to high	none	none
Potential for Impact of Water Treatment Chemicals	moderate	moderate	none
Costs	low	high	high

Although cooling water can be completely eliminated by converting to 100 percent air cooling systems, this may be impractical or uneconomical for some refineries due to space availability and the orientation of the heat exchanger systems. There are also real process limitations in that many processes designed for cooling water systems (more efficient cooling systems) can not be retrofitted for air cooling systems.

4.1.9 Once-Through Cooling Water Systems

In once-through cooling water (OTCW) systems, due to the use of chlorine and chlorine derivatives as additives, dechlorination using sulfide or sulfite compounds may be necessary to remove residual chlorine. In recent years, as concerns about the environmental impacts of chlorine and chlorination by-products have increased, the use of bromine an bromine compounds for OTCW treatment has also received consideration.

4.1.10 Cooling Tower Systems

There are several methods to minimize cooling tower blowdown streams. Cooling tower blowdown can contribute up to one third of total refinery wastewaters. Although cooling tower systems vary from plant to plant, the following general recommendations were made in the study to reduce cooling tower blowdown:

- Recycle cooling water from pumps, compressors, and sample boxes that use blowdown.
- Replace existing oil-leaking pump gland packing with mechanical seals to permit collection and recycle of blowdown to cooling tower.
- Reduce use of pump gland cooling water where presently overused or eliminate service completely.
- Upgrade maintenance of existing systems to reduce leakage and sump overflow.

Refineries can pretreat raw water to improve the initial quality of the influent which in turn will significantly increase the number of reuse cycles in cooling towers and reduce blowdown amounts. The toxicity of the blowdown can also be reduced. Water treatment chemicals containing zinc and chromate compounds used in the recirculating waters can be replaced with less toxic organic compounds. In the last ten years chromates have been virtually eliminated by substitution for less toxic chemicals. Zinc levels in the effluent discharge average 0.15 mg/l as shown in Table 4.5.

4.2 End-of-Pipe Treatment Technologies

All wastewater treatment that immediately follows the oil/water gravity separators (API or oily water separator) is considered end-of-pipe treatment. (The API separator is recognized as part of the refinery process equipment for the economic recovery of oil and, as such, is not considered a treatment unit.) Conventional end-of-pipe treatment technologies are addressed in this section and are classified as preliminary, biological, and effluent polishing.

4.2.1 Preliminary Treatment

Preliminary treatment commonly consists of equalization, followed by chemical treatment and supplemental oil removal. Filtration may also be included as part of the preliminary treatment system to limit the loading of soils to downstream units.

Equalization is one of the first, and one of the most important steps in the treatment of wastewater. Fluctuations in contaminant concentrations are leveled and the flow and pH of the waste stream are adjusted to provide the optimum conditions for further treatment. Unusually high flows or high contaminant concentrations, which cannot be handled by equalization, may be diverted to auxiliary holding facilities and slowly re-introduced in the treatment system when conditions warrant.

Supplemental oil removal is often accomplished by using parallel plate separators or chemically assisted dissolved air flotation (DAF) units, whereby emulsified oil in the waste stream is dispersed and removed. A parallel plate separator is a device which is very similar to the API separator. It was developed to improve oil and solids removal by mounting parallel plates at an angle along the length of the separator. By vastly increasing surface area, this device permits more efficient collection of oils and solids.

Dissolved air flotation consists of saturating a portion of the wastewater feed, or a portion of the feed or recycled effluent from the flotation unit, with air. The wastewater or effluent recycle is held at elevated pressure, typically for one to five minutes, in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles in the wastewater in the flotation chamber. This results in agglomerates which rise to the surface to form a froth layer.

Chemical flocculation agents, such as salts of iron and aluminum, with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification. Induced air flotation (IAF) is similar to DAF systems but IAF adds air to a flotation tank by using impellers rather than by adding dissolved air to a recirculation tank.

Chemical precipitation can be used to remove metals from selected refinery wastewater streams, such as cooling tower blowdown. Most metals are relatively insoluble as hydroxides, sulfides, or carbonates, an can be precipitated in one of these forms. The sludge formed is then separated from solution by physical means such as clarification or filtration. Hydroxide precipitation is the conventional method of removing metals from wastewater. Most commonly, caustic soda (NaOH) or lime ($Ca(OH)_2$) is added to the wastewater to adjust the pH to the point where metal hydroxides exhibit minimum solubilities and are thus precipitated. Sulfide precipitation has also been demonstrated to be an alternative to hydroxide precipitation for removing metals from certain wastewaters. Sulfide, in the form of hydrogen sulfide, sodium sulfide, or ferrous sulfide, is added to the wastewater to precipitate metal ions as insoluble metal sulfides.

4.2.2 Biological Treatment

Biological treatment is the basic process for treating oxygen-demanding compounds, usually measured as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). There are a number of variations of which the most common are described below.

- Oxidation Ponds. The oxidation pond is practical where land is plentiful and relatively inexpensive. An oxidation pond has a large surface area and a shallow depth, usually not exceeding two meters. These ponds have long detention periods of 11 to 110 days. This process is not reliable in very cold climates.

- Aerated Lagoons. The aerated lagoon is a smaller, deeper oxidation pond equipped with mechanical aerators or diffused air units. The addition of oxygen enables the aerated lagoon to have a higher concentration of microbes than the oxidation pond. Where effluent standards are stringent, final clarification is necessary. However, since the effectiveness of conventional clarification on such effluent is often poor, filtration may be necessary to comply with limitations. However, refiners have often addressed this problem by adding polishing ponds after the lagoon.

- Trickling Filters. A trickling filter is an aerobic biological process. It differs from other processes in that the biomass is attached to the bed medium, which may be rock, slag or plastic. When the biomass reaches a certain thickness, part of it sloughs off. When the filter is used as the major treatment process, a clarifier is used to remove the sloughed biomass.

- Rotating Biological Contactors (RBCs). RBCs are analogous to trickling filters, in that they are fixed-film reactors. Bacterial slime is grown on plastic discs rotating through the wastewater. Approximately half of the circular disc is out of the water at any one time, being aerated, and half is under water supporting biological growth.

- Activated Sludge. Activated sludge is an aerobic biological treatment process in which newly grown and recycled microbial biomass are suspended uniformly throughout a holding tank to which raw wastewaters are added. Oxygen is introduced by mechanical aerators, diffused air systems or a combination of the two. The organic materials in the waste are removed from the aqueous phase by the microbial biomass and stabilized by biochemical synthesis and oxidation reactions. The basic activated sludge process consists of an aeration tank followed by a clarification step.

4.2.3 Effluent Polishing

The function of effluent polishing is to remove residual suspended solids (biological floc) which may be carried over from the clarification step. The biological floc will add BOD and certain toxic organic compounds (which are adsorbed onto or absorbed into the floc) to the final effluent, and must be removed.

Most end-of-pipe treatment systems at petroleum refineries include effluent polishing in the form of polishing filters, polishing ponds, or both. Effluent polishing filters are often single-media (sand), however, dual-media (sand, anthracite) and multi-media filters are also used. Both gravity and pressure filtration systems are utilized in refinery applications.

Polishing ponds can be equipped with baffles and oil skimmers on overflows to remove traces of free oil which may have evaded upstream treatment systems. In the event that the final effluent does not meet discharge limitations or standards, some refinery treatment systems allow the transfer of effluent from the polishing ponds back to preliminary treatment.

4.2.3 Activated Carbon Treatment

There are two forms of activated carbon treatment, Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC). Each is discussed below.

- Granular Activated Carbon. Adsorption on granular activated carbon (GAC) is currently being used for effluent polishing following biological treatment at some refineries to remove trace level toxic organic pollutants, and at least three U.S. refineries to meet bioassay permit requirements based on toxicity for trout or fat-head minnows.

  The adsorption process typically requires preliminary filtration or clarification to remove suspended solids. Next, the wastewaters are placed in contact with carbon so adsorption can take place. Normally, two or more beds are used so that adsorption can continue while a depleted bet is reactivated. Reactivation is accomplished by heating the carbon to 870° to 980°C (1600° to 1800°F) to volatilize and/or oxidize the adsorbed contaminants.

- Powdered Activated Carbon. This technology consists of the addition of powdered activated carbon (PAC) to biological treatment systems. The adsorbent quality of the carbon aids in the removal of soluble organic materials in the biological treatment unit. This treatment technique also enhances color removal, clarification and system stability. BOD and COD removal may be enhanced but, it is not certain, depending on the treatment system. This treatment technology is currently being used at one U.S. refinery at least.

4.2.5 Technologies Used at EPA/OAR Survey Refineries

A summary of the treatment technologies that are in place at the 27 refineries covered by the OAR survey plants is presented in Table 4.3. Of the 27 refineries, 20 are direct dischargers and 7 are indirect dischargers. All of the 20 direct discharging refineries have some form of biological treatment. Three have sand filtration and one facility has an in-plant activated carbon system in addition to biological treatment.

Table 4.3 Summary of Current Wastewater Treatment Technologies for 27 Refineries Surveyed

	Treatment Type	Direct Discharge Refineries (total 20)	Indirect Discharge Refineries (total 7)
In-Plant Controls	Oil-Water Separator	15	4
	Stripper	16	5
	Oxidizer	2	0
	Activated Carbon	1	1
Primary Treatment	API Separator	9	5
	Air Flotation	5	1
	Coagulation	1	0
	Chemical Precipitation	1	0
	Dissolved Air Flotation	10	1
	Equalization	16	4
	Flocculation	1	1
	Grit Chamber	0	1
	Gas Flotation	0	1
	Induced Air Flotation	4	2
	Settling & Skimming	0	1
Secondary Treatment	Activated Sludge Unit	11	0
	Bio Treatment Ponds	6	2
	PAC Bio-Treatment	1	0
	RBC's	1	1
	Secondary Clarifier	12	0
	Lagoons	3	0
	Filtration (Media & Sand)	3	1
	Aeration & Other Biological Treatment	5	0

Source: EPA Office of Air and Radiation Survey (1992)

4.2.6 Performance of End-of-Pipe Systems

There are virtually no available data from this industry on the performance of individual treatment units within a treatment system. Therefore, performance must be assessed using effluent data only. However, since most direct discharging plants use the basic treatment train of preliminary treatment (oil removal), biological treatment and effluent polishing (filtration or ponds), effective comparisons of performance can be made using effluent data.

Table 4.4 presents a summary of the effluent data collected from the six refineries visited as part of this study, and compares the pollutants covered by BPT with the concentrations used as a basis to develop BPT limitations in 1974. Table 4.5 summarizes effluent concentration data for a number of pollutants obtained from the following three data sources:

- Average concentration data (over a one-year period) collected during Canada's "Seven Refineries Study" conducted in 1989,

- Long-term average data collected from seven U.S. refineries during the Canadian study,

- A summary of PCS data from 138 direct discharging refineries for 1992.

EPA's PCS system was accessed for priority pollutant data only. The data in this table indicate higher levels of priority pollutants in the PCS data base for chromium (in 1991 only), benzene, toluene, copper and nickel than from the other data sources.

Table 4.4 Summary of Effluent Data: Six Site Visits, 1992

Pollutant Average Values (in mg/l)	4 California Refineries	Pennsylvania Refinery	Texas	BPT/BAT Equiv.* Concentrations
TSS	8.75	11	12	10
COD	--	51	59.5	
Oil & Grease	2.7	2.7	4.2	5
NH_3 (as N)	1.43	0.94	1.42	
Sulfide	< 0.05	0.14	0.018	0.1
Phenols (4AAP)	< 0.02	0.005	0.012	0.1
Chrome, Total	< 0.02	0.02	0.015	0.25
Lead	0.012	0.002	<0.001**	
Zinc	0.04	0.147	.025**	
Benzene	ND	--	<.005**	
Toluene	ND	--	<.005**	
Naphthalene	ND	--	--	
Copper	0.01	0.011	.013**	
Nickel	0.033	--	.039**	
Selenium	0.06	0.006	.008**	

Notes:
* These are concentrations used as a basis to develop the BPT production-based mass limitations using the BPT flow model.
** Data from permit renewal application (March 1993)
ND Non Detectable
-- No Data

Table 4.5 Summary of Refinery Effluent Data: Canadian Study and PCS Data

Pollutant (mg/l)	Canadian Study[1]		138 U.S. Refineries PCS Data (1992)[2]	
	Average of 7 Ontario Refineries	Average of 7 U.S. Refineries	Low	High
TSS	22	31	22.3	22.6
COD	49.2	85	93.1	93.1
Oil & Grease	2.17	4.08	3.34	3.42
NH_3 (as N)	1.7	5.21	4.83	4.83
Sulfide	0.08	< 0.03	0.044	0.052
phenols (4AAP)	0.0110	0.047	0.038	0.040
Chrome, Total	0.0068	0.028	00.011	0.013
Lead	0.0041		0.004	0.006
Zinc	0.29	0.09	0.15	0.15
Benzene	0.0008	< 0.005	0.0008	0.001
Toluene	0.0007	< 0.004 (max)	< 0.02	0.003
Naphthalene	0.0011	< 0.003 (max)	--	--
Copper	0.0048	< 0.012	0.0106	0.0112
Nickel	0.0034	< 0.08	0.0159	0.0166
Arsenic	0.009	--	0.202	0.202
Cyanide	0.007	--	0.041	0.041
Selenium	0.005	--	0.145	0.145

Notes

1. Source: Best Available Treatment Technology for Ontario Petroleum Refining Sector, August 1991.
2. Source: Appendix 1 and 2. Low non-detects equal zero, High non-detects equal one-half detection.

-- No Data

4.2.7 Storm Water Management

Storm water management at petroleum refineries can have a significant bearing on the mass discharge of conventional and toxic pollutants to receiving waters. In addition to increasing wastewater volumes, stormwater also often contributes high levels of total suspended solids (TSS).

Under ideal circumstances, all stormwater should be segregated into the categories identified in Table 4.6 and treated or discharged as indicated.

Storm water segregation can easily be incorporated into grass roots refineries, however, segregation at existing refineries can be difficult. Segregation measures may include sloped or curbed process unit pads, individual or discrete drain and piping systems, and holding ponds for testing and controlled releases of wastewater to treatment systems or direct discharge points.

Table 4.6 Refinery Storm Water Management Practices

Refinery Area	Storm Water Management
Immediate process areas	Collection and co-treatment with refinery process wastewaters.
Developed areas of refinery, but outside immediate process areas	Segregation, collection and diversion to storm water holding pond equipped with oil baffles and skimmers. Controlled discharge after examination and testing.
Undeveloped areas	Segregation and direct discharge.

5. Water Use

Historically, U.S. petroleum refineries have been large water users. Water is used for contact and non-contact cooling, steam production, and in process operations such as desalting. Up until the early 1970's, barometric condensers were commonly used, which generated large quantities of contaminated wastewater. However, during the 1970's, barometric condensers were mostly replaced by surface condensers which has eliminated this water source.

Since 1972 (the year of the original EPA study of this industry), the petroleum refining industry has been steadily reducing the amount of water that it uses, and consequently discharges. Figure 5.1 (from EPA's 1982 Development Document for this industry) presents water use in this industry from 1972 projected to 1984 as a percent of the water use in 1972. This graph indicates a steady reduction of water use, such that only 45 percent of the water used in 1972 was projected to be used in 1984. The BAT regulations promulgated in 1982 did not require any further flow reductions, however, as a result of litigation, the 1986 amendment to BAT and NSPS incorporated additional flow reduction as part of the basis for limitations for phenol and total chromium.

Since the early 1980's, it is believed that refineries have continued to undertake flow reductions. Data collected as part of this study show water use at many refineries well below 50 percent of the flows predicted by the BPT and BAT flow models. Some refineries are as low as 15 percent of their water use rates predicted by the BPT flow model. Table 5.1 presents a water use comparison for the 27 refineries surveyed in the EPA/OAR refineries survey between reported water use and that predicted by the BPT and BAT flow models. The water use rates shown in Table 5.1 for the 27 refineries average 62 percent of their predicted BPT flows, and 66 percent of their BAT predicted flow rates.

Further review of the data presented in Table 5.2 indicates that the unit process water use basis for the BPT and BAT flow models may not represent actual refinery practices. As can be seen in Figure 5.2, the flows predicted by the BPT and BAT flow models for a given refinery can vary by a factor of over 2 to 1. Although the model accounts for some of this difference, many refineries have reduced water consumption by using techniques not directly related to specific refining processes. Techniques such as water reuse, condensate recovery, elimination of leaks, etc., are not necessarily process unit-specific.

Figure 5.1   Water Use Trends

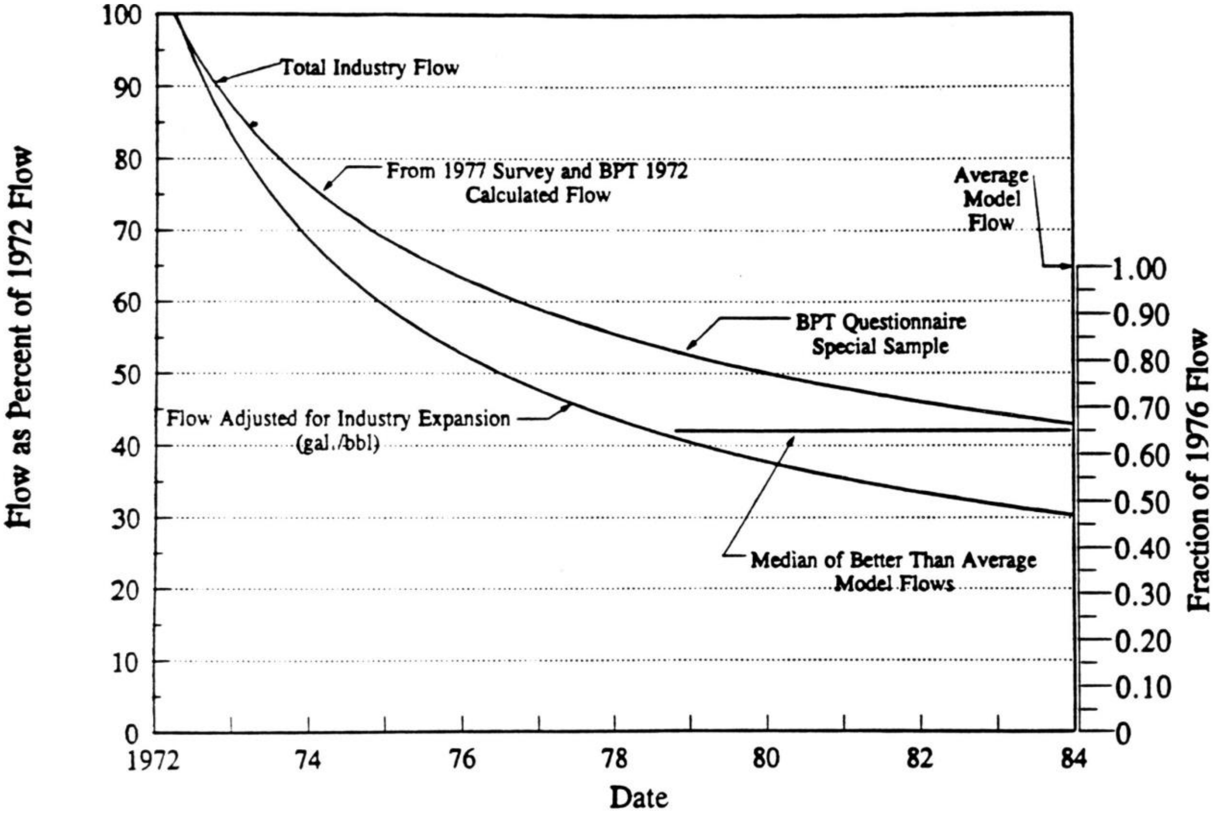
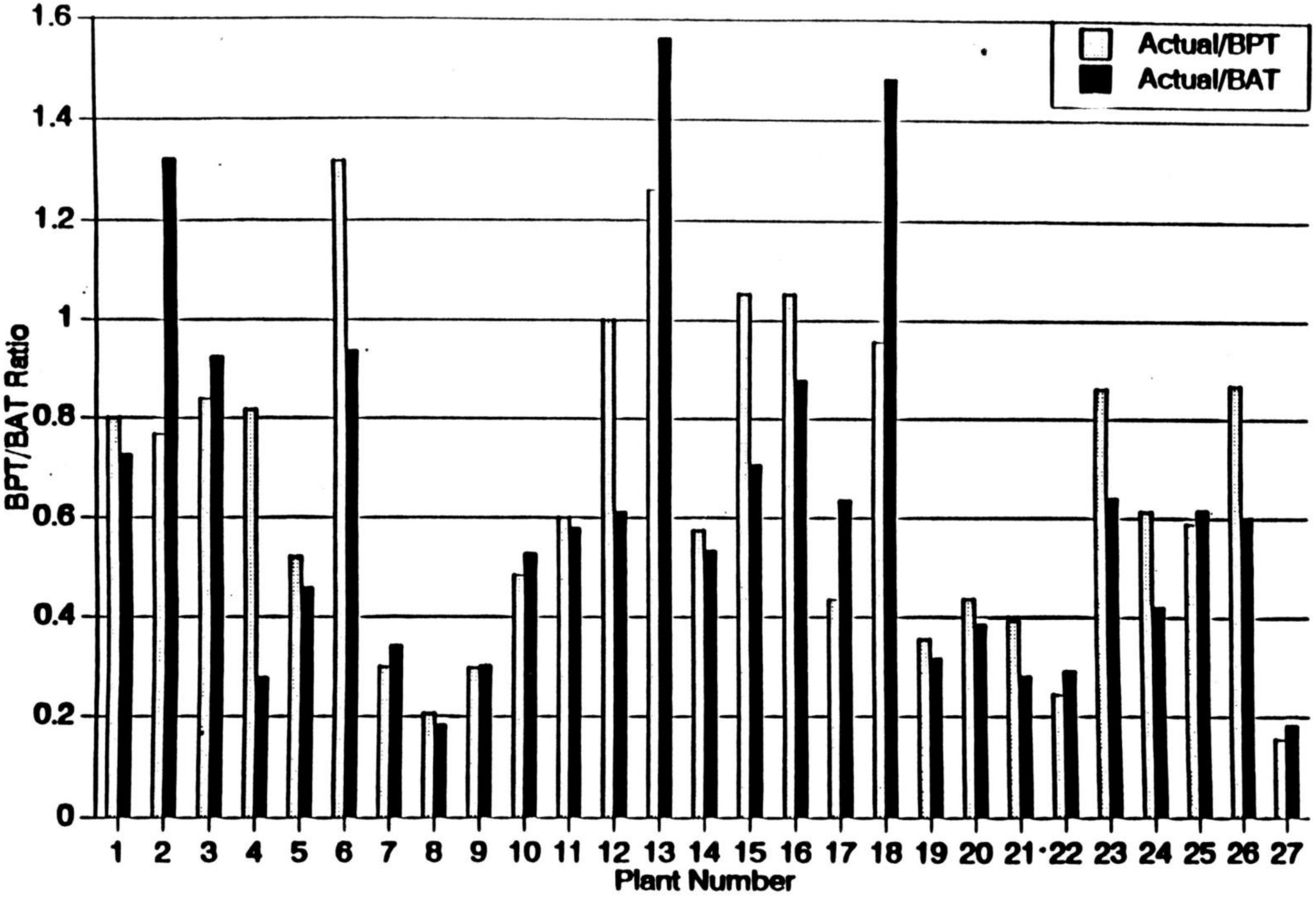


Table 5.1 Predicted and Actual Wastewater Flows for 27 Refineries in Ascending Order of Actual/BPT Ratio

No.	Refinery	Size (bbl/day	BPT Subcategor	BPT Flow (MGD)	BAT Flow (MGD)	Actual Flow (MGD)	$	Ratio Actual/ BPT	Ratio Actual/ BAT
8	50202	111,765	D	4.40	3.90	0.80	*	0.18	0.21
27	50801	64,000	B	2.20	2.60	0.40		0.18	0.15
4	50102	45,400	A	1.45	0.49	0.40		0.28	0.82
21	50602	127,600	B	3.80	2.70	1.06		0.28	0.39
22	50603	100,000	B	2.70	3.20	0.78		0.29	0.24
9	50301	255,000	B	9.00	9.10	2.70		0.30	0.30
19	50503	209,966	E	7.00	6.20	2.20		0.31	0.35
7	50201	46,467	D	1.50	1.70	0.51		0.34	0.30
20	50601	74,200	B	1.43	1.26	0.55		0.38	0.44
24	50703	161,500	B	6.20	4.24	2.60		0.42	0.61
5	50103	316,600	B	14.40	12.57	6.60		0.46	0.53
10	50302	50,000	B	1.14	1.24	0.60	*	0.53	0.48
14	50402	175,877	B	5.45	5.05	2.90		0.53	0.57
11	50303	70,000	B	2.80	2.70	1.62	*	0.58	0.60
26	50705	120,300	B	6.20	4.30	3.73	*	0.60	0.87
12	50304	68,381	D	1.80	1.10	1.10		0.61	1.00
25	50704	151,359	C	4.60	4.80	2.83		0.62	0.59
17	50501	22,319	D	0.63	0.92	0.40	*	0.63	0.43
23	50701	217,200	D	12.67	9.41	8.10		0.64	0.86
15	50403	132,187	D	4.67	3.13	3.30		0.71	1.05
1	50001	73,100	B	2.07	1.88	1.50		0.72	0.80
16	50404	44,000	B	1.14	0.95	1.00		0.88	1.05
3	50101	57,000	B	1.30	1.43	1.20	*	0.92	0.84
6	50104	187,033	D	8.44	6.00	7.90		0.94	1.32
2	50002	50,000	B	2.50	4.30	3.30	*	1.32	0.77
18	50502	105,000	B	2.84	4.40	4.21		1.48	0.96
13	50401	45,856	B	0.96	1.19	1.50		1.56	1.26
Totals				113.29	100.76	63.79	**Avg:**	0.62	0.66

* Discharge to POTW
Actual flow = Facilities total washwater flow - (stormwater and once through cooling water)

Figure 5.2. Comparison of Flow Predicted by BPT and BAT Models



The EPA/OAR survey obtained water use information from the 27 refineries surveyed. Each facility supplied a water balance diagram from which specific water flows were obtained. Table 5.2 summarizes these data. Flow information for the wastewater sources are summarized below:

Water Source	**Percent of Total Discharge**
Sour water stripper	19.6
Ballast water	4.2
Cooling tower blowdown	18.4
Pump compressors	1.94
Boiler blowdown	6.9
Water treatment	3.1
Desalter	20
Land farm	0.02
Cat. Reformer Scrubber	2.2
Tank draw down	2.4
Total	78.76

The remaining 21 percent cannot be accounted for. This is because most refineries do not have flow monitoring stations at their in-process discharge points, and therefore cannot complete a detailed water balance.

