

SECTION V

WASTE CHARACTERIZATION

General

After developing an understanding of the fundamental production processes and their inter-