Data on water use was also collected from the six refineries visited as part of this study. Water use, as compared to their BPT and BAT flow model rates, is shown in Table 5.3. The four California refineries average 0.46 of their BPT flows, and 0.67 of their BAT model flows. The Texas and Pennsylvania refineries average 1.17 of their BPT model flows and 1.08 of their BAT model flows. Refineries located where there are water shortages and/or stringent local water quality standards have made great strides in reducing water usage.

Environmental concerns have driven refineries to produce additional, significant wastewater as a result of compliance efforts.

- Resource Conservation and Recovery Act (RCRA) or Clean Air Act regulations have resulted in refineries closing certain wastewater ponds, which has reduced evaporation of wastewater in the system.

- The need to more frequently and more rigorously test tank and pipeline integrity produces large quantities of hydrotest water, up to several million gallons at a time.
- Some refineries have discovered groundwater contamination (due to past failures in tank or pipeline integrity). To remediate this contamination may generate up to several million gallons of groundwater per day, which may need to be treated and discharged through the NPDES outfall.
- Additional U.S. Coast Guard requirements for accepting ballast water from vessels.

Table 5.2 Selected Sources of Wastewaters

Facil. No.	BPT Sub.	Dry Wt Process Flow*	Wastewater Sources in gallons per day										
			Stripper	Ballast	Cooling Tower Blowdn	Pumps Com-press.	Boiler B.D.	Storm	Water Treatmt	Desalter	Land Farm	Cat Reform Scrub	Tank Draw Down
50001	B	0.44	270,720	30,420	139,680	N/A	30,240		N/A	86,000	N/A	23,040	3,600
50002	B	3.3	N/A	N/A	N/A	N/A	N/A	6,067	N/A	N/A	N/A	N/A	N/A
50101	B	1.4	N/A	23,040	191,520	27,340	158,400	N/A	N/A	130,000	0	14,247	1,370
50102	A	0.40	None	N/A	28,800	N/A	21,600	604,800	N/A	144,000	N/A	N/A	28,800
50103	B	6.6	1,022,400	20,000	706,000	None	None	1,380,000	N/A	N/A	N/A	28,800	864,00
50104	D	6.57	475,200	N/A	N/A	N/A	N/A	476,640	N/A	N/A	N/A	N/A	140,00
50201	D	0.5	104,000	N/A	53,280	N/A	40,000	17,280	N/A	54,900	90	9,700	4,526
50202	D	0.5	720	N/A	193,000	N/A	25,200	214,000	N/A	254,900	N/A	21,600	5,600
50301	B	2.7	N/A	N/A	500,000	N/A	497,000	374,000	N/A	625,000	None	150,000	144,00
50302	D	0.6	1,440	0	260,000	N/A	86,400	102,000	N/A	95,000	N/A	N/A	1,440
50303	B	0.33	142,000	N/A	N/A	N/A	N/A	N/A	N/A	104,000	N/A	N/A	613
50304	D	1.1	None	N/A	N/A	N/A	N/A	N/A	N/A	144,000	N/A	535	432
50401	B	0.7	172,800	N/A	64,800	8,640	7,200	20,160	N/A	93,600	N/A	N/A	1,440
50402	B	2.9	230,400	330	900,000	N/A	None	170,000	N/A	N/A	N/A	128,000	4,320
50403	D	3.3	201,600	N/A	606,240	4,320	20,160	233,300	N/A	N/A	N/A	1,440	N/A
50404	B	1.0	1,350,000	N/A	100,000	N/A	10,000	75,000	N/A	110,000	N/A	N/A	100
50501	B	0.40	None	N/A	115,200	N/A	43,300	390,000	N/A	56,160	N/A	18,720	2,850

Table 5.2 Selected Sources of Wastewaters

Facil. No.	BPT Sub.	Dry Wt Process Flow*	Wastewater Sources in gallons per day										
			Stripper	Ballast	Cooling Tower Blowdn	Pumps Com-press.	Boiler B.D.	Storm	Water Treatmt	Desalter	Land Farm	Cat Reform Scrub	Tank Draw Down
50502	C	5.2	705,600	N/A	2,400,00	N/A	400,000	N/A	N/A	280,000	N/A	5,000	100,00
50503	E	2.2	None	N/A	400	N/A	1,444	720,000	N/A	443,000	N/A	3,000	288,00
50601	B	0.55	259,200	72,000	144,000	N/A	21,600	43,200	36,000	221,760	N/A	7,200	
50602	B	0.73	259,200	72,000	144,000	N/A	43,200	43,200	7,200	161,280	N/A	1,440	7,200
50603	B	1.64	504,000	72,000	28,800	N/A	43,200	72,000	28,800	316,810	N/A	7,200	7,200
50701	D	8.10	1,670,000	89,300	1,340,00	N/A	735,900	2,082,200	N/A	N/A	N/A	500	
50702	Did not answer the questionnaire												
50703	D	2.6	1,186,300	N/A	684,000	N/A	360,000	43,200	N/A	470,000	N/A	55,000	38,500
50704	C	2.83	221,800	N/A	223,200	N/A	278,000	1,641,600	N/A	N/A	N/A	266,300	1,440
50705	B	3.73	907,200	N/A	82,100	165,16	59,040	N/A	N/A	527,000	N/A	90,410	116,50
50801	B	0.5	37,500	1,440	None	None	50,000	N/A	N/A	150,000	N/A	7,200	1,472
* million gallons per day													

Table 5.3 Water Use: Six Site Visits

Refinery	Flow Ratios	
	Actual/BPT	Actual/BAT
Chevron, Richmond, CA	0.285	0.50
Shell, Martinez, CA	0.51	0.74
Unocal, Rodeo, CA	0.72	0.80
Tosco, Martinez, CA	0.31	0.63
Phillips, Borger, TX	1.48	0.86
Chevron, Philadelphia, PA	0.86	1.31

6. Pretreatment Standards Review And Catalytic Reformer Issues

6.1 Indirect Discharging Refineries

EPA's 1976 survey of this industry identified 44 indirect discharging refineries. Table 6.1 lists these facilities, along with their location and refining capacities. This list was compared to the *Oil and Gas Journal* 1991 list of operating refineries. Only 22 indirect discharging facilities are now believed to be in operation, and their 1991 refinery capacities are also shown in Table 6.1. As can be seen, a greater proportion of smaller refineries have closed since 1976. Although the number of indirect dischargers have been reduced by one half, total capacity of indirect discharge refineries has only dropped by 25 percent.

6.1.1 Treatment Technologies

The current pretreatment standards (PSES and PSNS) are based on the use of oil/water gravity separators and in-plant sour water stripping for ammonia. However, indirect discharging refineries use a variety of technologies. Table 4.3 presents a summary of the technologies in place at the seven indirect refineries included in the EPA/OAR survey. These seven facilities use a range of technologies including enhanced oil removal (four facilities), biological treatment (three facilities), sand filtration and activated carbon (one facility).

Effluent Characteristics

Two data collection efforts were undertaken as part of this study to obtain effluent quality data from indirect discharging refineries. The first source of data was the Los Angeles County Sanitation Districts (LACSD) which have 14 indirect discharging refineries. LACSD has developed a comprehensive pretreatment program, in which the refineries have had to install enhanced oil removal systems such as dissolved air flotation. Table 6.2 presents a detailed summary of the data collected from these 14 facilities.

Data was also obtained from three other indirect discharging refineries and is summarized in Table 6.3. The facilities--La Gloria Oil and Gas Company, Tyler, Texas; Derby Refinery, Wichita, Kansas; and Clark Oil, Blue Island, Illinois--were selected to represent refinery discharges to smaller sewer systems that do not have as comprehensive a pretreatment program as LACSD.

Table 6.1 Summary Comparison of Locations and Capacities for Indirect Dischargers Between 1976 and 1991

Name	Location	1976 Capacity (1000 bbl/day)	1991 Capacity (1000 bbl/day)
Flint Chemical Co.	San Antonio, TX	1.0	1.9
Mid-America Refining Co., Inc.	Chanute, KS	3.0	-
Lunday Thagard Oil Co.	South Gate, CA	3.2	7.0
Eddy Refining Co.	Houston, TX	3.250	-
Chevron U.S.A., Inc.	Richmond Beach, WA	5.0	-
Northland Oil & Refining Co.	West Dickinson, ND	5.25	-
CRA, Inc.	Scottsbluff, NE	5.38	-
Lakeside Refining Co.	Kalamazoo, MI	5.92	5.6
Crystal Refining Co.	Carson City, MI	6.0	4.0
Edgington Oil Co., Inc.	Long Beach, CA	10.0	41.6
Sigmor Refinery Co.	Three Rivers, TX	10.0	53.0
Western Refining Co.	Woods Cross, UT	10.0	-
MacMillan Ring-Free Oil Co.	Long Beach, CA	12.2	-
Beacon Oil Co.	Hanford, CA	12.4	-
Saber Refining Co.	Corpus Christi, TX	13.0	-
Chevron U.S.A. Inc.	Portland, OR	14.0	16.0
U.S.A. Petrochem Corp.	Ventura, CA	15.2	-
Golden Eagle Refining Co., Inc.	Carson, CA	16.0	-
Amoco Oil Co.	Baltimore, MD	17.0	-
Ashland Petroleum Co.	Findlay, OH	20.0	-
Fletcher Oil & Refining Co.	Carson, CA	20.0	29.657
Winston Refining Co.	Fort Worth, TX	20.0	-

Table 6.1 Summary Comparison of Locations and Capacities for Indirect Dischargers Between 1976 and 1991

Name	Location	1976 Capacity (1000 bbl/day)	1991 Capacity (1000 bbl/day)
Continental Oil Co.	Wrenshall, MN	24.0	-
Ashland Petroleum Co.	Louisville, KY	25.0	-
Husky Oil Co. of Delaware	North Salt Lake, UT	25.0	-
LaGloria Oil & Gas Co.	Tyler, TX	29.3	49.5
Derby Refining Co.	Wichita, KS	29.9	29.925
Pride Refining, Inc.	Abiline, TX	36.5	45.5
Amoco Oil Co.	Salt Lake City, UT	40.4	40.0
Delta Refining Co.	Memphis, TN	43.9	-
Mobil Oil Corp.	Buffalo, NY	44.0	-
Powerine Oil Co.	Santa Fe Springs, CA	44.1	46.5
Rock Island Refining Corp.	Indianapolis, IN	44.5	50.0
Quintana-Howell Joint Venture	Corpus Christi, TX	46.0	-
Douglas Oil Co.	Paramount, CA	48.0	42.7
Gulf Oil Co., U.S.A.	Santa Fe Springs, CA	53.8	44.0
Ashland Petroleum Co.	Tonawanda, NY	63.0	-
Marathon Oil Co.	Detroit, MI	66.0	70.0
Clark Oil and Refining Corp.	Blue Island, IL	70.0	66.5
Texaco Inc.	Wilmington, CA	80.0	95.0
Shell Oil Co.	Carson, CA	93.0	133.3
Crown Central Petroleum Corp.	Pasadena, TX	100.0	-
Union Oil Co. of California	Wilmington, CA	111.0	108.0
Mobil Oil Corp.	Torrance, CA	131.1	123.0
Totals		1,476.3	1,102.7

Table 6.2 Summary of Discharge Data for Major Refineries Discharging to Los Angeles County Sanitation Districts (LACSD)

January 1, 1990 through February 9, 1993

Analyte	Maxim	Minim	Average
pH	10.08	6.50	7.89
Suspended Solids (mg/l)	222.37	11.42	62.45
Ammonia Nitrogen (mg/l)	99.97	4.09	29.73
Total Cyanide (mg/l)	0.74	0.05	0.12
Soluble Sulfide (mg/l)	1.99	0.05	0.15
Thiosulfate (mg/l)	61.19	0.80	9.59
Sulfate (mg/l)	984.19	888.64	935.57
Sulfite (mg/l)	2.20	0.50	0.62
Mercaptans (mg/l)	2.25	0.10	0.65
Phenols (mg/l)	66.06	2.73	22.77
Total COD (mg/l)	1613.05	159.05	632.96
Oil & Grease (mg/l)	272.20	4.12	51.14
Non-polar Oil & Grease	53.75	27.40	40.59
Benzene (µg/l)	5523.89	87.71	1419.90
Toluene (µg/l)	7400.56	97.30	1783.86
Ethyl Benzene (µg/l)	572.64	42.73	167.82
o-xylene (µg/l)	1357.78	47.94	340.39
p-xylene (µg/l)	1366.25	674.37	1066.53
m+p xylene (µg/l)	2385.88	79.69	630.60
Chloroform (µg/l)	800.00	800.00	800.00
Naphthalene (µg/l)	143.60	143.60	143.60
2,4 Dimethyl phenol (µg/l)	359.50	359.50	359.50
Chrysene (µg/l)	10.50	10.50	10.50
Fluorene (µg/l)	6.50	6.50	6.50
Phenanthrene (µg/l)	15.00	15.00	15.00
2-Chlorophenol (µg/l)	22.00	22.00	22.00
2,4,6-Trichlorophenol (µg/l)	54.00	54.00	54.00
Acenaphthene (µg/l)	2.00	2.00	2.00
Pyrene (µg/l)	1.00	1.00	1.00
Total Chromium (mg/)	0.16	0.03	0.04
Lead (mg/l)	0.48	0.11	0.36
Zinc (mg/l)	2.00	0.19	0.42
Note: In calculating averages, one-half of the detection limit was used when "Less than" values were reported.			

Table 6.3 Summary of Discharge Data for Major Refineries Discharging to Local POTWs

Analyte	LaGloria Oil and Gas Co.	Derby Refining	Clark Oil	Average
Suspended Solids (mg/l)	720.00	248.00		484.00
Maximum	40.00	1.00		20.50
Minimum	126.61	25.68		76.14
Mean				
Ammonia Nitrogen (mg/l)	38.00	32.6	85.30	51.96
Maximum	0.60	10.6	0.90	4.03
Minimum	9.72	21.35	18.38	16.48
Mean				
Total Cyanide (mg/l)		0.19	0.12	0.15
Maximum		0.01	0.09	0.05
Minimum		0.04	0.10	0.07
Mean				
Phenols (mg/l)				
Maximum	3.50	190.00		96.75
Minimum	<0.02	11.70		<5.86
Mean	0.45	62.05		31.25
Total COD (mg/l)				
Maximum	2597.00	1196.22		1896.61
Minimum	82.00	244.00		163.00
Mean	328.31	557.46		442.88
Oil & Grease (mg/l)	47.00	326.00	95.00	156.00
Maximum	1.05	7.80	2.00	3.61
Minimum	8.07	78.60	36.16	40.94
Mean				
Total Chromium (mg/l)		1.36	2.18	1.77
Maximum		0.36	1.01	0.68
Minimum		0.86	1.62	1.24
Mean				

Table 6.3 Summary of Discharge Data for Major Refineries Discharging to Local POTWs

Analyte	LaGloria Oil and Gas Co.	Derby Refining	Clark Oil	Average
Lead (mg/l)				
Maximum	<0.10	0.10		<0.10
Minimum	<0.10	0.06		<0.08
Mean	<0.10	0.08		<0.09
Zinc (mg/l)				
Maximum			0.99	0.99
Minimum			0.13	0.13
Mean			0.58	0.58
Sulfide				
Maximum	12.00	13.10		12.55
Minimum	<0.50	0.10		<0.30
Mean	1.43	3.35		2.39
BOD				
Maximum	246.00			343.00
Minimum	21.50			16.25
Mean	99.08			165.08
Total VOC's				
Maximum		8.72		8.72
Minimum		1.46		1.46
Mean		4.98		4.98
Total Dissolved	2160.00			2160.00
Solids	130.00			130.00
Maximum	1121.61			1121.61
Minimum				
Mean				
pH	9.60	9.20	9.80	9.53
	5.90	8.20	8.00	7.36
	7.54	8.90	8.77	8.40

A summary is contained in Table 6.4 comparing effluent values for seven selected pollutants for which the data is shown in Tables 6.2 and 6.3. This comparison of the data indicates that the LACSD refineries are doing slightly better in the removal of oil (oil and grease) and total suspended solids.

Table 6.4 Data Comparison: Indirect Discharging Refineries

Pollutant	Average Data (mg/l)	
	LACSD	Other Refineries
Oil & Grease	37.5	40.94
Suspended Solids	62.45	76.14
Benzene	0.83	
Toluene	1.00	
Phenols	21.64	31.25
Lead	0.36	0.09
Zinc	0.35	0.58

6.2 Dioxins in Catalytic Reformer Wastewaters

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (CDDs and CDFs, respectively) are closely related families of highly toxic and persistent organic chemicals which are formed as unwanted by-products in some commercially significant chemical reactions, during high temperature decomposition and combustion of certain chlorinated organic chemicals, and through other reactions involving chlorine and organic materials. CDDs and CDFs constitute a family of over 200 related chemical compounds with varying chemical, physical, and toxicological properties. The congener that appears to be the most toxic and has generally raised the greatest health concerns is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, abbreviated as 2378-TCDD.

Unfortunately, CDDs and CDFs are among the most persistent as well as the most toxic pollutants. Certain congeners, including 2378-TCDD, are highly bioaccumulative and lipophilic. The U.S. Centers for Disease Control has estimated the half life of 2378-TCDD in the environment to be about 12 years.

In 1988, CDDs and CDFs were found in internal waste streams at refineries in Canada. Further studies at refineries in the United States and Canada located the source of the CDDs and CDFs to be the regeneration of catalyst for the catalytic reforming operations. In particular the source was identified as the caustic and rinse wastewaters from certain types of regeneration processes.

One such study was conducted by the EPA Engineering and Analysis Division. The objective of this study was to verify the analytical method for measuring CDD's and CDF's in refinery wastewater matrices, and to screen and characterize the wastewaters from the catalytic reforming catalyst regeneration processes for formulation of CDD's and CDF's. This report is included as Appendix G to this Preliminary Data Summary.

Catalytic reformers can be categorized by the type of catalyst regeneration system employed. The three major types of regeneration are:

1. Semi-Regenerative. Characterized by the shutdown of the entire reforming unit at specified intervals for in situ regeneration of the catalyst. Regenerations are generally limited to one or two per year.

2. Cyclic. Characterized by continual regeneration of the catalyst in situ in one of several reactors that is isolated from the naptha feed during regeneration. The remaining reactors continue reforming naphtha while regeneration of the catalyst occurs in the isolated reactor. There may be several regeneration cycles each year since one of the reactors is usually being operated in a regeneration mode.

3. Continuous. A portion of the catalyst is continually removed from the reformer, regenerated in a separate reactor, and returned to the reformer.

In all cases, the purpose of catalyst regeneration is to remove accumulated coke from the catalyst under controlled combustion conditions and to replenish the catalyst with chlorine which is necessary for catalytic reactions to occur. Chlorine may be added in the form of chlorine gas, hydrochloric acid, or any of a number of chlorinated compounds including carbon tetrachloride, trichloromethane, dichloropropane, and dichlorethane. Reactions conditions of temperature, pressure and presence of free chlorine radicals and CDD and CDF precursors (various unchlorinated polycyclic compounds) are such that the potential exists for the formation of CDD's and CDF's during the catalyst regeneration cycle.

The off-gases from the regeneration processes contain combustion products, hydrochloric acid, and water vapor. Depending upon design considerations (materials of construction, etc.) off-gases may be scrubbed with a caustic or water solution, or vented directly to the atmosphere. Caustic scrubbing is more common at semi-regenerative reformers and generally not practiced at refineries with cyclic reformers.

6.2.1 Waste Characterization

As a result of these discoveries, refineries in both Canada and the U.S. have conducted waste characterization studies of their catalytic reformer regeneration wastes and their refinery final effluents in order to identify the presence of CDD’s and CDF’s.

Tables 6.5 and 6.6 present data resulting from sample and analysis from two Canadian refineries.

Table 6.5 Shell Canada Products Limited, Sarnia Refinery Range of Dioxins/Furans in Internal Shell Wastewaters

all figures in parts per billion

Sample	New Caustic	Spent Caustic	Scrubber Water	Biological Sludge	Combined Effluent
2,3,7,8,8-4 CDD	ND**	0.0046 - 0.0054	ND	ND	ND
4CDD (Total)	ND	0.350 - 5.900*	0.0052 - 0.012	9.9 - 15	ND
5CDD	ND	0.400 - 8.200*	0.00076 - 0.002	9.0 - 17	ND
6CDD	ND	0.530 - 5.300*	0.00076 - 0.0012	17.0 - 23	ND
7CDD	ND	0.290 - 1.500*	0.00091 - 0.0014	8.7 - 12	ND
8CDD	ND	0.230 - 1.300*	0.00052 - 0.00071	7.0 - 8.4	ND
Total Dioxins ***		1.810 - 22.200	0.00815 - 0.01731	51.6 - 75.4	
4CDF	ND	0.380 - 6.1*	0.0051 - 0.010	8.2 - 10.0	ND
5CDF	ND	0.680 - 8.9*	0.0016 - 0.0038	12.0 - 16.0	ND
6CDF	ND	1.200 - 5.6*	0.0031 - 0.0057	24.0 - 31.0	ND
7CDF	ND	1.400 - 4.2*	0.0049 - 0.0084	28.0 - 40.0	0.00034 - 0.00022
8CDF	ND	0.760 - 2.5*	0.00071 - 0.0008	20.0 - 28.0	ND
Total Furans ***		4.420 - 27.3	0.01541 - 0.0287	92.2 - 125	

* July samples by Shell; others are November Samples taken by Ontario MOE; all November samples were done in duplicate

** Non-detectable

*** Totals may not add because highest and lowest concentrations for individual types of dioxins and furans did not occur in same samples.

Table 6.6 Esso Petroleum Canada, Sarnia Refinery
Powerformer Regeneration Study
Dioxin and Furan Concentrations, December 16, 1988
(parts per trillion)

PCDF/PCDD Isomer Group	**Scrubber Water**		**BIOX Inlet**		**BIOX Outlet**	
	1st 24 hours	**2nd 24 hours**	**1st 24 hours**	**2nd 24 hours**	**1st 24 Hours**	**2nd 24 Hours**
2378-TCDD	< 0.0005	< 0.012				
4-TCDD	0.11	0.111	< 0.002	< 0.009	< 0.003	< 0.008
5-PCDD	0.030	0.072	< 0.005	< 0.005	< 0.008	< 0.004
6-HCDD	0.015	0.027	< 0.004	< 0.007	< 0.007	< 0.004
7-HCDF	0.042	0.041	< 0.04	< 0.02	< 0.01	< 0.01
8-OCDF	0.037	0.063	< 0.04	< 0.06	< 0.03	< 0.03
Total Dioxins	0.243	0.308	0.000	0.000	0.000	0.000
4-TCDF	0.32	0.48	< 0.002	0.051	< 0.002	< 0.002
5-PCDF	0.14	0.17	< 0.003	0.029	< 0.008	< 0.004
6-HCDF	0.071	0.11	< 0.02	< 0.007	< 0.006	< 0.002
7-HCDF	0.026	0.077	< 0.01	< 0.008	< 0.007	< 0.004
8-OCDF	0.071	0.21	< 0.02	< 0.03	< 0.02	< 0.02
Total Furans	0.628	1.038	0.000	0.080	0.000	0.000
2378-TCDD Toxic Equivalent	0.243	0.345	0.000	0.040	0.000	0.000

Notes
4-TCDD includes 2378-TCDD
Totals and toxic equivalents do not include values below MDL. Assume less than detectable means zero.

CDD and CDF information was also collected as part of the six refinery visits conducted as part of this study. Table 6.7 presents a summary of catalytic reformer usage in the six refineries visited, and the availability of CDD/CDF analytical data. Table 6.8 through Table 6.10 present CDD/CDF analytical data obtained from three of the refineries from which information was obtained. In all cases, 2378-TCDD and 2378-TCDF levels in the refinery effluents were non-detectable.

Table 6.7 Catalytic Reforming Data: Six Site Visits

Refinery	Catalytic Reforming	Semi-Regeneration	Sample Data Available
Chevron Richmond, CA	yes	yes	yes
Shell Martinez, CA	yes	no	N/A
Unocal Rodeo, CA	yes	yes	yes
Tosco Martinez, CA	yes	yes	yes
Phillips Borger, TX	yes	yes	no
Chevron Philadelphia, PA	yes	yes	no

Table 6.8 Summary of CDD/CDF Data for Chevron Richmond Refinery

Furans	**Grab - 1**	**Grab - 2**
TCDFs (total)	86,000	19,000
2,3,7,8-TCDF	5,500	1,200
PeCDFs (total)	120,000	23,000
1,2,3,7,8-PeCDF	15,000	3,300
2,3,4,7,8-PeCDF	7,600	1,600
HxCDFs (total)	87,000	20,000
1,2,3,4,7,8-HxCDF	24,000	5,400
1,2,3,6,7,8-HxCDF	9,400	2,200
2,3,4,6,7,8-HxCDF	2,000	640
1,2,3,7,8,9-HxCDF	2,600	800
HpCDFs (total)	61,000	14,000
1,2,3,4,6,7,8-HpCDF	28,000	6,500
1,2,3,4,7,8,9-HpCDF	12,000	3,000
OCDF	17,000	3,500
Dioxins	**Grab - 1**	**Grab - 2**
TCDDs (total)	11,000	2,300
2,3,7,8-TCDD	280	58
PeCDDs (total)	12,000	2,700
1,2,3,7,8-PeCDD	1,200	270
HxCDDs (total)	13,000	2,900
1,2,3,4,7,8-HxCDD	1,200	280
1,2,3,6,7,8-HxCDD	1,500	340
1,2,3,7,8,9-HxCDD	710	180
HpCDDs (total)	7,900	1,800
1,2,3,4,6,7,8-HpCDD	4,300	990
OCDD	1,900	440

Notes
1. Two grab samples taken on July 16, 1991, from one batch of all wastewaters resulting from a catalytic regeneration. The analysis was by Method 8290.
2. Units in picograms/liter or parts per quadrillion (pg/l or ppg)

Table 6.9 Summary of CDD/CDF Data for Tosco Martinez Refinery

Furans	**#2 Ref Prim. Burn**	**#2 Ref Mkup H20**	**#2 Ref Mkup H20**	**#3 Ref Regen**	**#3 Ref clean cond.**	**E-001 Back-grnd**	**E-001 Post**	**E-001 Post Reana**
TCDFs (total)	170	2.00	ND	750	0.081	ND	0.023	ND
2,3,7,8-TCDF		0.580	ND		ND	ND	0.013	ND
PeCDFs (total)	270	2.40	ND	1100	0.100	ND	ND	ND
1,2,3,7,8-PeCDF	13.0	0.120	ND	75.0	ND	ND	ND	ND
2,3,4,7,8-PeCDF	43.0	0.250	ND	180	ND	ND	ND	ND
HxCDFs (total)	450	3.40	ND	2300	0.140	ND	ND	ND
1,2,3,4,7,8-HxCDF	30.0	0.290	ND	227	ND	ND	ND	ND
1,2,3,6,7,8-HxCDF	37.0	0.270	ND	225	ND	ND	ND	ND
1,2,3,7,8,9-HxCDF	54.0	0.130	ND	300	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	21.0	0.290	ND	29.0	ND	ND	ND	ND
HpCDFs (total)	240.0	1.50	ND	1800	0.068	ND	ND	ND
1,2,3,4,6,7,8-HpCD	98.0	0.750	ND	1100	ND	ND	ND	ND
1,2,3,4,7,8,9-HpCD	32.0	0.150	ND	1100	ND	ND	ND	ND
OCDF	59.0	0.280	ND	500	ND	ND	ND	ND
Dioxins								
TCDDs (total)		0.100	ND	3.00	ND	ND	ND	ND
2,3,7,8-TCDD	ND	ND	ND	ND	ND	ND	ND	ND
PeCDDs (total)		0.350	ND	ND	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	0.020	ND	ND	ND	ND	ND	ND
HxCDDs (total)	18.0	0.460	ND	270	ND	ND	ND	ND
1,2,3,4,7,8-HxCDD		0.021	ND	7.60	ND	ND	ND	ND
1,2,3,6,7,8-HxCDD		0.042	ND	29.0	ND	ND	ND	ND
1,2,3,7,8,9-HxCDD		0.026	ND	32.0	ND	ND	ND	ND
HpCDDs (total)		0.330	ND	230	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCD	12.90	0.170	ND	110	ND	ND	ND	ND
OCDD		0.170	ND	130	ND	ND	ND	1.20
All results in picograms/milliliter (parts per trillion)								

Table 6.10 Summary of CDD/CDF Data for Unocal Rodeo Refinery

Test Parameters	Refinery # 231		Refinery # 244
	9/16/90	2/23/91	6/27/91
Furans			
TCDFs (total)	1200	2300	2900
2,3,7,8-TCDF	230	61	160
PeCDFs (total)	1500	2800	270
1,2,3,7,8-PeCDF	170	160	36
2,3,4,7,8-PeCDF	240	260	38
HxCDFs (total)	3100	2000	48
1,2,3,7,8,9-HxCDF	830	190	11
2,3,4,6,7,8-HxCDF	430	290	11
2,3,4,6,7,8-HxCDF	390	190	5.4
1,2,3,7,8,9-HxCDF	340	330	9.3
HpCDFs (total)	2600	1600	58
1,2,3,4,6,7,8-HpCDF	2100	790	35
1,2,3,4,7,8,9-HpCDF	1300	260	13
OCDF	5300	440	17
Dioxins			
TCDDs (total)	550	600	65
2,3,7,8-TCDD	47	14	5.3
PeCDDs (total)	500	1500	22
1,2,3,7,8-PeCDD	120	130	3.9
HxCDDs (total)	1700	1100	15
1,2,3,4,7,8-HxCDD	150	120	ND (1.9)
1,2,3,6,7,8-HxCDD	250	200	ND (3.1)
1,2,3,7,8,9-HxCDD	370	190	ND (2.4)
HpCDDs (total)	2600	1700	14
1,2,3,4,6,7,8-HpCDD	1700	950	8.3
OCDD	3300	890	21

Note: Results in picograms/liter (ppq) for samples of regeneration wastewater

6.2.2 Available Treatment Technologies

The discovery of the presence of CDD/CDF's in refinery wastewaters only occurred in the last three to five years. As a result, there have been limited studies of this problem, and only limited data on available technologies. The following sections present a summary of currently available control information.

Flow Reduction

There is a very large range in water use found during regeneration of the catalyst from refinery to refinery. As a result, there may be opportunities to minimize the volumes of scrubber waters used at certain facilities. Modifications to off-gas cooling an scrubbing systems may be possible.

As can be seen by the waste characterization data presented earlier, there is a wide range in concentrations found. This may be caused by various process techniques used at each facility. Investigation into the causes of these variations in pollutant concentrations would be needed in order to determine whether there are in-process techniques that can reduce the quantities of CDD/CDF's generated.

Pretreatment

Since available data from Ontario and U.S. refineries indicate the more toxic CDD's and CDF's are found only in wastewaters from catalytic reforming (regeneration) operations, the most effective means to achieve minimum mass discharge of these compounds is to isolate an treat the low volume catalytic reforming regeneration process wastewaters prior to mixing with other refinery process or cooling waters, or stormwater. Accordingly, the regeneration process wastewaters should be collected and isolated in each refinery in appropriately sized equalization or holding tanks prior to treatment. The principal purposes of the holding or equalization tanks are to provide for temporary storage of reforming regeneration wastewaters and to provide for low volume constant feeds, thus allowing for design of downstream treatment systems at low hydraulic loading rates.

Based upon investigations by Shell Canada Products Limited, catalytic reforming regeneration wastewaters are characterized by relatively low concentrations of very fine suspended particulates. CDD's and CDF's are most often associated with particulate matter in wastewater matrices. Hence, relatively simple technologies such as conventional gravity settling or mixed media filtration that are incapable of fine particulate removal would not be effective for removal of CDD's and CDF's from catalytic reforming wastewaters.

The more advanced adsorption and membrane technologies require fairly clean feed streams in terms of TSS to prevent fouling and plugging. Although it appears that untreated catalytic reforming regeneration wastewaters do not contain TSS at levels likely to cause operating problems in downstream units, consideration of pretreatment by filtration is recommended. Also, depending upon the reforming operation and the type of regeneration system and gas scrubbing system, the untreated wastewaters may be highly alkaline and unsuitable for direct feed to downstream treatment units. In these cases, neutralization with acid may be necessary.

Granular Activated Carbon

Adsorption on granular activated carbon offers several advantages over membrane technologies for removal of CDD's and CDF's from catalytic reforming wastewater. The technology is suitable for treatment of relatively large volumes of wastewaters contaminated with adsorbable organic contaminants at low levels. Aside from spent carbon, there are no by-product sludges or concentrated aqueous streams requiring further processing or treatment for ultimate disposal. Multiple carbon units can be used in parallel or series to ensure maximum removal. Finally, since catalytic reformer wastewater streams are relatively low in organic content, the life of the carbon beds should be relatively long, on the order of a few years as opposed to weeks or months.

Two Canadian refineries have installed temporary activated carbon treatment facilities and have applied for Certificates of Approval for permanent wastewater treatment facilities. Treatability and performance data from these systems are summarized in Tables 6.11 and 6.12. These data indicate consistently high removal rates for CDD's and CDF's (> 95 percent). Suncor recently reported consistent removal from current operations to non-detectable levels in the low parts per quadrillion range (ppq). Shell reported more than 96 percent removal during recent testing. All Ontario refineries have reported consistently no detection of the more toxic CDD and CDF congeners in treated refinery process wastewater effluents.

Table 6.11 Suncor-Sarnia Catalytic Reformer Wastewater Treatment August 3, 1990 Samples

Analyte	Carbon Filter	
	Influent	Effluent
2378-TCDD	ND (10)	ND (10)
TCDDs	260	ND (10)
PeCDDs	310	ND (10)
HxCDDs	700	ND (20)
HpCDDs	210	ND (30)
OCDD	83	ND (30)
2378-TCDF	300	ND (10)
TCDFs	1,400	ND (10)
PeCDFs	2,000	ND (10)
HxCDFs	3,900	ND (10)
HpCDFs	1,300	ND (20)
OCDF	530	ND (20)
2378-TCDD TEQ*	2,520	34.5

Results in parts per trillion (ppt)
* 2378-TCDD TEQ computed assuming CDDs and CDFs were present at detection levels when not-detected results were obtained.
Removal Efficiency >98.6%

Source: October 18, 1990, letter from T.A. Brown, Suncor to L.Van Asseldonk, Ontario MOE-Sarnia.

Table 6.12 Shell Canada-Sarnia, Catalytic Reformer Wastewater Treatment Spent Caustic, May 9, 1991

Analyte	Carbon Filter	
	Influent	Effluent
2378-TCDD	< 5.5	0.21
TCDDs	95	5.9
12378-PeCDD	15	0.3
PeCDDs	120	7.3
123478-HxCDD	8.5	0.35
123678-HxCDD	25	0.8
123789-HxCDD	< 5.8	0.84
HxCDDs	140	8
1234678-HpCDD	86	3.9
HpCDDs	140	7.2
OCDD	90	4.7
2378-TCDF	54	0.43
TCDFs	210	8.5
12378-PeCDF	13	1.6
23478-PeCDF	27	1.3
PeCDFs	350	16
123478-HxCDF	220	9.2
123678-HxCDF	120	3.5
234678-HxCDF	47	1.8
123799-HxCDF	27	< 0.057
HxCDFs	580	28
1234678-HpCDF	400	18
1234789-HpCDF	69	3.2
HpCDF	590	29
OCDF	260	15
2378-TCDD TEQ	431	4.54

Results in parts per trillion (ppt) Removal Efficiency 98.9%

Source: June 26, 1991, letter from D. Atwell, Shell Canada to A. Peterson, Ontario MOE-Sarnia.

7. Evaluation of Pollutant Discharges And Environmental Issues

The purpose of this section is to present a preliminary assessment of the pollutant loadings and potential water quality impacts of discharges from petroleum refining facilities to surface waters and publicly-owned treatment works (POTWs). Using readily available data and information sources on refinery wastewater volume and constituents, annual loadings and average concentration are estimated. In addition, potential aquatic life and human health impacts are summarized based on a review of documented environmental impacts and a review of the physical-chemical properties and toxicity of pollutants associated with wastewater discharges from the petroleum refining industry. The following sections of this report describe the methodology and results (including data sources and assumptions/limitations) used in the identification of documented environmental impacts, the identification and quantification of pollutant releases, and the evaluation of the fate and toxicity of released pollutants. Additional details on specific information addressed in this section are presented in the Appendices.

7.1 Identification And Quantification of Pollutant Releases

Petroleum refining wastewater constituents are identified using two EPA data bases: the Permit Compliance System (PCS) and the Toxic Release Inventory (TRI). The identified constituents are listed on Table 7.1. Annual loadings are obtained from both PCS and TRI data for a variety of parameters including conventional, priority, and non-conventional pollutants. TRI encompasses direct and indirect discharges, whereas PCS covers direct discharges only. Average pollutant concentrations are also retrieved from PCS for analysis. A brief description of each data base, the methodology to identify and quantify releases, add the assumptions and limitations of the analyses are described below.

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
1,1,1-Trichloroethane	71556	0	1	1
1,1,2-Trichloroethane	79005	0	1	1
1,2-Dibromoethane	106934	0	1	1
1,2-Dichlorobenzene	95501	1	0	0
1,2-Dichloroethane	107062	0	1	1
1,2,4-Trimethylbenzene	95636	0	1	1
1,3-Butadiene	106990	0	1	1
1,4-Dichlorobenzene	106467	1	0	0

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
2-Methoxyethanol	109864	0	1	1
2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin	1746016	1	0	0
2,4-Dimethylphenol	105679	0	1	1
2,4,6-Trichlorophenol	88062	1	0	0
Acetone	67641	0	1	1
Acetonitrile	75058	0	1	1
Alkalinity		1	0	0
Alkalinity/Hardness (CaCO3)		2	0	0
Aluminum	7429905	1	0	0
Ammonia	7664417	4	1	1
Ammonium Sulfate (Solution)	7783202	0	1	1
Anthracene	120127	1	1	1
Antimony	7440360	0	1	1
Arsenic	7440382	2	1	2
Barium	7440393	0	2	2
Benzene	71432	1	1	1
Benzene,Toluene,Ethylbenzene,Xylene (BTEX)		1	0	0
Benzo(a)anthracene	56553	1	0	0
Benzo(a)pyrene	50328	1	0	0
Biological Oxygen Demand (BOD)		3	0	0
Biphenyl	92524	0	1	1
Bis (2-ethylhexyl) Phthalate	117817	1	0	0
Bromide	24959679	1	0	0
Cadmium	7440439	1	0	0
Carbon Tetrachloride	56235	0	1	1
Chemical Oxygen Demand (COD)		5	0	0

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
Chloride	16887006	1	0	0
Chlorine	7782505	1	1	1
Chlorine Dioxide	10049044	0	1	1
Chloroform	67663	1	0	1
Chromium	7440473	1	2	2
Chromium, Hexavalent	18540299	1	0	0
Chromium, Trivalent	16065831	1	0	0
Chrysene	218019	1	0	0
Cobalt	7440484	1	2	1
Copper	7440508	1	2	2
Cresol (Mixed Isomers)	1319773	0	1	1
Cumene	98828	0	1	1
Cyanide	57125	3	0	1
Cyclohexane	110827	0	1	1
Diethanolamine	111422	0	1	1
Dissolved Oxygen (DO)		1	0	0
Ethylbenzene	100414	1	1	1
Ethylene	74851	0	1	1
Ethylene Glycol	107211	0	1	1
Fluoride	16984488	1	0	0
Formaldehyde	50000	0	1	1
Glycol Ethers		0	1	1
Hexachlorobenzene	118741	1	0	0
Hydrocarbons		3	0	0
Hydrogen Cyanide	74908	0	1	1
Hydrogen Fluoride	7664393	0	1	0
Iron	7439896	3	0	0

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
Isophorone	78591	1	0	0
Lead	7439921	2	2	2
Manganese	7439965	3	2	2
M-Cresol	108394	0	1	0
Mercury	7439976	1	1	0
Methanol	67561	0	1	1
Methyl Ethyl Ketone	78933	0	1	1
Methyl Isobutyl Ketone	108101	0	1	1
Methyl Tert-Butyl Ether	1634044	1	1	1
Molybdenum Trioxide	1313275	0	1	1
M-Xylene	108383	0	1	1
Naphthalene	91203	1	1	1
N-Butyl Alcohol	71363	0	1	1
Nickel	7440020	2	2	2
Nitrite Plus Nitrate	14797558	1	0	0
Nitrogen	17778880	2	0	0
O-Cresol	95487	0	1	0
Oil And Grease		4	0	0
O-Xylene	95476	0	1	1
PAH Compounds		1	0	0
P-Cresol	106445	0	1	0
Phenanthrene	85018	1	0	0
Phenol	108952	1	1	1
Phenolic Compounds		3	0	0
Phosphate	14265442	1	0	0
Phosphoric Acid	7664382	0	1	0
Phosphorus	7723140	1	0	0

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
Polychlorinated Biphenyls	1336363	1	0	0
Polyram	9006422	1	0	0
Propylene	115071	0	1	1
P-Xylene	106423	0	1	1
Residual Oxidants		1	0	0
Selenium	7782492	2	2	1
Silver	7440224	1	1	1
Sodium Chloride (Salt)	7647145	1	0	0
Styrene	100425	0	1	1
Sulfate	14808798	1	0	0
Sulfide	18496258	2	0	0
Sulfite	14265433	1	0	0
Sulfuric Acid	7664939	0	1	1
Surfactants (MBAS)		1	0	0
Tetrachlorodibenzofuran, 2,3,7,8-	51207319			
Tetrachloroethylene	127184	1	0	0
Thallium	7440280	0	1	0
Toluene	108883	1	1	1
Total Dissolved Solids (TDS)		2	0	0
Total Organic Carbon (TOC)		1	0	0
Total Oxygen Demand (TOD)		1	0	0
Total Suspended Solids (TSS)		1	0	0
Total Toxic Organics (TTO)		1	0	0
Trichloroethylene	79016	1	0	0
Trichlorophenol	25167822	1	0	0
Vanadium	7440622	1	1	0
Xylene	1330207	1	1	1

Table 7.1 Refinery Wastewater Constituents

Constituent	CAS Number	Number of 1992 PCS Parameters	Number of 1991 TRI Parameters	Number of 1992 TRI Parameters
Zinc	7440666	2	2	2

7.1.1 Permit Compliance System

EPA's Office of Wastewater Management (OWM) oversees the NPDES program on a national level. EPA has authorized 39 States and the Virgin Islands to administer the NPDES program. EPA regional offices administer the program in non-delegated States. More than 65,000 active NPDES permits have been issued to facilities throughout the nation. PCS has extensive records on approximately 7,000 permits which are classified as "major". Facilities are classified as "major" based on consideration of many factors, including effluent design flow, physical and chemical characteristics of the wastestream, and location of discharge. Each permit record in PCS may contain information that:

- Identifies and describes the facility to which the permit has been granted (including a primary Standard Industrial Classification (SIC) code);
- Specifies the pollutant discharge limits for that facility;
- Records the actual amounts of pollutants measured in the facility's wastewater discharges; and
- Tracks the facility's history of compliance with construction, pollutant limits, and reporting requirements.

Major facilities must report compliance with NPDES permit limits, usually on a monthly basis, via Discharge Monitoring Reports (DMRs). DMRs provide detailed information on measured concentrations, including those that are in violation of established limits for the permit. DMR data entered into PCS include the type of violation (if any), concentration and quantity values, and monitoring period. The PCS data base is revised and updated twice weekly and, therefore, data retrieved at a specific time are subject to subsequent alteration. In addition, because of data entry delays, a complete set of data for a particular time period may not exist until a year or more afterwards.

Among the permits listed in PCS are specific discharge limits or monitoring requirements for over 200 individual chemicals.

7.1.2 Estimation of Annual Pollutant Loads from PCS

It is important to recognize that, unlike TRI, PCS is a permit tracking system, rather than a repository of pollutant release amounts. However, an optional report in PCS called "Effluent Data Statistics" (EDS) can process PCS data to produce annual loading values. EDS uses the following hierarchy to derive a loading for each measured parameter: (1) reported loading value in PCS (i.e., mass-based permit limit); and (2) loading estimate based on discharge flow and concentration measurement. Depending on the monitoring requirements imposed by the permit, flows and concentrations may be reported in many different ways. Measurements from PCS are selected in the following order of preference: (1) average concentration; (2) maximum concentration; and (3) minimum concentration. Estimated loadings are produced for records with valid concentrations (as defined by PCS-EDS) and corresponding flow data assuming 30 operating days per month for each facility. Loadings are estimated using the following general equation:

Load = Flow * Conc * Conversion Factors

Where:

Load = Specific pollutant load from a facility per unit time;
Flow = Facility effluent flow per unit time;
Conc = Concentration of a pollutant; and
Conversion Factors = Appropriate factors to convert reported units to standard units.

The Engineering and Analysis Division identified 138 permitted direct dischargers as petroleum refineries potentially subject to effluent guidelines regulations. For these facilities, EDS processed loading data for the calendar year 1992 were retrieved at the discharge pipe level for each PCS parameter addressed in the permit with sufficient quantity or concentration/ discharge flow information. The loads for each parameter were summed across discharge pipes to yield the total facility load. Concentration measurements recorded as below a detection limit were treated in two ways: (1) for a low end estimated loading data set, values below detection were set equal to zero; and (2) for a high end estimated loading data set, values below detection were set equal to one-half the recorded detection limit. Parameters loadings based on concentration measurements always below detection at a given discharge pipe were set equal to zero for both data sets. The low end and high end data sets are presented in Table 7.2 for all petroleum refining parameters. Multiple parameters sometimes exist for the same pollutant. For example, zinc is represented by parameters for "total recoverable zinc" and "total zinc" as (Zn).

Table 7.2 1992 Annual Loading Data from PCS

Sorted by Parameter Name

Parameter Number	Parameter Name	Number of Facilities	Annual Load Low-End (lbs/yr)	Annual Load High-End (lbs/yr)	Selected for Production-Weighting
34536	1,2-dichlorobenzene	1	0.00	0.00	
34571	1,4-dichlorobenzene	1	0.00	0.00	
34675	2,3,7,8-tetrachloro-dibenzo-*p*-dioxin	1	0.00	0.00	
34621	2,4,6-trichloro-phenol	1	0.00	0.00	
415	Alkalinity, Phenol- Phthaline Method	2	50,709.60	50,709.60	
410	Alkalinity, Total (as $CaCO_3$)	1	327,630.01	327,630.01	
1105	Aluminum, Total (as Al)	5	3,625.64	3,869.49	●
619	Ammonia, unionized	1	4.38	4.38	
34220	Anthracene	1	0.00	0.00	
1002	Arsenic, Total (as As)	9	2,512.36	2,524.06	●
978	Arsenic, Total Recoverable	1	562.30	562.30	
34030	Benzene	6	67.52	67.88	●
30383	Benzene, Ethylbenzenetoluene, Xylene Combn	1	0.00	0.00	
34526	Benzo(A)Anthracene	1	0.00	0.00	
34247	Benzo(A)Pyrene	1	0.00	0.00	
39100	Bis (2-Ethylhexyl) Phthalate	1	14.19	14.19	●
310	BOD, 5-Day (20 Deg. C)	100	9,552,282.39	9,579,814.21	●
311	BOD, 5-Day Dissolved	1	47,619.34	47,619.34	
80082	BOD, Carbonaceous 5 Day, 20 Deg.C	5	81,823.31	81,823.31	
71870	Bromide (as Br)	1	4,750.17	4,750.17	●
1027	Cadmium, Total (as Cd)	7	33.09	48.17	●
680	Carbon, Tot Organic (TOC)	54	15,728,883.65	15,811,467.64	●
81017	Chemical Oxygen Demand (COD)	8	5,157,384.29	5,157,384.29	
940	Chloride (as Cl)	12	26,851,306.87	26,851,306.87	●
50060	Chlorine, Total Residual	15	469,150.37	469,165.52	●
32106	Chloroform	3	3.76	3.76	●
1032	Chromium, Hexavalent (as Cr)	84	5,731.06	6,246.07	●
1034	Chromium, Total (as Cr)	93	21,081.95	21,666.80	●
1033	Chromium, Trivalent (as Cr)	3	159.30	181.90	
34320	Chrysene	1	0.00	0.00	
1037	Cobalt, Total (as Co)	5	10.25	40.35	●
1042	Copper, Total (as Cu)	17	4,017.84	4,180.82	●

Table 7.2 1992 Annual Loading Data from PCS

Sorted by Parameter Name

Parameter Number	Parameter Name	Number of Facilities	Annual Load Low-End (lbs/yr)	Annual Load High-End (lbs/yr)	Selected for Production-Weighting
81208	Cyanide, Free (not amenable to chlorination)	1	78.13	109.16	
720	Cyanide, Total (as Cn)	9	2,353.27	2,384.00	●
722	Cyanide, Free (amen. to chlorin.)	4	521.70	521.70	
34371	Ethylbenzene	2	224.96	1,237.05	●
56	Flow Rate	3	31,776.87	31,776.87	
50050	Flow, in conduit or thru treatment plant	108	1,583,221.78	1,583,221.78	
951	Fluoride, Total (as F)	5	208,305.59	208,305.59	●
900	Hardness, Total (as $CaCO_3$)	1	1,632,518.41	1,632,518.41	
39700	Hexachlorobenzene	1	0.05	0.05	●
39942	Hydrocarbons, Aromatic	2	10.55	10.55	
46116	Hydrocarbons, Total Gas Chromat.	1	12,293.02	12,293.02	
551	Hydrocarbons, in H_2O, IR, CC14 Ext. Chromat.	3	13,509.68	13,536.22	●
980	Iron, Total Recoverable	1	2,377.94	2,377.94	
1046	Iron, Dissolved (as Fe)	1	34.78	49.05	
1045	Iron, Total (as Fe)	1	15.89	15.89	●
34408	Isophorone	1	0.00	0.00	
1114	Lead, Total Recoverable	1	67.80	140.47	
1051	Lead, Total (as Pb)	12	1,266.47	2,688.44	●
1056	Manganese, Dissolved (as Mn)	1	4,998.97	4,998.97	
1055	Manganese, Total (as Mn)	1	483.75	483.75	●
11123	Manganese, Total Recoverable	1	5,097.37	5,097.37	
71900	Mercury, Total (as Hg)	10	827.28	832.39	●
22417	Methyl Tert-Butyl Ether	2	1,334.15	1,334.15	●
34696	Naphthalene	1	0.00	0.00	
1074	Nickel, Total Recoverable	1	143.87	178.51	
1067	Nickel, Total (as Ni)	7	2,021.08	2,140.30	●
630	Nitrite Plus Nitrate Total	1	12,701.94	12,701.94	
610	Nitrogen, Ammonia, Total (as N)	102	3,015,792.35	3,031,910.08	●
71845	Nitrogen, Ammonia, Total (as NH_4)	1	19,448.10	19,448.10	
612	Nitrogen, Ammonia, Tot. Unionized (as N)	2	4,136.28	4,136.28	

Table 7.2 1992 Annual Loading Data from PCS

Sorted by Parameter Name

Parameter Number	Parameter Name	Number of Facilities	Annual Load Low-End (lbs/yr)	Annual Load High-End (lbs/yr)	Selected for Production-Weighting
600	Nitrogen, Total (as N)	1	118,681.20	118,681.20	
560	Oil & Grease (Freon Extr.-IR Meth) Tot,Rc	1	121,980.00	121,980.00	
3582	Oil And Grease	1	3,001.56	3,001.56	
550	Oil And Grease (Soxhlet Extr.) Tot.	21	475,731.79	478,588.98	
556	Oil And Grease Freon Extr-Grav Meth	89	4,805,765.77	4,924,117.65	●
78141	Organics, Total Toxic (TTO)	1	1,919.19	1,925.73	
34044	Oxidants, Total Residual	2	9,524.47	9,524.47	
82210	Oxygen Demand First Stage	2	601,690.79	601,690.79	
341	Oxygen Demand, Chem. (COD), Dissolved	1	133,851.00	133,851.00	
340	Oxygen Demand, Chem. (High Level) (COD)	77	48,012,895.91	48,012,952.25	●
335	Oxygen Demand, Chem. (Low Level) (COD)	7	2,734,385.34	2,734,385.34	
343	Oxygen Demand, Total (TOD)	1	1,206,525.79	1,206,525.79	
300	Oxygen, Dissolved (DO)	14	9,342,790.99	9,342,790.99	
34461	Phenanthrene	1	0.00	0.00	
34694	Phenol, Single Compound	19	1,506.46	1,521.75	●
78218	Phenolic Compounds, Unchlorinated	4	226.73	235.25	
32730	Phenolics, Total Recoverable	87	19,157.48	19,646.59	●
46000	Phenols	2	78.57	78.57	
650	Phosphate, Total (as PO_4)	1	16,234.99	16,234.99	●
665	Phosphorus, Total (as P)	5	40,216.87	40,216.87	
38528	Poly-Nuclear Aromatics (Polyram)	1	0.00	0.00	
39516	Polychlorinated Biphenyls (PCBs)	1	1.33	1.33	
22456	Polynuc Aromatic HC per Method 610	1	21.59	86.13	
1147	Selenium, Total (as Se)	9	5,442.65	5,483.49	●
981	Selenium, Total Recoverable	2	5.38	5.38	
1077	Silver, Total (as Ag)	9	43.32	81.40	●
32017	Sodium Chloride (Salt)	1	356,129.31	356,129.31	
70295	Solids, Total Dissolved	4	174,189,544.43	174,189,544.43	
70300	Solids, Total Dissolved- 180 Deg.C	3	14,639,211.69	14,639,211.69	
530	Solids, Total Suspended	107	29,597,956.57	29,613,328.78	●

Table 7.2 1992 Annual Loading Data from PCS

Sorted by Parameter Name

Parameter Number	Parameter Name	Number of Facilities	Annual Load Low-End (lbs/yr)	Annual Load High-End (lbs/yr)	Selected for Production-Weighting
81395	Storm Water Flow	3	835.87	835.87	
945	Sulfate, Total (as SO_4)	6	1,951,597.35	1,951,597.35	
81621	Sulfide, Total	5	6,329.89	6,415.89	
745	Sulfide, Total (as S)	93	27,861.12	30,592.20	●
741	Sulfite (as S)	1	221.70	226.35	
38260	Surfactants (MBAS)	2	828.92	828.92	
34475	Tetrachloroethylene	1	0.00	0.00	
17	Thermal Discharge, million BTUs per day	1	1,344,075.39	1,344,075.39	
34010	Toluene	3	1,093.01	2,022.41	●
39180	Trichloroethylene	1	0.00	0.00	
1087	Vanadium, Total (as V)	5	27,379.00	27,680.95	●
81551	Xylene	1	0.89	0.89	●
1094	Zinc, Total Recoverable	3	1,416.01	1,416.01	
1092	Zinc, Total (as Zn)	19	13,841.55	14,078.59	●

To support EPA's industry selection process for future effluent guidelines development, further refinement of the EDS loading data was conducted as follows:

- Exclude conventional and classical parameter loads (e.g., TSS, BOD, Oil and Grease, COD) that represent groups of individual chemicals;
- Exclude relatively non-toxic anion and cation parameter loads (e.g., phosphorus, phosphate, chloride, sulfate, sulfite nitrogen, nitrite, sodium chloride, and sodium);
- Exclude nonconventional parameter loads that represent groups of individual chemicals (e.g., total recoverable phenolics);
- Include the parameter with the maximum loading reported if multiple parameters are reported for the same chemical at the same discharge pipe;
- Sum chemical parameter loads across all discharge pipes to calculate a facility pollutant load; and
- Include only reported loadings, representing the high-end estimated data, and not extrapolated national projections.

A listing of pollutant loadings used in the industry selection is presented in Appendix H.

Many of the parameters listed on Table 7.2 are measured at only a portion of the petroleum refineries. Therefore, the loading values represent a sample of all petroleum refining wastewater discharges. Based on the assumption that the constituents listed on Table 7.2 are present in the effluent of all refineries, the loading data for several parameters were extrapolated to a national level for two sets of facilities: (1) facilities in California, and (2) facilities not in California. Total loads for California facilities were estimated separately because these facilities employ significantly different practices with respect to water conservation and treatment systems (i.e., activated carbon). To assist in verifying the presence of wastewater constituents in petroleum refining effluent, EPA undertook a limited review of Form 2C NPDES Applications, which require a chemical analysis of current or proposed discharges. This review, summarized in Appendix F, indicates the presence of 37 individual wastewater constituents, 20 of which are among the constituents selected for production weighting. Five of the chemicals reported as above detection on at least one Form 2C are represented by less than five facilities in the 1992 PCS loadings data set. The extrapolation procedure is based on the ratio of petroleum production level at the facilities measuring a given parameter to the overall industry production level. Production levels (in barrels per day) were obtained from data presented for 138 direct dischargers (13 in California) in the *Oil and Gas Journal* (Thrash, 1991). The set of 138 facilities, listed on Table 7.3 with production data, is assumed to represent all direct dischargers. The total production level for direct dischargers in California is 1,619,950 barrels per day; the total production level for direct dischargers not in California is 12,376,556 barrels per day. In general, parameters representing individual chemicals, and parameters representing conventional pollutants or pollutant groups that have a large sample size, are selected for inclusion in the production weighted data set. These parameters are identified in Table 7.2. The general equation for production weighted extrapolation is given as:

$$TOTLOAD = SMPLOAD * \left[\frac{TOTPROD}{SMPPROD} \right]$$

Where: TOTLOAD = Total extrapolated load
SMPLOAD = Sample load based on facilities reporting the parameter in PCS
TOTPROD = Total production level
SMPPROD = Sample production level

Table 7.3 Crude Production for 138 Direct Discharging Petroleum Refineries

Sorted by State and Company Name

NPDES Permit No.	Company	City	State	Crude Production (bbl/day)
AK0000841	Tesoro Alaska Petroleum Co	Kenai	AK	72,000
AL0000574	Gamxx Energy, Inc., Theodore	Mobile County	AL	26,500
AL0000973	Hunt Refining Company	Tuscaloosa	AL	33,500
AL0055859	LL&E Petroleum Marketing Inc	Saraland	AL	80,000
AR0000663	Berry Petroleum Corp-Stephens	Stephens	AR	5,700
AR0000591	Cross Oil-Smackover	Smackover	AR	6,770
AR0000647	Lion Oil Company	El Dorado	AR	48,000
CA0000680	ARCO	Carson	CA	223,000
CA0005134	Chevron U.S.A. Products Co.	Richmond	CA	205,000
CA0000337	Chevron U.S.A., Inc.	El Segundo	CA	254,000
CA0005550	Exxon Co., USA	Benicia	CA	128,000
CA0005096	Pacific Refining Co.	Hercules	CA	52,250
CA0057177	Powerine Oil Co.	Santa Fe Springs	CA	46,500
CA0005789	Shell Oil Co.	Martinez	CA	140,100
CA0003778	Texaco Refining/Marketing Inc.	Wilmington	CA	95,000
CA0055387	Torrance Refinery	Torrance	CA	123,000
CA0004961	Tosco Refining Co.	Martinez	CA	132,000
CA0005053	Union Oil Co. Of Ca.	Rodeo	CA	56,550
CA0000809	Unocal	Carson	CA	108,000
CA0000051	Unocal Corporation	Arroyo Grande	CA	56,550
CO0001210	Colorado Refining Company	Commerce City	CO	28,000
CO0001147	Conoco, Inc.	Commerce City	CO	48,000
CO0000078	Landmark Petroleum, Inc.	Fruita	CO	15,200
DE0000256	Star Enterprises	Delaware City	DE	140,000
GA0001902	Young Refining Corp	Douglasville	GA	7,500
HI0000329	Chevron U.S.A., Inc.	Honolulu	HI	52,800
IL0001244	Clark Oil-Wood River	Hartford	IL	57,000
IL0004219	Indian Refining-Lawrenceville	Lawrenceville	IL	54,000
IL0004073	Marathon Oil-Robinson	Robinson	IL	170,000
IL0002861	Mobil Oil-Joliet Ref	Joliet	IL	180,000
IL0000205	Shell Oil Co.-Wood River	Roxana	IL	274,000
IL0001589	Uno-Ven Company-Lemont	Lemont	IL	147,000
IN0000108	American Oil Company (Amoco)	Whiting	IN	350,000
IN0002470	Countrymark Cooperative, Inc.	Mount Vernon	IN	20,600
IN0001244	Laketon Refining Corporation	Laketon	IN	8,300

Table 7.3 Crude Production for 138 Direct Discharging Petroleum Refineries

Sorted by State and Company Name

NPDES Permit No.	Company	City	State	Crude Production (bbl/day)
IN0002364	Marathon Petroleum Co., Ird	Indianapolis	IN	50,000
KS0000205	Coastal Ref. & Marketing	Butler County	KS	30,400
KS0000248	Farmland-Coffeyville Refinery	Coffeyville	KS	59,600
KS0050997	Farmland-Phillipsburg Refinery	Phillipsburg	KS	26,400
KS0000761	Texaco Refining & Marketing Inc	El Dorado	KS	80,000
KS0000434	Total Petroleum, Inc	Arkansas City	KS	56,000
KY0000388	Ashland Petroleum Co	Ashland	KY	213,400
KY0094579	Somerset Refinery Inc	Somerset	KY	5,500
LA0032417	Atlas Processing Co-Shreveport	Shreveport	LA	46,200
LA0003115	BP Oil Company	Belle Chasse	LA	218,500
LA0052370	Calcasieu Refining Co.	Lake Charles	LA	13,500
LA0046612	Calumet Refining Co.	Princeton	LA	4,376
LA0006963	Canal Refining-Church Point	Church Point	LA	9,865
LA0005941	Citgo Petroleum Corp.	Lake Charles	LA	320,000
LA0003026	Conoco Inc-Lake Charles Refine	Westlake	LA	159,500
LA0005584	Exxon Co USA-Baton Rouge	Baton Rouge	LA	421,000
LA0005312	Kerr-Mcgee Corp-Cotton Valley	Cotton Valley	LA	7,800
LA0045683	Marathon Oil Co	Garyville	LA	225,000
LA0004260	Mobil Oil Corp-Chalmette	Chalmette	LA	160,000
LA0003646	Murphy Oil USA Inc	Meraux	LA	97,000
LA0051942	Phibro Energy USA, Inc-Krotz	Krotz Springs	LA	56,700
LA0054216	Phibro Energy USA, Inc-St.Rose	St Rose	LA	28,300
LA0039390	Placid Refining Co-Port Allen	Port Allen	LA	48,000
LA0003522	Shell Oil Co-Norco	Norco	LA	215,000
LA0006041	Star Enterprise	Convent	LA	225,000
MI0003778	Lakeside Refining Co	Kalamazoo	MI	5,600
MI0001066	Total Petroleum Inc	Alma	MI	45,600
MN0000256	Ashland Oil Inc	Saint Paul Park	MN	67,100
MN0000418	Koch Refining Co-Rosemount	Rosemount	MN	218,500
MS0002984	Amerada Hess Corp Purvis	Purvis	MS	30,000
MS0001481	Chevron USA	Pascagoula	MS	295,000
MS0034711	Ergon Refining Incorporated	Vicksburg	MS	16,800
MS0001686	Southland Oil Company	Sandersville	MS	11,000

Table 7.3 Crude Production for 138 Direct Discharging Petroleum Refineries

Sorted by State and Company Name

NPDES Permit No.	Company	City	State	Crude Production (bbl/day)
MS0001678	Southland Oil Lumberton	Lumberton	MS	5,800
MT0000264	Cenex-Laurel Refinery	Laurel	MT	40,400
MT0000256	Conoco Inc	Billings	MT	24,750
MT0029742	Conoco, Inc	Billings	MT	24,750
MT0000477	Exxon Co USA (Billings Refin.)	Billings	MT	42,000
MT0000434	Montana Refining Co-Blackeagle	Black Eagle	MT	7,000
ND0000248	Amoco Oil Company	Mandan	ND	58,000
NJ0001511	Bayway Refining Company	Linden	NJ	13,000
NJ0000221	Chevron USA Inc	Perth Amboy	NJ	80,000
NJ0005401	Coastal Eagle Point Oil Co	West Deptford	NJ	109,520
NJ0005029	Paulsboro Refinery	Paulsboro	NJ	100,000
NJ0028878	Port Reading Refining Fac	Port Reading	NJ	50,000
NY0028592	Cibro Petroleum Products, Inc	Albany	NY	39,900
OH0005657	Ashland Oil, Inc.	Canton	OH	66,000
OH0002461	BP Oil Company	Toledo	OH	120,650
OH0002623	BP Oil Company	Lima	OH	142,500
OH0002763	Sun Refining & Marketing Co	Toledo	OH	125,000
OK0000256	Conoco Inc.-Ponca City Refiner	Ponca City	OK	140,000
OK0000825	Kerr-Mcgee Corp-Garvin	Wynnewood	OK	43,000
OK0001309	Sinclair Oil Corporation	Tulsa	OK	50,000
OK0000876	Sun Refining & Marketing Compa	Tulsa	OK	85,000
OK0001295	Total Petroleum	Ardmore	OK	68,000
PA0012637	BP Oil Inc.	Marcus Hook	PA	171,000
PA0011533	Chevron U.S.A. Products, Co.	Philadelphia	PA	175,000
PA0002551	Pennzoil United Inc Rouseville	Rouseville,	PA	15,700
PA0011096	Sun Refining & Marketing, Inc	Philadelphia	PA	130,000
PA0005304	United Refining Co-Warren	Warren	PA	64,600
PA0002674	Witco Chem Corp	Bradford	PA	10,000
PR0000370	Caribbean Gulf Refining Corp	Bayamon	PR	38,000
PR0000400	Puerto Rico Sun Oil Co.	Yabucoa	PR	85,000
TN0059226	Mapco Petroleum,Inc	Shelby County (Mbo)	TN	75,000
TX0002984	Amoco Texas Refining Company	Texas City	TX	433,000
TX0004847	Chevron USA Inc		TX	66,000

Table 7.3 Crude Production for 138 Direct Discharging Petroleum Refineries

Sorted by State and Company Name

NPDES Permit No.	Company	City	State	Crude Production (bbl/day)
TX0005991	Chevron USA Inc Port Arthur	Port Arthur	TX	315,300
TX0006211	Citgo Refining & Chemicals Inc	Corpus Christi	TX	132,500
TX0066591	Coastal Refinig & Marketing, I	Corpus Christi	TX	45,125
TX0006904	Coastal Refining & Marketing,	Corpus Christi	TX	45,125
TX0004626	Crown Central Petr-Houston	Pasadena	TX	100,000
TX0088331	Diamond Shamrock Refining & Ma	Three Rivers	TX	53,000
TX0006271	Exxon Corp-Houston	Baytown	TX	396,000
TX0104515	Fina Oil & Chem-Big Spr	Big Spring	TX	55,000
TX0004201	Fina Oil & Chem-Port A	Jefferson County	TX	110,000
TX0084778	Howell Hydrocarbons & Chem. In	Houston	TX	1,900
TX0006289	Koch Refining Co	Corpus Christi	TX	125,000
TX0001449	La Gloria Oil & Gas Co-Tyler	Tyler	TX	49,500
TX0003247	Lyondell Petrochemical Co.	Houston	TX	265,000
TX0003697	Marathon Oil Company	Texas City	TX	70,000
TX0004227	Mobil Chem-Beaumont	Jefferson County	TX	275,000
TX0002976	Phibro Energy USA, Inc-Houston	Houston	TX	67,000
TX0006009	Phibro Energy USA, Inc-Tx City	Texas City	TX	123,500
TX0009148	Phillips 66 Co-Hutchins	Borger	TX	105,000
TX0007536	Phillips 66 Co-Sweeny Refinery	Sweeny	TX	175,000
TX0004871	Shell Oil Co-Deer Park	Harris County	TX	215,900
TX0006599	Southwestern Refining-Corpus C	Corpus Christi	TX	104,000
TX0005835	Star Enterprise-Port Arthur	Port Arthur	TX	250,000
TX0063355	Valero Refining Co.-Corpus Chr	Corpus Christi	TX	27,000
UT0000175	Chevron U.S.A., Inc	Salt Lake City	UT	45,000
UT0000507	Phillips 66 Company	West Bountiful	UT	25,000
VA0003018	American Oil Yorktown	Yorktown	VA	53,000
VI0000019	Hess Oil Virgin Islands Corp	St. Croix	VI	545,000
WA0022900	ARCO Petroleum Products Co	Ferndale	WA	167,000
WA0002984	BP Oil Company	Ferndale	WA	90,250
WA0000761	Shell Oil Co		WA	89,300

Table 7.3 Crude Production for 138 Direct Discharging Petroleum Refineries

Sorted by State and Company Name

NPDES Permit No.	Company	City	State	Crude Production (bbl/day)
WA0003204	Sound Refining Co	Tacoma	WA	11,900
WA0002941	Texaco Inc	Anacortes	WA	132,000
WA0001783	US Oil & Refining Company	Tacoma	WA	32,775
WI0003085	Murphy Oil USA Inc Superior Re	Superior	WI	32,000
WV0004626	Quaker State Oil Refining Corp	Newell	WV	10,500
WY0000442	Frontier Oil & Refining Co	Cheyenne	WY	35,000
WY0001163	Wyoming Refining Co	Denver	WY	11,900

The low-end (zero for non-detects) production-weighted loadings are given by parameter on Table 7.4 and for the high-end estimate (half detection limit) is presented on Table 7.5. These summaries identify pollutants as classical or conventional, organics or metals. The designation as classical is given to parameters which have been measured historically as part of refinery discharge permits and are neither an organic nor a metal. Parameters that represent conventional pollutant parameters such as BOD are listed at the bottom of both Table 7.4 and 7.5. National totals of metals and organics for 1992 are between 2.1 and 2.6 million lbs/yr. (Double counting may occur in the reported national total loadings reported for organics. Hydrocarbons and total recoverable phenolics are listed with other individual organics and are included in the total). Over 577,000 pounds of hydrocarbons and approximately 28,000 pounds of total recoverable phenolics were estimated to be released in 1992. Annual releases of priority pollutants were projected to be between 1.0 and 1.6 million pounds. In general, the average releases per facility are greater for non-California facilities. Notable exceptions are nickel, selenium, and phenolics. Note the significance of values below detection in the estimated ethylbenzene load for non-California facilities.

Assumptions and Limitations

Several assumptions and limitations of the above described analyses include:

- Only refineries considered as “major facilities” that directly discharge to surface waters and have a NPDES permit are included in PCS. Consequently, PCS may be incomplete in terms of petroleum refining facilities, pollutants, or wastestreams.

- Facilities are not required by their NPDES permit to report on all chemicals actually discharged. A facility is only required to report on a particular chemical if it is specified in the permit conditions.
- Although EDS converts all values to standard units, there are an undetermined number of unit code/measurement value mismatches in PCS, as well as invalid discharge flow records and analytical test results, that cannot be readily identified after EDS processing.
- National production-weighted load estimates assume that all petroleum refineries in a particular grouping discharge similar waste streams. The fewer the data points in a parameter sample set, the greater the uncertainty that the parameter loading rate is representative of refinery discharge in general.

Table 7.4 Comparison of California and Non-California PCS Loads after Production Weighting (Low-End Estimate)

Parameter Name	Poll. Type *	Non-Calif. Loads		California Loads		Total Load (lb/yr)	Priority Pollutants (lb/yr)
		Total (lb/yr)	**Average (lb/fac/yr)**	**Total (lb/yr)**	**Average (lb/fac/yr)**		
Bromide (as Br)	C	1,187,691	9,502			1,187,691	
Chloride (as Cl)	C	146,706,014	1,173,648	107,420,130	8,263,087	254,126,144	
Chlorine, Total Residual	C	3,717,957	29,744	39,083	3,006	3,757,040	
Cyanide, Total (as CN)	C	10,050	80	5,488	422	15,538	15,538
Fluoride, Total (as F)	C	6,911,812	55,294			6,911,812	
Nitrogen, Ammonia, Total (as N)	C	3,552,591	28,421	178,232	13,710	3,730,823	
Phosphate, Total (as PO_4)	C	1,148,190	9,186			1,148,190	
Sulfide, Total (as S)	C	35,723	286	1,738	134	37,461	
Subtotal		**163,270,028**	**1,306,160**	**107,644,672**	**8,280,359**	270,914,700	**15,538**
Aluminum, Total (as Al)	M	11,368	91	14,736	1,134	26,104	
Arsenic, Total (as As)	M	78,851	631	764	59	79,615	79,615
Cadmium, Total (as Cd)	M	780	6	19	1	799	799
Chromium, Hexavalent (as Cr)	M	7,433	59	89	7	7,522	7,522
Chromium, Total (as Cr)	M	24,450	196	3,088	238	27,537	27,537
Cobalt, Total (as Co)	M			33	3	33	
Copper, Total (as Cu)	M	27,787	222	625	48	28,412	28,412
Iron, Total (as Fe)	M	2,459	20			2,459	
Lead, Total (as Pb)	M	13,840	111	117	9	13,957	13,957
Manganese, Total (as Mn)	M	70,437	563			70,437	
Mercury, Total (as Hg)	M	14,600	117	9	1	14,609	14,609
Nickel, Total (as Ni)	M	11,298	90	3,975	306	15,274	15,274
Selenium, Total (as Se)	M	7,758	62	11,691	899	19,449	19,449

Table 7.4 Comparison of California and Non-California PCS Loads after Production Weighting (Low-End Estimate)

Parameter Name	Poll. Type *	Non-Calif. Loads Total (lb/yr)	Non-Calif. Loads Average (lb/fac/yr)	California Loads Total (lb/yr)	California Loads Average (lb/fac/yr)	Total Load (lb/yr)	Priority Pollutants (lb/yr)
Silver, Total (as Ag)	M	520	4	24	2	544	544
Vanadium, Total (as V)	M			87,154	6,704	87,154	
Zinc, Total (as Zn)	M	76,744	614	9,308	716	86,053	86,053
Subtotal		**348,326**	**2,787**	**131,631**	**10,125**	479,957	**293,771**
Benzene	O	1,507	12			1,507	1,507
Bis (2-ethylhexyl) Phthalate	O	1,405	11			1,405	1,405
Chloroform	O	250	2			250	250
Ethylbenzene	O	214,124	1,713	1	0.1	214,125	214,125
Hexachlorobenzene	O	12	0			12	12
Hydrocarbons, in H_2O, IR, CC14 Ext. Chromat	O	577,519	4,620			577,519	
Methyl Tert-butyl Ether	O	217,266	1,738			217,266	
Phenolics, Total Recov.	O	23,769	190	3,411	262	27,180	
Phenol, Single Compound	O	10,070	81			10,070	10,070
Toluene	O	46,957	376	4	0.3	46,962	46,962
Xylene	O			12	1	12	
Subtotal		**1,517,949**	**12,144**	**144,366**	**11,105**	1,662,316	**654,153**
BOD, 5-day (20 Deg. C)	C	11,399,374	91,195	970,502	74,654	12,369,876	
Carbon, Total Organic (TOC)	C	27,928,894	223,431	2,591,416	199,340	30,520,310	
Oil and Grease Freon Extr-grav Meth	C	6,709,057	53,672	207,957	15,997	6,917,013	
Oxygen Demand, Chem. (High Level) (COD)	C	86,050,803	688,406	5,213,221	401,017	91,264,025	
Solids, Total Suspended	C	33,744,172	269,953	1,385,076	106,544	35,129,248	

* Pollutant Type: (C) Classical/Conventional; (M) Metal; (O) Organic

Table 7.5 Comparison of California and Non-California PCS Loads after Production Weighting (High-End Estimate)

Parameter Name	Poll. Type *	Non-Calif.Loads		California Loads		Total Load (lb/yr)	Priority Pollutants (lb/yr)
		Total (lb/yr)	Average (lb/fac/yr)	Total (lb/yr)	Average (lb/fac/yr)		
Bromide (as Br)	C	1,187,691	9,502			1,187,691	
Chloride (as Cl)	C	146,706,014	1,173,648	107,420,130	8,263,087	254,126,144	
Chlorine, Total Residual	C	3,717,957	29,744	39,220	3,017	3,757,177	
Cyanide, Total (as CN)	C	10,050	80	5,586	430	15,636	15,636
Fluoride, Total (as F)	C	6,911,812	55,294			6,911,812	
Nitrogen, Ammonia, Total (as N)	C	3,561,088	28,489	197,629	15,202	3,758,717	
Phosphate, Total (as PO_4)	C	1,148,190	9,186			1,148,190	
Sulfide, Total (as S)	C	38,317	307	3,930	302	42,247	
Subtotal		163,281,118	1,306,249	107,666,496	8,282,038	270,947,615	15,636
Aluminum, Total (as Al)	M	11,368	91	15,773	1,213	27,141	
Arsenic, Total (as As)	M	78,851	631	790	61	79,642	79,642
Cadmium, Total (as Cd)	M	788	6	55	4	843	843
Chromium, Hexavalent (as Cr)	M	7,896	63	556	43	8,452	8,452
Chromium, Total (as Cr)	M	25,107	201	3,209	247	28,316	28,316
Cobalt, Total (as Co)	M			128	10	128	
Copper, Total (as Cu)	M	27,910	223	957	74	28,867	28,867
Iron, Total (as Fe)	M	2,459	20			2,459	
Lead, Total (as Pb)	M	28,882	231	360	28	29,243	29,243
Manganese, Total (as Mn)	M	70,437	563			70,437	
Mercury, Total (as Hg)	M	14,679	117	11	1	14,690	14,690
Nickel, Total (as Ni)	M	11,298	90	4,246	327	15,544	15,544
Selenium, Total (as Se)	M	7,758	62	11,784	906	19,542	19,542
Silver, Total (as Ag)	M	685	5	87	7	772	772
Vanadium, Total (as V)	M			88,115	6,778	88,115	
Zinc, Total (as Zn)	M	76,755	614	9,810	755	86,565	86,565
Subtotal		364,874	2,919	135,882	10,452	500,755	312,475
Benzene	O	1,515	12			1,515	1,515
Bis (2-ethylhexyl) Phthalate	O	1,405	11			1,405	1,405
Chloroform	O	250	2			250	250
Ethylbenzene	O	1,177,682	9,421	1	0	1,177,682	1,177,682

Table 7.5 Comparison of California and Non-California PCS Loads after Production Weighting (High-End Estimate)

		Non-Calif.Loads		California Loads		Total	Priority
Hexachlorobenzene	O	12	0			12	12
Hydrocarbons, in H_2O, IR, CC14 Ext. Chromat	O	578,654	4,629			578,654	
Methyl Tert-butyl Ether	O	217,266	1,738			217,266	
Phenolics, Total Recov.	O	24,308	194	3,577	275	27,885	
Phenol, Single Compound	O	10,172	81			10,172	10,172
Toluene	O	86,898	695	4	0	86,902	86,902
Xylene	O			12	1	12	
Subtotal		2,098,161	16,785	3,593	276	2,101,755	1,277,938
BOD, 5-day (20 Deg. C)	C	11,402,040	91,216	1,017,120	78,240	12,419,160	
Carbon, Tot Organic (TOC)	C	28,081,112	224,649	2,591,416	199,340	30,672,527	
Oil and Grease Freon Extr-grav Meth	C	6,863,165	54,905	223,355	17,181	7,086,520	
Oxygen Demand, Chem. (High Level) (COD)	C	86,050,909	688,407	5,213,221	401,017	91,264,131	
Solids, Total Suspended	C	33,746,916	269,975	1,402,484	107,883	35,149,400	
* Pollutant Type: (C) Classical/Conventional; (M) Metal; (O) Organic							

7.1.3 Analysis of Average Measured Pollutant Concentrations from PCS

In addition to EDS-generated loadings, measured average concentration values from monthly monitoring data were retrieved separately from PCS for 1992. Theres data set may include data not participating in the loadings analysis because of lack of corresponding discharge flow data. Conversely, parameters with large predicted loads may not have corresponding high concentrations because the load estimate may be a direct measurement (mass based limit) or may be based on a minimum or maximum concentration. Also, because the concentration data set is based on single measured values (rather than a formula as with the loadings data set) limited QA/QC procedures can be employed. For the concentration data, the range of measured values at the pollutant/discharge pipe level and at the overall pollutant level (i.e., for all discharge pipes) were examined. If either range exceeded three orders of magnitude, the concentration data at the discharge pipe level were checked for potential unit code/measurement value mismatches. In eight cases, obvious unit code errors were corrected; in an additional 13 cases, there were not enough data points to clearly identify a unit code error, yet the values were so extreme that they were considered highly questionable and were excluded from subsequent analysis. As with the loadings analysis, two sets of data were prepared: (1) a low-end estimate based on assigning zero to measurements below detection, and (2) a high-end estimate based on assuming half the detection limit. Measurements always below detection for a particular parameter at a particular discharge pipe were set equal to zero for both data sets.

Comparisons of average concentrations at California and non-California facilities at the low-end and high-end for the 20 parameters with data available for both groups are presented on Tables 7.6 and 7.7. Most parameters are measured at higher concentrations outside of California. Some parameters, such as cadmium, mercury, and arsenic are significantly higher on the average at non-California facilities. A few parameters, including selenium and cyanide, are significantly higher at California facilities. Additional tables summarizing concentration data by parameter for California, non-California, and all facilities combined are presented in Appendix B. These tables include all of the 74 parameters with measured average concentration data available, and also present the range and standard deviation. For comparison, Table 7.8 presents the average concentrations for 27 pollutants reported in the petroleum refining development document (US EPA, 1982a). These data reflect sampling done at current/BPT treatment levels prior to implementation of the 1982 BAT regulations (US EPA, 1982b). As with the PCS data, these data are limited by the frequency of detection. In general, the high-end PCS concentration averages for all facilities are on-line with or slightly lower than the levels reported in the 1982 development document. Exceptions to this are arsenic at both California and non-California facilities, mercury and cadmium at non-California facilities, and selenium at California facilities.

In the case of arsenic and mercury, the 1982 document reports high variability in the data that may reflect low confidence. In addition, the PCS parameters are measuring total mercury, total arsenic, and total cadmium. Much of this may include metal bound in compounds and complexes that may not be included in the 1982 measures. It is interesting to note that the high-end "total recoverable selenium" average concentration for non-California facilities (see Appendix B) matches the 1982 average almost exactly, whereas the high-end "total selenium" average concentration for California facilities is much higher.

Table 7.6 Comparison of California and Non-California PCS Concentration Data (Low-End Estimate)

(Parameters Available for Both Groups, all concentrations in µg/L)

Parameter	California				Non-California			
	Number of Facilities	Number of Observ.	Number of Non-Detects	Measured Average	Number of Facilities	Number of Observ.	Number of Non-Detects	Measured Average
Arsenic, Total (as As)	3	25	11	3.60	2	24	0	408.42
BOD, 5-day (20 Deg. C)	6	58	20	6,281.03	25	241	2	14,264.70
Cadmium, Total (as Cd)	3	25	24	0.02	2	8	1	34.79
Carbon, Tot. Organic (TOC)	4	65	1	9,177.54	15	366	17	10,219.05
Chromium, Hexavalent (as Cr)	5	84	72	0.41	21	189	65	2.92
Chromium, Total (as Cr)	6	63	42	2.06	22	192	59	13.53
Copper, Total (as Cu)	4	36	9	9.53	4	44	6	11.39
Cyanide, Total (as Cn)	3	31	12	54.77	2	24	7	23.42
Lead, Total (as Pb)	3	32	29	3.44	1	8	0	8.38
Mercury, Total (as Hg)	3	25	23	0.03	2	16	0	8.75
Nickel, Total (as Ni)	4	39	9	11.38	2	13	1	29.69
Nitrogen, Ammonia Total (as N)	5	43	3	3,110.70	26	234	6	5,140.18
Oil and Grease Freon Extr-grav Meth	7	76	24	2,626.84	31	464	43	3,451.35
Oxygen Demand, Chem. (High Level) (COD)	5	45	0	72,844.44	17	165	0	126,609.21
Phenolics, Total Recoverable	6	89	31	18.62	25	231	21	45.76
Selenium, Total (as Se)	4	40	1	155.50	1	3	1	3.90
Silver, Total (as Ag)	3	25	24	0.02	1	3	1	2.10
Solids, Total Suspended	7	69	12	13,872.46	33	457	17	23,981.16
Sulfide, Total (as S)	5	45	44	1.11	20	175	23	55.48
Zinc, Total (as Zn)	5	50	8	165.50	4	50	1	136.36

Table 7.7 Comparison of California and Non-California PCS Concentration Data (High-End Estimate)

(Sorted by Parameter Name for Parameters Available for Both Groups, All concentrations in µg/L)

Parameter	California				Non-California			
	Number of Facilities	Number of Observ.	Number of Non-detects	Measured Average	Number of Facilities	Number of Observ.	Number of Non-detects	Measured Average
Arsenic, Total (as As)	3	25	11	4.46	2	24	0	408.42
BOD, 5-day (20 Deg. C)	6	58	20	7,462.07	25	241	2	14,273.00
Cadmium, Total (as Cd)	3	25	24	0.02	2	8	1	37.91
Carbon, Tot. Organic (TOC)	4	65	1	9,189.85	15	366	17	10,244.59
Chromium, Hexavalent (as Cr)	5	84	72	4.24	21	189	65	3.88
Chromium, Total (as Cr)	6	63	42	3.10	22	192	59	17.19
Copper, Total (as Cu)	4	36	9	10.45	4	44	6	11.93
Cyanide, Total (as Cn)	3	31	12	54.77	2	24	7	25.67
Lead, Total (as Pb)	3	32	29	5.13	1	8	0	8.38
Mercury, Total (as Hg)	3	25	23	0.09	2	16	0	8.75
Nickel, Total (as Ni)	4	39	9	12.22	2	13	1	29.69
Nitrogen, Ammonia Total (as N)	5	43	3	3,110.70	26	234	6	5,149.82
Oil and Grease Freon Extr-grav Meth	7	76	24	2,705.79	31	464	43	3,533.83
Oxygen Demand, Chem. (High Level) (COD)	5	45	0	72,844.44	17	165	0	126,609.21
Phenolics, Total Recoverable	6	89	31	21.47	25	231	21	46.79
Selenium, Total (as Se)	4	40	1	155.50	1	3	1	4.23
Silver, Total (as Ag)	3	25	24	0.02	1	3	1	5.43
Solids, Total Suspended	7	69	12	13,944.93	33	457	17	24,261.24
Sulfide, Total (as S)	5	45	44	8.44	20	175	23	62.65
Zinc, Total (as Zn)	5	50	8	170.77	4	50	1	136.86

Table 7.8. Direct Discharge Pollutant Concentration Levels Reported in 1982 Effluent Guidelines Development Document (Current/BPT)

Pollutant	Average Flow-Weighted Pollutant Concentration (µg/L)	Maximum Pollutant Concentration (µg/L)	Frequency of Detection
Chloroform	3.1	66	2/17
Benzene	2.3	11	3/17
Toluene	10.1	35	1/17
2,4-Dichlorophenol[c]	0.2	10	1/17
p-chloro-m-cresol[c]	0.3	10	1/17
Dimethyl phthalate[c]	0.1	3	1/17
Diethyl phthalate	1.4	30	1/17
Di-n-butyl phthalate	0.04	10	2/17
Acanaphthene	1.1	6	1/17
Benzo(a)pyrene[c]	0.1	3	2/17
Chyrsene	0.02	1	2/17
Phenanthrene	0.2	1	1/17
Pyrene	0.1	7	1/17
Arsenic[b]	0.01	31	3/17
Beryllium	0.04	2	2/51
Cadmium[c]	0.25	20	3/93
Chromium (Trivalent)	107.8	1230	41/53
Chromium (Hexavalent)	7.7	110	8/48
Copper	9.8	199	25/50
Cyanide	45.5	320	26/39
Lead	5.2	113	10/54
Mercury	0.9	6	20/45
Nickel	3.4	74	13/55
Selenium	17.2	32	17/20
Silver[c]	0.04	4	1/47
Thallium[c]	3.2	12	5/14
Zinc	104.6	620	43/59

Notes

a. All 129 priority pollutants were analyzed during the sampling of the Current/BPT wastestream. Thirteen organic pollutants and fourteen inorganic pollutants were detected. The Current/BPT concentrations were calculated by flow-weighting the data available for the seventeen direct dischargers sampled.

b. Low values were not included, and were assumed to be not quantifiable. High values were not included because laboratory contamination was suspected; therefore, data were assumed to be invalid.

c. The Current/BPT pollutant concentration is greater than that in the Pretreated Raw wastestream because of the variability of the data during sampling.

7.1.4 Toxic Release Inventory

In October 1986, Congress enacted the Emergency Planning and Community Right-to-know Act (EPCRA), as Title III of the Superfund Amendments and Reauthorization Act (SARA). Section 313 of EPCRA requires manufacturing facilities to report their annual use and releases of more than 300 toxic chemicals to State and local Emergency Planning Commissions, and to the EPA’s Toxic Release Inventory (TRI).

Facilities are required to report releases and offsite transfers of EPCRA Section 313 chemicals to TRI, if they meet all of the following criteria:

- They conduct manufacturing operations in SIC codes 20 through 39.
- They have ten or more full-time employees or the equivalent.
- They manufacture or process the EPCRA Section 313 chemical in an amount greater than 25,000 pounds/year.
- They otherwise use the EPCRA Section 313 chemical in an amount greater than 10,000 pounds/year.

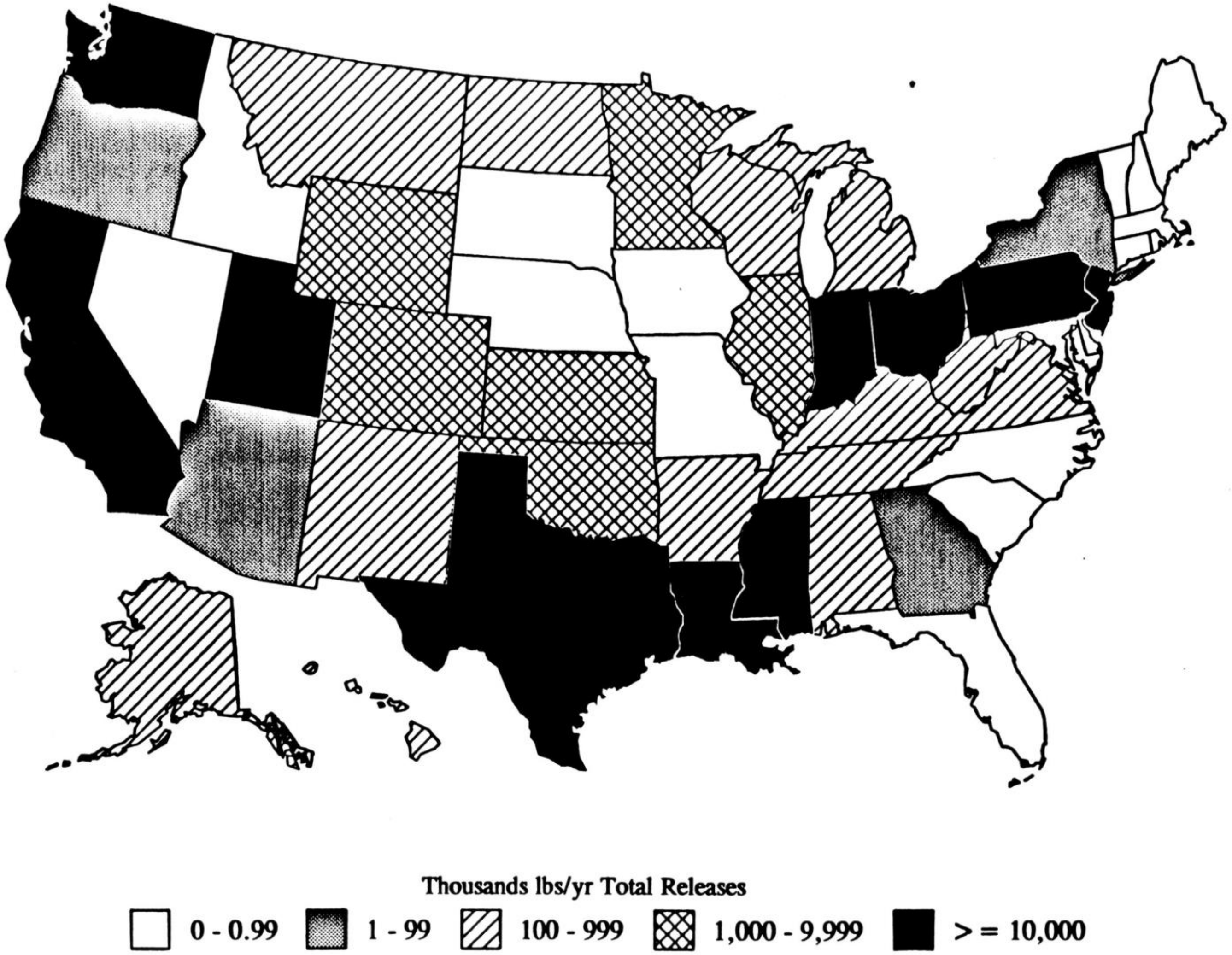
EPCRA requires reporting of five types of onsite releases: (1) fugitive air emissions; (2) stack air emissions; (3) surface water discharges; (4) underground injections; and (5) land disposal. EPCRA also requires reporting of two types of offsite waste transfers containing listed chemicals; (1) transfers to POTWs; and (2) transfers to other treatment or disposal facilities. In addition, EPCRA specifies that EPA must compile these release reports into an annual inventory of releases and transfers and make this inventory available to the public. EPA stores reported release data in the Toxics Release Inventory System (TRIS) which is maintained by EPA's Office of Pollution Prevention and Toxics (OPPT).

7.1.5 Reported Annual Pollutant Loads from TRI

Two hundred five (205) petroleum refining facilities, identified by primary SIC code 2911, reported data to TRI in 1991; some facilities may not have been required to report because they did not meet employment or chemical use thresholds during 1991. Releases and transfers from the 205 facilities, located in 37 states, total 738.8 million pounds. The highest releases are from ten states: California, Indiana, Louisiana, Mississippi, New Jersey, Ohio, Pennsylvania, Texas, Utah, and Washington (Figure 7.1). The top two reporting states are Indiana and Pennsylvania with 201.8 and 110.9 million pounds, respectively.

The largest releases and transfers are to offsite locations other than POTWs (e.g. to recycling, energy recovery or treatment and disposal) (85 percent), air (10 percent) and underground injections (3 percent). Releases to surface waters, transfers to POTWs, and land disposal each represent less than 1 percent. The chemical with the highest reported amount of releases or transfers is sulfuric acid (a byproduct of processing), accounting for 84 percent of the total chemicals released or transferred. However, because refineries are required to neutralize their wastes prior to discharge, the sulfate would not be in an acidic form and would be present as a more benign the salt of inorganic cations in the wastewater. A total of 119 chemicals and compounds are identified, 65 of which are released to either surface waters or POTWs.

Figure 7.1 Geographic Distribution of 1991 TRI Chemical Releases and Transfers



Forty-four priority pollutants discharged by petroleum refining facilities are reported to TRI in 1991. Releases and transfers from these facilities total 33.5 million pounds. The largest releases and transfers are to air (70 percent), offsite locations other than POTWs (15 percent), POTWs (8 percent), underground injections (5 percent), and land (2 percent). Releases to surface waters are less than 1 percent. The priority pollutant with the highest reported amount of releases or transfers is toluene (44 percent). Seventy-seven (77) percent of the releases are from three priority pollutants (toluene, benzene, and phenol).

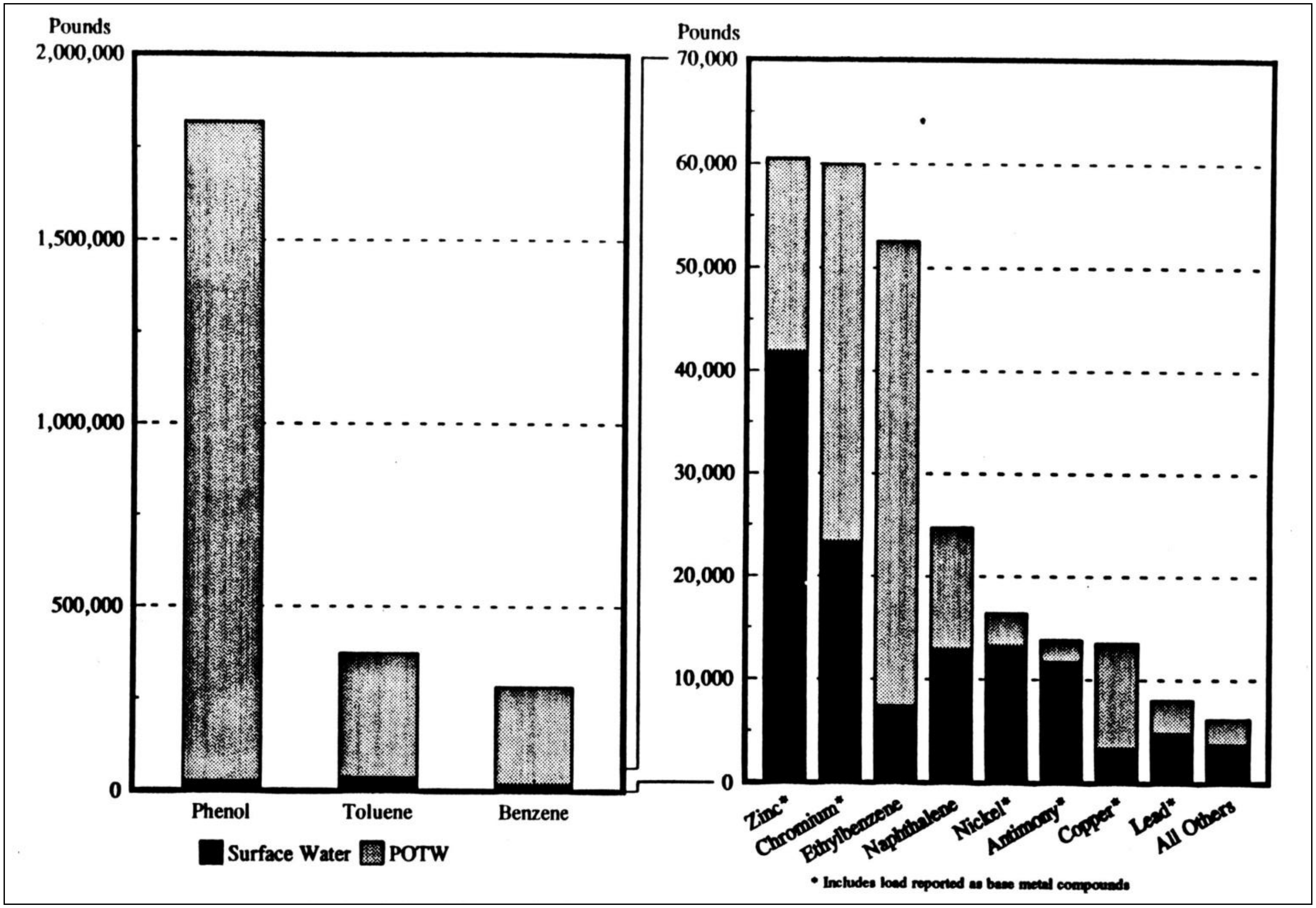
Releases and transfers to POTWs and surface waters are identified from 112 direct dischargers, 32 indirect dischargers, and 15 that discharge to both surface water and POTWs. National totals for 1991 are 4.33 million lbs/yr, or 34,100 lbs/yr/facility to surface waters, and 6.94 million lbs/yr, or 148,000 lbs/yr/facility to POTWs. A table presenting TRI surface water releases and POTW transfers by pollutant is presented in Appendix C. Annual loads of priority pollutants are 207,000 lbs/yr, or 1,600 lbs/yr/facility to surface waters, and 2.52 million lbs/yr, or 53,200 lbs/yr/facility to POTWs. Transfers to POTWs (92 percent of all releases) far exceed releases to surface waters. Figure 7.2 depicts the priority pollutants with the highest reported amount of surface water releases or POTW transfers. Three priority pollutants (phenol, toluene, benzene) account for 91 percent of the total releases and transfers. The vast majority of this load (over 90 percent) would likely biodegrade or volatilize during typical secondary wastewater treatment.

Assumptions and Limitations

Several assumptions and limitations of this analysis include:

- Only facilities reporting releases of Section 313 chemicals, and meeting threshold requirements, are required to report in TRI. Consequently, TRI may be incomplete in terms of petroleum refining facilities, pollutants, or wastestreams.
- Facilities in TRI with releases under 1,000 pounds for any one chemical may submit a range of the release/transfer amount for that chemical. For this study, OPPT standards are followed by using 5 pounds for loads of 0 to 10 pounds; 250 pounds for loads of 10 to 499; and 750 pounds for loads of 500 to 999.
- Data reported by industrial facilities are determined by a variety of methods. Therefore, the accuracy, precision, and comparability of TRI data are unknown.
- Data are based only on facilities identified by primary SIC code 2911. Because many facilities engage in numerous industrial activities, this may exclude some releases generated from petroleum refining and include some releases not attributable to refining activities.

Figure 7.2 1991 TRI Priority Pollutant Releases to Surface Water and POTWs



Total Priority Pollutant Surface Water/POTW Releases = 2.73 Million Pounds

7.2 Fate and Toxicity Evaluation of Released Pollutants

The environmental fate and toxicity of pollutant releases are evaluated by: (1) compiling physical-chemical and toxicity data, and POTW inhibition and sludge contamination values for identified pollutants; (2) categorizing the pollutants based on their potential toxicity and environmental fate; (3) weighting loads from PCS and TRI according to toxicity and bioaccumulation potential; and (4) evaluating whole effluent toxicity test data.

7.2.1 Compilation of Physical-Chemical and Toxicity Data and Information to Evaluate Indirect Discharges

Physical-chemical properties and toxicity data, both measured and estimated, are compiled for toxic pollutants currently being discharged by petroleum refining facilities according to available sources. These data are compiled from Standards and Applied Science Division's (SASD) Toxics Data Base (TDB) which contains aquatic toxicity, human health, physical-chemical properties, and other information for over 1,600 toxic chemicals. The chemical specific data needed to conduct the fate and toxicity evaluation for this study include:

- Aquatic life criteria or toxic effect data for native aquatic species;
- Human health reference doses (RfD);
- Human health cancer potency slope factors;
- EPA maximum contaminant levels (MCLs) for drinking water protection;
- Henry's Law constants, vapor pressure and solubility values;
- Soil/sediment adsorption coefficients (K_{oc});
- Octanol-water partition coefficients (K_{ow});
- Bioconcentration factors (BCF) for native aquatic species; and
- Aqueous aerobic biodegradation rate constants.

Sources for the TDB include EPA ambient water quality criteria documents and updates, EPA's Assessment Tools for the Evaluation of Risk (ASTER) and the associated Aquatic Information Retrieval System (AQUIRE) and Environmental Research Laboratory-Duluth fathead minnow data base, EPA's Integrated Risk Information System (IRIS), the Registry of Toxic Effects of Chemical Substances (RTECS) data base, the Superfund Chemical Data Matrix (SCDM), Syracuse Research Corporation's CHEMFATE and BIODEG data bases, EPA and other government reports, scientific literature, and other primary and secondary data sources. To ensure that the examination is as comprehensive as possible, alternative measures are taken to compile data for chemicals for which physical-chemical property and/or toxicity data do not exist. Therefore, where necessary, values are estimated using quantitative structure-activity relationship (QSAR) models, or for some physical-chemical properties, utilizing published linear regression correlation equations, if available.

Information needed to evaluate adverse effects on POTW operations and sewage sludge quality includes inhibition values, sludge partitioning factors, and sludge contamination levels.

The lower values for POTW removal rate indicate less removal at the POTW, and therefore a higher portion of the pollutant reaches the receiving water. Inhibition values are the concentration of influent to the POTW likely to interfere with treatment. Sludge partitioning factors represent the proportion of a constituent load that will be found in primary or secondary sewage sludge. EPA recently established sludge criteria for lead, chromium and zinc, which restrict certain applications of sludge above criteria values. Inhibition values and sludge partitioning factors are obtained from the *Domestic Sewage Study* (US EPA, 1986), *Guidance Manual for Preventing Interference at POTWs* (US EPA, 1987), and *CERCLA Site Discharges to POTWs* guidance (US EPA, 1990). Data to determine allowable sludge contamination levels are obtained from the Agency's final rule on "Standards for the Use or Disposal of Sewage Sludge" (US EPA, 1993). Pollutant limits established for the final use or disposal of sewage sludge via application to agricultural and non-agricultural land are reported.

Information is compiled and summarized from the TDB for pollutants regulated in the discharge from 14 petroleum refining facilities located in Los Angeles County, California, which discharge their wastewaters to POTWs (Table 7.9). Removal rates for these 25 pollutants vary from a low of 0.52 (52 percent) for 2,4,6-trichlorophenol to a high of 0.98 (98 percent) for both toluene and acenaphthene. The inhibition concentrations for these pollutants are generally high, with the exception of lead and chromium. The sludge partitioning factors indicate that lead, chromium, zinc and cyanide will remain in sludge. Sludge with contaminant levels that exceed EPA criteria for less expensive disposal by land application must be disposed of through higher cost alternatives, such as incineration.

Table 7.9. POTW Information for Selected Indirect Discharges

(Sorted by CAS Number)

CAS Number	Pollutant Name	POTW Removal	Inhibition Value (µg/l)	Partition Factor	Sludge Criteria Value (mg/kg)
57125	Cyanide	0.704	5,000	1	
67663	Trichloromethane	0.676	500,000	0.015	
71432	Benzene	0.941	125,000	0.019	
74931	Methanethiol*	0.77		0.1	
83329	Acenaphthene	0.983	500,000		
85018	Phenanthrene	0.949	500,000		
86737	Fluorene	0.698	500,000		
88062	Trichlorophenol, 2,4,6-	0.516	50,000	0.079	
91203	Naphthalene	0.947	500,000	0.275	
95476	Xylene, o-	0.951	5,000	0.149	
95578	Chlorophenol, 2-	0.65	5,000	0.079	
100414	Ethylbenzene	0.938	200,000	0.06	
105679	Dimethylphenol, 2,4-	0.85	40,000	0.079	
106423	Xylene, p-		5,000	0.149	

Table 7.9. POTW Information for Selected Indirect Discharges

(Sorted by CAS Number)

108383	Xylene, m-	0.654	5,000	0.149	
108883	Toluene	0.976	200,000	0.278	
108952	Phenol	0.967	200,000	0.146	
129000	Pyrene	0.95	500,000		
218019	Chrysene	0.97	500,000		
7439921	Lead	0.918	100	1	300
7440473	Chromium	0.754	1,000	1	1200
7440666	Zinc	0.78	5,000	1	2800
7664417	Ammonia	0.6319	480,000		
14808798	Sulfate				
18496258	Sulfide		25,000		
Note: * = Representative of Mercaptans					

Assumptions and Limitations

Several assumptions and limitations of this compilation include:

- Data are used from readily available electronic data bases; other primary and secondary sources are not searched.
- Many of the data are estimated and therefore have a high degree of associated uncertainty.
- For some chemicals, neither measured nor estimated data are available for key categorization parameters. As a result, this study is an incomplete assessment of potential fate and toxicity of petroleum refining discharge.

7.2.2 Categorization of Pollutants

Human and ecological exposure and risk from toxic chemical releases is primarily a function of toxic potency, inter-media partitioning, and chemical persistence. These factors are dependant on chemical-specific properties relating to pharmocokinetic effects on living organisms, physical state, hydrophobicity/lipophilicity, and reactivity; as well as the mechanism and media of release and site-specific environmental conditions. The potential fate and toxicity of pollutants associated with petroleum refining, based on chemical-specific data, are examined in this portion of the study.

The objective of this generalized evaluation of fate and toxicity potential is to place chemicals into qualitative groups based on their potential environmental fate and impact. These categorization groups are based on techniques derived for:

- Acute aquatic toxicity (highly, moderately, or slightly toxic);

- Volatility from water (highly, moderately, slightly, or non volatile);
- Adsorption to soil/sediment (highly, moderately, slightly, or non adsorptive);
- Bioaccumulation potential (high, moderate, slight, or no significant potential); and
- Biodegradation potential (fast, moderately fast, slow, or resistant).

The primary advantage of the categorization methods is that the results allow the user to identify the potential impact/threat of a chemical. The methods effectively group chemicals based on their potential to harm the environment. Using key parameters, these categorization methods identify the relative aquatic toxicity and bioaccumulation fate for each chemical constituent (with sufficient data) of petroleum refining discharges. In addition, the potential to partition to various media (air, sediment/sludge, or water) and persist in the environment is identified for each organic constituent. The acute aquatic toxicity, volatility from water, soil/sediment adsorption, and bioconcentration categorization methods have been reviewed by EPA staff (Offices of Water; Health and Environmental Assessment; and the former Office of Toxic Substances), as well as by Dr. Warren J. Lyman, principal author of *Handbook of Chemical Property Estimation Methods* (Lyman et al, 1982). The biodegradation categorization method is based on *Handbook of Environmental Degradation Rates* (Howard et al, 1991). These methods are used for screening purposes only, and do not take the place of detailed pollutant assessments that analyze all fate and transport mechanisms.

This evaluation also identifies chemicals which (1) are known, probable, or possible human carcinogens; (2) are systemic human health toxicants; and (3) have EPA human health drinking water standards. The results of this analysis can provide a qualitative indication of potential risk posed by the release of these chemicals. Actual risk depends on the magnitude, frequency, and duration of pollutant loading; site-specific environmental conditions; proximity and number of human and ecological receptors; and relevant exposure pathways. The categorization schemes and ranges of parameter values defining the categories are presented in Appendix D.

The categorization assessment addresses the 96 individual pollutants identified from PCS data and TRI releases to surface water and POTW transfers. Inorganic constituents include heavy metals, halogens and other anionic species. The organic constituents encompass a broad class of aliphatic and aromatic alkanes, alcohols, acids, ketones, and ethers. Also represented are several polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and 2378-TCDD.

Aquatic toxicity data are available for most pollutants, with the exception of inorganic acids and anionic species. Discharges of these chemicals may cause indirect adverse ecological effects by altering receiving water chemistry. However, these potential effects are not addressed in this study. Fate and transport data (i.e., volatility from water, adsorption to soil/sediment, and biodegradation potential) are available for most organic pollutants and some inorganic pollutants (e.g., Henry's Law constant for mercury in its methylated form), therefore, the fate assessment is applicable primarily to organic pollutants. Bioconcentration factors are available for over half of the inorganic pollutants and all but two organic pollutants.

A summary of the categorization results is presented on Tables 7.10 and 7.11. Approximately one quarter of the pollutants exhibit high or moderate acute toxicity to aquatic life (Table 7.10). Pollutants notable for their aquatic toxicity include CDD/CDF, mercury, anthracene, cadmium, silver, and hexachlorobenzene (HCB). The most potent carcinogens include CDD/CDF, hexavalent chromium, arsenic, 1,3-butadiene, and HCB. Antimony, cadmium, and mercury are highly potent systemic toxicants. In total, 29 of the pollutants are potential carcinogens, 56 are recognized by EPA as human systemic toxicants, and 45 have EPA-assigned concentration limits for drinking water protection (Table 7.11).

Table 7.10 Number of Pollutants by Categorization Group (96 pollutants evaluated)

Environmental Effects and Projected Fate	High	Moderate	Slight or Slow	Not Significant	No Data
Acute Aquatic Toxicity	18	7	57		14
Volatility from Water	25	17	12	4	38
Adsorption to Solids	11	2	43	6	34
Bioaccumulation Potential	10	18	26	22	20
Biodegradation Potential	12	21	12	15	36

Table 7.11 Number of Pollutants with Health Effect Designations (96 pollutants evaluated)

Health Effect Designation	Number of Pollutants
Carcinogenic Effects[a]	29
Human Systemic Effects[b]	56
Drinking Water Values[c]	45

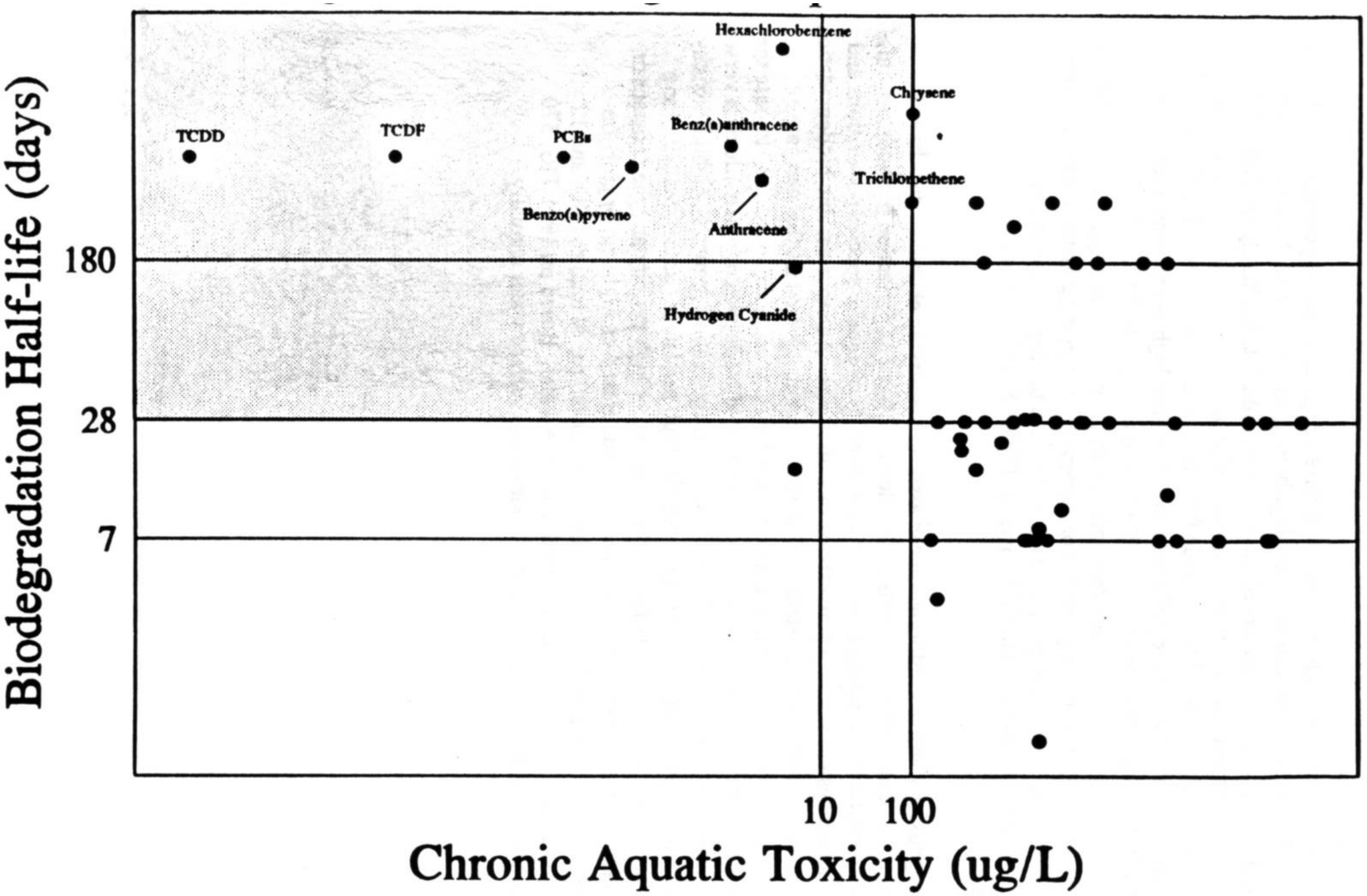
a. Chemicals with EPA classification as a human carcinogen (A), probable human carcinogen (B1, B2), or possible human carcinogen (C). Dioxins/furans with a TEF are also considered to be carcinogens.
b. Chemicals for which EPA has established a verified or provisional chronic reference dose (RfD).
c. Chemicals for which EPA has established a concentration limit or goal under the Safe Drinking Water Act (SDWA).

About three-quarters of the organic pollutants have a high to moderate potential to volatilize. Most of the likely volatile chemicals are only slightly toxic to aquatic life. Notable exceptions are HCB and mercury. Only 14 percent of the pollutants with data are highly or moderately adsorptive to soil/sediment. However, most of the highly adsorptive chemicals are also highly or moderately toxic to aquatic life. These include PAH compounds, phthalates, TCDD/TCDF, HCB, and mercury. One third of the pollutants with data have high to moderate bioaccumulation potential, which is strongly correlated with soil/sediment adsorption. TCDD/TCDF, HCB, mercury, and phenanthrene have the greatest potential to bioaccumulate. Approximately half of the pollutants are expected to biodegrade fast or moderately fast in oxygenated water. However, several highly to moderately toxic pollutants are resistant to biodegradation or only slowly biodegrade. These chemicals include HCB, pyrene, TCDD/TCDF, anthracene, and phenanthrene.

Combining toxicity and fate information can assist in identifying chemicals that have the greatest potential to cause adverse impacts upon release. In the categorization methods, chronic aquatic toxicity indicates the potential to reduce the viability of aquatic species populations and adversely affect ecosystem stability downstream of a discharge. Aqueous aerobic biodegradation half-life is used as a measure of persistence in the environment. Chemicals that can cause chronic toxic effects in small amounts and persist for a long period of time are likely to pose the greatest ecological threat. Figure 7.3 depicts a scatter plot of biodegradation half-life data versus chronic aquatic toxicity levels. The gridlines show the categorization groups, with high toxicity associated with low chronic aquatic toxicity levels and high persistence associated with long half-lives. The names of chemicals falling in the moderate or high toxicity and the resistant or slow biodegradation ranges (shaded region) are provided.

Based on high-end production-weighted 1992 PCS data, approximately 16 thousand pounds/year of total cyanide and 12 pounds/year of hexachlorobenzene are released to surface water. Based on 1991 TRI, 570 pounds of anthracene and hydrogen cyanide are released to surface water annually.

Figure 7.3. Ecological Impact Potential

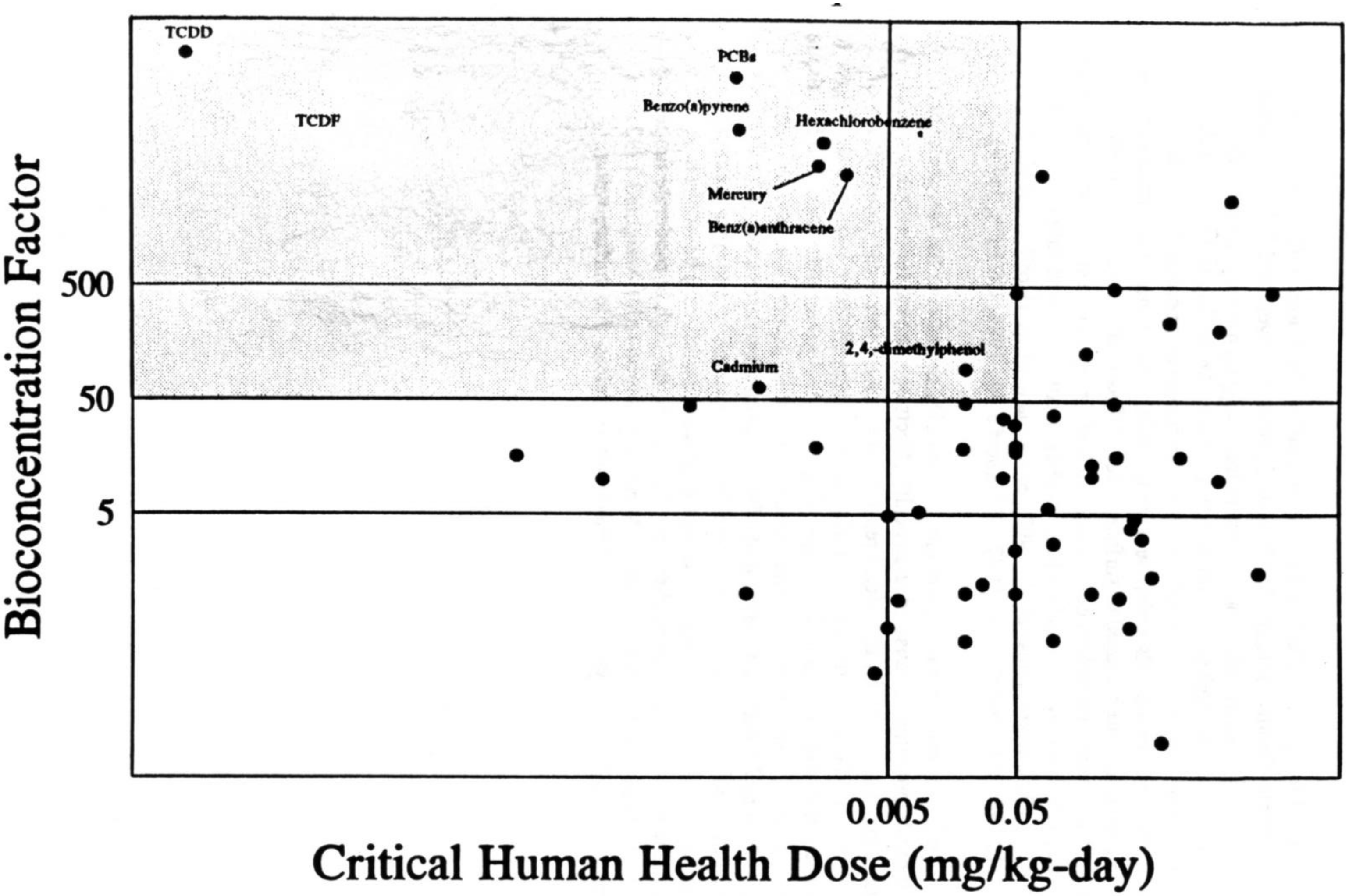


Shading indicates pollutants in high/moderate toxicity and resistant/slow degradation ranges

An additional 13 inorganic pollutants that may or may not have long-term bioavailability, have high or moderate chronic toxicity. The high-end production-weighted 1992 PCS load of 9 inorganic chemicals (aluminum, chlorine, selenium, lead, copper, mercury, chromium hexavalent, silver, and cadmium) is 3.9 million pounds/year. According to 1991 TRI data, 45,000 pounds/year of inorganic chemicals (chlorine, antimony compounds, lead and compounds, copper and compounds, cobalt and compounds, silver compounds, selenium and compounds, and mercury) are released to surface water. Of particular note is selenium. Selenium is shown to cause mortality, deformities, lack of embryonic development, and severe reproductive impacts in a range of species (Harris 1991), including plants, amphibians, fish (Hermanutz et al., 1992; Marcogliese et al., 1992), and aquatic birds (Hoffman et al., 1988; Ohlendorf et al., 1986; Ohlendorf, et al., 1987; Ohlendorf et al., 1989; US EPA, 1989).

Cancer slope factor, reference dose, and mammalian LD_{50} are used in the categorization methods to indicate potential to cause adverse health effects on exposed human populations. A primary human exposure route for chemicals released to surface water is the consumption of contaminated fish. In the categorization methods, bioconcentration factor indicates the degree to which a chemical may accumulate in fish tissue. Chemicals that accumulate in edible fish tissue and may cause adverse health effects in small amounts are likely to pose the greatest threat to human health. Figure 7.4 depicts a scatter plot of bioconcentration factors versus "critical doses" for human health toxicity. Critical human health doses are derived by converting cancer slope factors and LD_{50} values to an equivalent reference dose unit (mg/kg-day) based on the categorization methods. The names of chemicals falling into the high or moderate ranges for both parameters (shaded region) are provided. According to production-weighted 1992 PCS data, as much as 16,000 pounds/year of these chemicals are released to surface water.

Figure 7.4. Human Health Impact Potential



Shading indicates pollutants in high/moderate toxicity and bioaccumulation potential ranges

Assumptions and Limitations

Assumptions and limitations of this analysis include:

- Placement into groups is based on arbitrary order of magnitude delineations for several categorization schemes. Combined with data uncertainty, this may lead to an overstatement or understatement of the characteristics of a chemical.
- Receiving waterbody characteristics, pollutant loading amounts, exposed populations, and potential exposure routes explicitly are not considered.
- Bioavailability of inorganic pollutants is not assessed. Ionic specification, dissolved-solid phase equilibrium, and attachment to clay particles or organic matter are largely functions of waterbody characteristics.
- Human health toxicity assessment is based on an ingestion exposure route, and may not accurately reflect the hazard posed by inhalation or dermal contact.
- Biodegradation potential may not be a good indicator of persistence for organic chemicals that rapidly photooxidize or hydrolyze, since these degradation mechanisms are not considered.
- Available aquatic toxicity and bioconcentration test data may not represent the most sensitive species.
- Data derived from laboratory tests may not accurately reflect conditions in the field.

7.2.3 Toxic Weighting Factor Analysis

EPA's Office of Water uses toxic weighting factors (TWFs) analysis to compare the relative toxicity of industrial effluent discharges. Toxic weighting factors are derived using the same methodology employed for other effluent guidelines (US EPA, 1992a), but are based on updated toxicity information.

Originally, TWFs were used to calculate copper based pound-equivalents, and were derived from chronic aquatic life criteria (or toxic effect levels) and human health criteria (or toxic effect levels) established for the consumption of fish. For carcinogenic substances, the human health risk level was set at 10^{-5}, i.e. protective to a level allowing 1 in 100,000 excess cancer cases over background. These toxicity levels were related to a benchmark value, or toxicity level associated with a single pollutant. Copper, a toxic metal pollutant commonly detected and removed from industrial effluent, was selected as the benchmark pollutant (i.e., the basis to which others are compared). EPA had used copper previously in TWF calculation for the cost-effectiveness analysis of effluent guidelines. While the water quality criterion for copper has been revised (to 12.0 µg/L), the TWF method used the former criterion (5.6 µg/L) to facilitate comparisons with cost-effectiveness values calculated for other regulations. The criterion for copper was reported in the *Ambient Water Quality Criteria for Copper* (US EPA, 1980).

In the original method, a TWF for aquatic life effects and a TWF for human health effects were added for pollutants of concern. The calculation was performed by dividing aquatic life and human health criteria (or toxic effect levels) for each pollutant, expressed as a concentration in micrograms per liter (µg/L), into the former copper criterion of 5.6 µg/L:

$$\mathrm{TWF} = \frac{5.6}{?}AQ + \frac{5.6}{?}HHOO$$

Where:

TWF = Original toxic weighting factor
AQ= Chronic aquatic life value (µg/L)
HHOO= Human health (ingesting organisms only) value (µg/L)

With the new method, pollutant weighting factors (PWFs) are derived from either chronic aquatic life criteria (or toxic effect levels), or human health criteria (or toxic effect levels) established for the consumption of water and fish. For carcinogenic substances, the human health risk level is 10^{-6}, that is, protective to a level allowing 1 in 1,000,000 excess cancer cases over background. In contrast to original TWFs, PWFs are not related to a benchmark pollutant. PWFs are derived by taking the reciprocal of the more stringent (smallest value) of the aquatic life or human health criterion or toxic effect level, both expressed in concentration units of micrograms per liter (µg/L):

$$\mathrm{PWF} = \frac{1}{?}AQ \text{ , } if \text{ AQ} < \text{HHWO}$$

$$\mathrm{PWF} = \frac{1}{?}HHWO \text{ , } if \text{ HHWO} < \text{AQ}$$

or

Where:

PWF = Pollutant weighting factor
AQ = Aquatic life chronic value (µg/L)
HHWO = Human health (ingesting water and organisms) value (µg/L)

Individual TWFs and PWFs for petroleum refinery wastewater constituents are presented in Appendix E. The differences between original TWFs and new PWFs are summarized below:

Feature	**TWF**	**PWF**
Benchmark Value (numerator)	5.6 (former freshwater chronic criterion for copper)	1
Carcinogenic Risk Level	10^{-5} (1 in 100,000 excess cancer cases)	10^{-6} (1 in 1,000,000 excess cancer cases)
Human Health Exposure	Fish consumption only	Drinking water and fish consumption
Aquatic Life Effects vs. Human Health Effects	TWFs are added	More stringent PWF is used

Application to PCS and TRI Load Estimates

TWFs are applied to the PCS and TRI load estimates given in Section 7.1. Toxic-weighted loads provide a measure for comparison between industries. Based on TWFs, approximately 75 percent of the high-end PCS production-weighted load is categorized as being a priority pollutant and a much smaller percentage is classified as carcinogenic. Based on PWFs, more than 90 percent of the PCS weighted load is from priority pollutants, and carcinogens dominate this total (Table 7.12). TRI loads to surface water show a lower proportion of priority pollutants, due to the difference in the set of pollutants reported to TRI and those that are reported to PCS. Transfers to POTWs have a higher percentage of priority pollutant TWF load (80 percent) than those to surface water (60 percent). Average TWF loads per facility to surface water and to POTWs show that indirect wastestreams have hazard potentials that are almost three times greater than direct wastestreams (1,854 vs. 728 lbs-eq/yr/fac).

Table 7.12 Petroleum Refining Annual Loads from PCS and TRI

	All Pollutants Total	All Pollutants Average*	Priority Pollutants Total	Priority Pollutants Average*	EPA Classified Carcinogens Total	EPA Classified Carcinogens Average*
Unweighted	*lb/yr*	*lb/yr/fac*	*lb/yr*	*lb/yr/fac*	*lb/yr*	*lb/yr/fac*
PCS Surface Water Releases (1992)	30,711,578		67,222		11,593	
Extrapolated PCS Surface Water Releases (1992)	272,726,320	1,976,278	1,606,049	11,638	121,361	879
TRI Surface Water Releases (1991)	4,330,091	34,095	206,553	1,626	33,362	263
TRI POTW Transfers (1991)	6,942,533	147,713	2,522,607	53,672	282,726	6,015
Standard TWFs	*lb-eq/yr*	*lb-eq/yr/fac*	*lb-eq/yr*	*lb-eq/yr/fac*	*lb-eq/yr*	*lb-eq/yr/fac*
Extrapolated PCS Surface Water Releases (1992)	10,157,542	73,605	7,889,816	57,173	389,684	2,824
TRI Surface Water Releases (1991)	92,454	728	54,564	430	23,450	185
TRI POTW Transfers (1991)	87,123	1,854	69,821	1,486	10,490	223
Optional TWFs	*lb-eq/yr*	*lb-eq/yr/fac*	*lb-eq/yr*	*lb-eq/yr/fac*	*lb-eq/yr*	*lb-eq/yr/fac*
Extrapolated PCS Surface Water Releases (1992)	6,226,774	45,122	5,821,318	42,183	4,579,868	33,187
TRI Surface Water Releases (1991)	497,817	3,920	59,992	472	484,834	3,818
TRI POTW Transfers (1991)	242,157	5,152	233,967	4,978	228,292	4,857

* Derived by dividing individual pollutant loads (lb/yr or lb-eq/yr) by:
1. 138 (number of facilities included in the PCS extrapolation), or
2. 127 (number of facilities reporting surface water releases in TRI), or
3. 47 (number of facilities reporting POTW transfers in TRI);

and summing for all pollutants.

7.2.4 Whole Effluent Toxicity Testing

EPA has advocated an integrated approach to water quality-based toxics control via chemical-specific testing, bioassessment, and whole effluent toxicity testing. These methods, taken in combination, are expected to provide a comprehensive biological evaluation of a water body (US EPA, 1992b). Whole effluent toxicity (WET) refers to the evaluation of toxic effects of an effluent on living organisms, and has primarily been used for the protection of aquatic life. Whole effluent toxicity is defined as the "aggregate toxic effect of an effluent as measured directly by a toxicity test."

Using the whole effluent approach for the protection of aquatic life involves using acute (usually 96-hours or less in duration with lethality as the typical endpoint) and/or chronic (generally 7-day with lethality, reproduction, and growth effects as test endpoints) toxicity tests to measure the aggregate effects of the pollutant discharge. See EPA's *Technical Support Document for Water Quality-Based Toxics Control* (US EPA, 1991). The acute toxicity endpoint (ATE) values are generally reported as LC_{50} values, defined as the concentration at which 50 percent of the test organisms died. In addition, an exposure duration is often reported along with the lethal concentration value such as a 96-hour LC_{50} value.

Chronic toxicity test results may be reported in terms of a number of different endpoint values. These commonly include the No Observed Effect Concentration (NOEC), Lowest Observed Effect Concentration (LOEC), or the Effect Concentration (EC). These and other chronic toxicity endpoints (CTEs) are defined by EPA in the *Technical Support Document.*

WET tests provide an indication of the ecological impacts of pollutants on receiving waters. Tests conducted by EPA's Complex Effluent Toxicity Testing Program, the University of Kentucky, the University of North Texas, and North Carolina Division of Environmental Management showed a strong correlation between actual receiving water impact and the predicted results from whole effluent toxicity tests. As acknowledged in the EPA *Technical Support Document,* the correlation has been strongest when related to maximum impact responses, or acute WET tests.

EPA's Region 6 Office typically requires that there be no statistically significant lethality in the 7-day chronic WET test at the critical effluent concentration (low flow). Effluent from 18 out of 47 petroleum refining facilities, Texas, Louisiana and Oklahoma (approximately 40 percent) failed at least one WET test for acute, chronic or sublethal effects. All but two of these facilities also showed a statistically significant lethality in their test results at least once, and 11 of these facilities (approximately 25%) showed persistent lethality (i.e., the facility also failed a re-test). California has stringent acute and chronic WET test requirements in place. These requirements typically stipulate that the median test result not reduce survival below 90 percent and the percentile test result not reduce survival below 70 percent during a 96 hour test conducted on fingerling trout, stickleback, and fathead minnows. Shallow water discharges must use 100 percent effluent, whereas deep water dischargers are typically given a 10:1 dilution. As a result of these testing requirements, many petroleum refineries now have activated carbon systems in place to achieve compliance. The State of California is currently compiling a data base of statewide WET test results, which may be available for data summarizing in the future. However, as of January 1994, all five refineries in the San Francisco Bay region with chronic WET test requirements were in compliance.

Assumptions and Limitations

There are several potential limitations to using WET tests as a measure of receiving water impact:

- WET test results are assumed to be valid independent of water body type.
- Biological, physical and chemical factors at any site will affect the true toxic effect of a given effluent, giving both false positives and false negatives.

7.3 Documented Impacts

Tables with supporting data for the following documented environmental impacts are presented in Appendix A. In a review of over 60 literature abstracts (accessed through the DIALOG data service), EPA found that four laboratory studies reported potential environmental impacts from petroleum refinery wastewaters. Impacts include aquatic life effects such as spinal curvature, co-carcinogenic activity, behavioral pattern changes in fish, and mutagenic activity. Tests using treated refinery effluent report a 48-hour LC_{50} for *Daphnia pulex* at 76 percent effluent (a 3:1 mixture of effluent to water), and a 14-day LC_{50} at 6.4 percent effluent, representing a threshold value for mortality. Sublethal effects, such as reproductive failure, ranged from a 14-day EC_{50} at 3.1 percent effluent to a 14-day EC_5 at 0.52 percent effluent. Chemical characterization studies using *Daphnia magna* static bioassays determine that the most toxic fraction of petroleum refinery wastewaters are steam volatiles, base-neutrals, and aromatic organics.

Twenty-three petroleum refining facilities (17 percent of the 138 direct dischargers identified in the *Oil and Gas Journal* (Thrash, 1991)) are identified by States as point sources impairing (or contributing to impairment of) water quality and are included on their CWA Section 304(l) Short List. Pollutants of concern include 10 metals (antimony, cadmium, chromium, hexavalent chromium, trivalent chromium, copper, lead, mercury, nickel, selenium, silver, and zinc), cyanide, phenol and toxicity as reflected by whole effluent-toxicity (WET). Section 304(l) requires States to identify waterbodies impaired by the presence of toxic substances, identify point source dischargers of these toxics, and develop Individual Control Strategies (ICSs) which identified dischargers were required to implement by July 30, 1993. In accordance with the statutory provisions, states must submit to EPA three lists of water bodies, one of which is termed the "short list." The "short list" (Section 304(l)(B)) is a list of waters for which a state does not expect applicable water quality standards (numeric or narrative) to be achieved after technology-based requirements have been met, due entirely or substantially to point source discharges of Section 307(a) toxics.

Three cases of sediment contamination are identified with petroleum refineries from *An Overview of Sediment Quality in the United States* (EPA, 1987b). The associated contaminants are cadmium, chromium, copper, cyanide, nickel, lead, zinc, PCBs, PAHs, petroleum hydrocarbons, and oil and grease. This report presents an overview of sediment quality and qualitatively describes the nature and extent of contaminated sediments (i.e., bottom deposits in rivers, lakes, harbors, and oceans) polluted from anthropogenic sources. Information for this report is from a review of the published literature and inquiries to environmental agencies. The data collection effort is not statistically designed or geographically complete; sites are chosen for inclusion based on the sources of information available.

Petroleum refining ranks second among 40 industrial categories (based on TRI data) as a source of sediment contaminants in EPA's 1995 draft report on sediment contamination (US EPA, 1995)(see Appendix I, "Analysis of TRI Data by Industrial Category"). In addition, the report ranks petroleum refining 11 out of 43 industrial categories based on 1992 PCS data (Appendix I, "Analysis of PCS Data by Industrial Category"). The rankings are based on industry loads weighted by individual chemical toxicity and fate specific to potential sediment contamination. Unitless relative hazard scores are developed for each chemical by multiplying chemical loads retrieved from PCS and TRI by a toxicity factor, based on relative potential toxicity to aquatic life or human health when present in sediment, and a fate factor, based on relevant fate and transport factors.

A review of the EPA/Army Corps of Engineers draft report, *Evaluation of Dredged Material Proposed for Discharge in Waters of the United States - Testing Manual* (US EPA, 1994a), reveal contaminants associated with petroleum refineries include ammonia, lead, selenium, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF). This report provides a matrix of potential correlations between industrial sources and specific contaminants of sediments based on a compilation of existing information. This matrix is, however, not all inclusive and makes no accounting for current pollution control practices. See Appendix I.

8. Economic Profile of the Petroleum Refining Industry

8.1 U.S. Petroleum Refinery Geographic Distribution and Trends

8.1.1 Number and Distribution of Refineries

Petroleum refineries in the United States are classified into five geographic groups called Petroleum Administration for Defense (PAD) Districts. All 50 states and the District of Columbia are distributed among these five districts (see Table 8.1). However, this does not imply that there are refineries in all 50 states. These districts were originally created for economic and geographic reasons as "Petroleum Administration for War (PAW)" districts, which were first established in 1942. In 1950 the nomenclature was changed to "PAD."

As of January 1, 1993[2] there were 187 operable refineries in the United States with a total atmospheric crude oil distillation capacity of 15,120,630 barrels per day (see Table 8.2). However, only 175 refineries were operating with an atmospheric crude oil distillation capacity of 14,776,880 barrels per day. The remaining 12 refineries were idle. During 1992, 2 new refineries were put into operation, 1 was reactivated, 15 were shut down, and 2 refineries were sold to new operators.

As observed in Table 8.1, PAD District III, the Gulf Coast, is the largest in terms of number of refineries and also in capacity, with 66 operable refineries with a capacity of 6,764,450 barrels per day, which amounts to 35 percent of the number of refineries and 45 percent of the entire capacity in the United States. PAD District II, the Midwest, is the second largest in terms of capacity, producing 3,398,800 barrels per day (22.5 percent) from 38 refineries (20 percent). The second highest number of refineries is found in PAD III, the West Coast, with 45 operable refineries (24 percent). This district ranks third in production with a capacity of 2,895,800 barrels per day (19 percent). The smallest district is PAD IV, the Mountain States, with 17 operable refineries (9 percent), and a capacity of 519,375 barrels per day (3 percent).

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[2] While 1993 data are available and exhibit a declining trend, the 1992 data from the draft report were not updated so as to maintain comparability with the technical data on refineries and the PCS system from 1992 summarized in the rest of the final report.

Table 8.1 Number and Capacity of Operable Petroleum Refineries by PAD District as of January 1, 1993

PAD District and State	Number of Operable Refineries			Atmospheric Crude Oil Distillation Capacity (bbl/calendar day)		
	Total	Operating	Idle	Total	Operating	Idle
PAD District I	21	17	4	1,542,805	1,352,955	189,850
Delaware	1	1	0	140,000	140,000	0
Georgia	2	1	0	33,540	5,540	28,000
New Jersey	6	4	2	527,500	407,500	120,000
New York	1	0	2	41,850	0	41,850
Pennsylvania	8	8	0	731,415	731,415	0
Virginia	1	1	0	53,000	53,000	0
West Virginia	2	2	0	15,500	15,500	0
PAD District II	**38**	**36**	**2**	**3,398,200**	**3,364,800**	**33,400**
Illinois	7	7	0	965,600	965,600	0
Indiana	4	4	0	474,900	474,900	0
Kansas	7	6	1	327,300	296,900	30,400
Kentucky	2	2	0	218,900	218,900	0
Michigan	3	2	1	118,600	115,600	3,000
Minnesota	2	2	0	267,100	267,100	0
North Dakota	1	1	0	58,000	58,000	0
Ohio	4	4	0	462,100	462,100	0
Oklahoma	6	6	0	396,500	396,500	0
Tennessee	1	1	0	76,000	76,000	0
Wisconsin	1	1	0	33,200	33,200	0
PAD District III	**66**	**64**	**2**	**6,764,450**	**6,722,450**	**42,000**
Alabama	3	2	1	119,500	104,500	15,000
Arkansas	3	3	0	61,700	61,700	0
Louisiana	20	20	0	2,358,900	2,358,900	0
Mississippi	6	6	0	371,800	371,800	0
New Mexico	3	3	0	94,600	94,600	0
Texas	31	30	1	3,757,950	3,730,950	27,000
PAD District IV	**17**	**16**	**1**	**519,375**	**509,375**	**10,000**
Colorado	3	2	1	95,500	85,500	10,000

Montana	4	4	0	139,650	139,650	0
Utah	6	6	0	154,500	154,500	0
Wyoming	4	4	0	129,725	129,725	0
PAD District V	**45**	**42**	**3**	**2,895,800**	**2,827,300**	**68,500**
Alaska	6	6	0	256,300	256,300	0
Arizona	2	1	1	14,000	10,000	4,000
California	26	24	2	1,933,900	1,869,400	64,500
Hawaii	2	2	0	146,300	146,300	0
Nevada	1	1	0	7,000	7,000	0
Oregon	1	1	0	0	0	0
Washington	7	7	0	538,300	538,300	0
U.S. Total	**187**	**175**	**12**	**15,120,630**	**14,776,880**	**343,750**

Source: U.S. DOE, Energy Information Administration

Table 8.2 Number and Capacity of Refineries in California, Louisiana, and Texas as of January 1, 1993

	Number of Refineries	**Capacity (bbl/day)**
California	26	1,933,900
Louisiana	20	2,358,900
Texas	31	3,757,950
Total CA, LA, TX	77	8,050,750
% of U.S. Total	41%	53%

Source: US DOE/EIA, *Petroleum Supply Annual*

Fifty-three percent of the nation's refining capacity is concentrated in 3 states: California, Louisiana, and Texas. These 3 states combined contain 77 refineries with a combined capacity of 8,050,750 barrels per day (see Table 8.2). The remaining 110 refineries (59 percent) are distributed among 32 other states with a combined capacity of 7,069,080 barrels per day (47 percent). As of January 1, 1993, 15 states did not have refining capacity (see Table 8.3).

Table 8.3 States with No Refining Capacity as of January 1, 1993

Connecticut	Nebraska
Florida	New Hampshire
Idaho	North Carolina
Iowa	Rhode Island
Maine	South Carolina
Maryland	South Dakota
Massachusetts	Vermont
Missouri	

8.1.2 Trends in the Number of Refineries

Since 1981 the number of refineries has decreased from 324 to 187. During this period 156 refineries have shut down, with 69 closures (44 percent) in PAD District III (Gulf Coast), making this the highest number of closures among all 5 districts.

The number of refineries reached a historical high of 324 in 1981. The growth in the number of refineries was largely the result of government regulatory policy. The combination of price controls and non-market allocative mechanisms were introduced in the Emergency Petroleum Allocation Act (EPAA) of 1973 and continued under the Energy Policy and Conservation Act (EPCA) of 1975 (Vogely, 1985; Bohi and Russell, 1978). With the adoption of EPAA, the primary problem was assigning rights to price controlled oil among refiners. An "entitlements" program was designed to equalize the effective cost of crude oil to all refiners at a level equal to the national weighted average of controlled and uncontrolled prices. Cash settlements were made from refiners with lower-than-average crude oil acquisition costs to refiners with higher-than-average acquisition costs. Under EPCA, refiners with crude runs of less than 50,000 bbl/day were exempted from any entitlements obligation, regardless of the small refiner's access to low-cost crude oil (Piccini, 1992). This was the so-called "small refiner bias." As a result of the program, many small refineries were created particularly in PAD district III (Gulf Coast), for access to low-cost crude oil, and typically with only crude distillation capability.

The program ended in 1981, eliminating special treatment for small refineries which eventually caused many of them to go out of business. Since 1981 the number of small refineries that produce under 10,000 barrels per day has decreased from 82 to 32 (a 61 percent decrease) (see

Table 8.4). However, the number of large refineries with capacities over 100,000 bbl/day has actually increased from 52 to 54 refineries between 1982 and 1993 (see Table 8.4).

Table 8.4 Number of Operable Refineries

Classified by Operable Atmospheric Crude Oil Distillation Capacity

Date	Refinery Capacity (bbl/day)				
	100,000 +	30,001 - 100,000	10,001 - 30,000	10,000 or less	Total per year
1/1/82	52	87	80	82	301
1/1/83	48	84	59	67	258
1/1/84	47	82	55	63	247
1/1/85	47	77	43	56	223
1/1/86	47	74	46	49	216
1/1/87	50	75	42	52	219
1/1/88	54	72	41	46	213
1/1/89	53	71	37	38	204 *
1/1/90	56	70	41	43	205 *
1/1/91	55	70	42	33	202 *
1/1/92	54	68	38	36	199 *
1/1/93	54	65	33	32	187 *

* The sum of the columns do not equal the total as some operable refineries possess only vacuum distillation capacity with no atmospheric crude oil distillation capacity.

Source: US DOE/EIA, *Petroleum Supply Annual*

8.2 Economic Profile

8.2.1 The FRS Companies

Financial Reporting System (FRS) companies comprise a number of the largest oil producing companies in the U.S. who report their annual performance to the Energy Information Administration (EIA). Thirty-three companies have submitted data to EIA since EIA started to collect this type of information in 1977.

These companies occupy a major position in the U.S. economy. In 1991 their sales were equal to 21 percent of the $2.3 trillion in sales by *Fortune* magazine's list of the 500 largest U.S. industrial corporations, and their profits and assets were each equal to 27 percent and 18 percent respectively of those of the "Fortune 500" companies. In 1991, The FRS companies accounted for 56 percent of total U.S. crude oil and natural gas liquids production, 44 percent of U.S. natural gas production, and 64 percent of the U.S. refinery capacity.

The Energy Information Administration uses the financial data from the FRS companies as a surrogate for the refining industry as a whole because of the ready availability, completeness, reliability, and continuity of the data. During the 1980's, FRS refineries accounted for between 75 and 80 percent of total domestic refining capacity, although this has fallen during the early 1990's to approximately 70 percent. As can be seen in Table 8.5, the net income derived from refining and marketing operations has experienced wide fluctuations during the period from 1979 to 1992, with the only loss recorded in 1992. Although FRS companies are large integrated entities, economic factors such as increases in raw material costs have a similar effect (in this case increased costs) on both FRS and non-FRS companies. However, the financial health of FRS and non-FRS companies may be significantly different.

Table 8.5 Income from Refining and Marketing Operations (FRS) (in Millions of dollars)

Year	**Net Income**
1979	2,301
1980	2,518
1981	1,278
1982	1,913
1983	1,636
1984	105
1985	2,281
1986	1,641
1987	1,073
1988	5,443
1989	4,522
1990	2,184
1991	903
1992	(200)

Source: US DOE/EIA, *Annual Energy Review*

8.2.2 Refined Product Margins

Refined product margins are a good indicator of overall refinery financial performance. Refined product margin is defined as the difference between the composite refiner acquisition price of crude oil and the price of refined products to resellers (i.e., wholesale prices). The composite price of refined products includes aviation gasoline, kerosene-type jet fuel, kerosene, motor gasoline, distillate fuel nos. 1, 2, and 4, and residual fuel. Price controls were in effect in late 1970's and early 1980's (ending in 1981), thus making interpretation of the margin difficult. As can be seen in Table 8.6, thereafter, margins have experienced significant volatility, reaching a peak of 22.1 cents per gallon in 1990 and a trough of 13.7 cents per gallon in 1984. The trough in 1984 can be largely attributed to weakened prices for motor gasoline. The peak in 1990 (the year of the Persian Gulf crisis) can be attributed to significant increases in prices for aviation gasoline, motor gasoline, and jet fuel.

Table 8.6 Composite Refiner Margin

Year	Margin (Cents per Gal)
1979	19.4
1980	22.4
1981	19.4
1982	19.4
1983	16.0
1984	13.7
1985	17.0
1986	15.8
1987	13.8
1988	18.7
1989	18.8
1990	22.1
1991	20.7
1992	19.8

Source: US DOE/EIA, *Annual Energy Review*

8.2.3 Refined Products Imports

The level of imports of refined products has remained stable throughout the 1980's and early 1990's, as shown in Table 8.7. Imports reached a peak of 2,295,000 barrels per day in 1988 and reached a trough of 1,625,000 barrels per day in 1982. No discernible long-term trend can be observed in the period.

Table 8.7 Refined Product Import Volumes (in thousands of barrels per day)

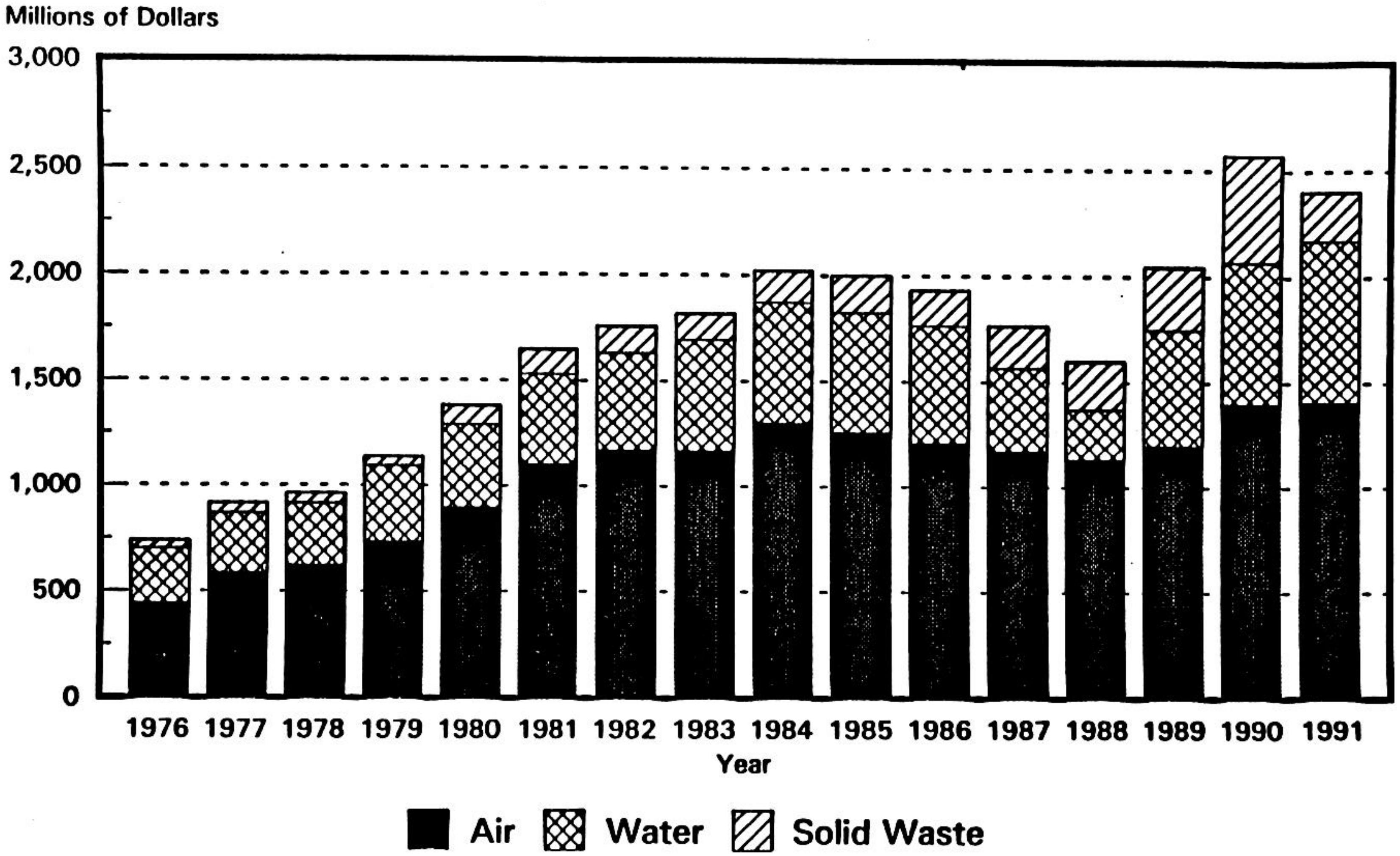
Year	Imports
1979	1,937
1980	1,646
1981	1,599
1982	1,625
1983	1,722
1984	2,011
1985	1,866
1986	2,045
1987	2,004
1988	2,295
1989	2,217
1990	2,123
1991	1,844
1992	1,805

Source: US DOE/EIA, *Annual Energy Review*

8.3 Impacts of Environmental Regulations

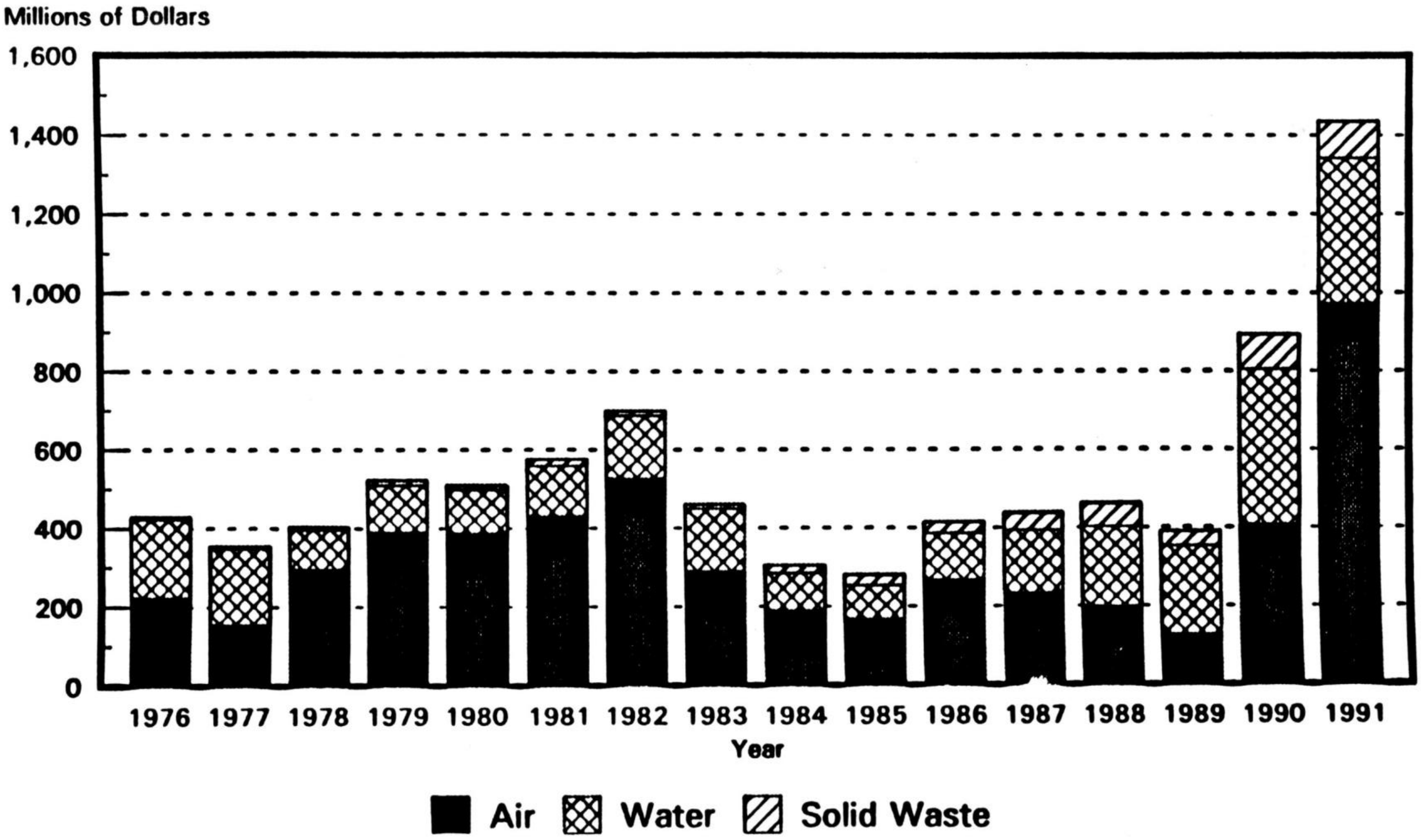
As observed in Figures 8.1 and 8.2, capital and operation and maintenance (O & M) costs for pollution abatement have been increasing since 1976. Solid waste pollution abatement expenditures have increased only slightly while pollution abatement expenditures for water and air have shown significant increases, especially in 1990 and 1991.

Figure 8.1. Refinery Pollution Abatement Operating Expenditures



Source: Bureau of the Census. 1987 costs are estimated.

Figure 8.2. Refinery Pollution Abatement Capital Expenditures



Source: Bureau of the Census. 1987 costs are estimated.

8.3.1 Air Pollution Abatement Expenditures

A major driving force in increased air pollutant abatement expenditures are the Clean Air Act Amendments of 1990 (CAAA). The Act establishes deadlines and procedures for bringing areas into compliance with National Ambient Air Quality Standards.

Ozone and carbon monoxide (CO) are two air pollutants targeted by the CAAA. EPA has identified areas of the country that are not in compliance with the ozone and CO standards ("non-attainment areas") and has categorized these areas according to the severity of their non-attainment. Petroleum refineries in these areas will be required to reduce air emissions from stationary sources. Refineries will be required to undergo modifications to equipment, increase inspection and maintenance programs in order to reduce fugitive emissions.

Table 8.8 shows one such estimate of the incremental costs for refineries to meet the new requirements of the CAAA. This estimate was a result of a 1993 environmental study covering the years 1991-2010 conducted by the National Petroleum Council (NPC), an advisory committee to the Secretary of Energy.

Table 8.8 National Petroleum Council Estimates of Incremental Cost to Meet the New CAAA Requirements

Item	**$ Millions**						
	1991-1995	**1995**	**1996-2000**	**2000**	**2001-2010**	**2010**	**Total**
Capital Investments	3,537	--	1,874	--	2,090	--	7,501
One-Time Costs	9	--	29	--	--	--	38
Total	3,546	--	1,903	--	2,090	--	7,539
O & M Expenses	--	228	--	454	--	152	--

Note: Costs are expressed in mid-1990 Gulf Coast Dollars
Source: National Petroleum Council

According to the NPC, the estimated capital investment of $7,501 million (or $7.5 billion) will be spread over four types of emissions as identified in Table 8.9.

Table 8.9 National Petroleum Council Estimate of Emission Control Investments (by Emission Type)

Emissions	$ millions	Percent
Volatile Organic Compounds (VOC)	3,760	50.1
Particulate Matter (PM_{10})	1,628	21.7
Sulfur Dioxide (SO_2)	965	12.9
Nitrogen Oxides (NO_X)	921	12.3
Toxics	227	3.0

8.3.2 Water Pollution Abatement Expenditures

As observed in Table 8.10, pollution abatement capital expenditures for water have also been on the increase. The NPC expected that a forthcoming reauthorization of the Clean Water Act would be a major driving force in future increased water pollution abatement expenditures. Table 8.10 shows the incremental cost estimates for the U.S. refining industry to meet the provisions of a revised Clean Water Act according to the NPC environmental study covering 1991-2010.

Table 8.10 National Petroleum Council Estimates of Incremental Cost to Meet the New Requirements of Clean Water Act Reauthorization

Item	$ Millions						
	1991-1995	1995	1996-2000	2000	2001-2010	2010	Total
Capital Investments	1,251	--	4,478	--	6,602	--	12,331
One-Time Costs	--	--	--	--	8	--	8
Total	1,251	--	4,478	--	6,610	--	12,339
O & M Expenses	--	44	--	405	--	573	--

Note: Costs are expressed in mid-1990 Gulf Coast Dollars
Source: National Petroleum Council

According to the NPC, these figures have been developed from existing and anticipated wastewater regulations.

The assumptions used to develop these costs based on Clean Water Act reauthorization work at the time of the NPC study include the following group of requirements:

- Reduction of wastewater toxicity and biomonitoring
- Elimination of chromium compounds from cooling towers
- Storm water permit requirements to exclude oil (in storm water) from tank draw offs
- Storm water requirements to exclude oil from sampling (in storm water)
- Storm water requirements to exclude exchanger cleaning wastes (from storm water)
- Storm water permit requirements to reduce discharge of suspended solids (in storm water)
- Store and treat quantity of contaminated storm water from 10-year storm

Other assumptions anticipated additional regulations applicable to water, wastewater and groundwater and include:

- Anticipated requirements for process wastewater reuse
- Mandated application of a revised Best Available Technology (Effluent Limitations Guidelines)
- Anticipated requirements to assess and remediate sediments in outfall areas
- Prevent ground water pollution from storage tank areas
- Prevent ground water pollution from underground process piping
- Prevent groundwater pollution from underground process sewers

The NPC estimate for capital investment over these three areas is shown in Table 8.11. Table 8.12 shows the time frame for the projected investments, estimated to total $12.3 billion.

Table 8.11 National Petroleum Council Estimate for Water Pollution Control Investments

Item	$ Million	Percent
CWA Reauthorization	1,251	10.1
Storm Water Quality	1,196	9.7
Ground Water Issues	3,549	28.8

Table 8.12 National Petroleum Council Projection

for Water Pollution Control Investments
by Time Period

Period	$ Million	Percent
1991-1995	1,251	10.1
1996-2000	4,478	36.3
2001-2010	6,602	33.6

The NPC study predicts that the major area of wastewater investment will be made to reduce and control the toxicity of refinery wastewater effluent during 1996 through 2010 time frame.

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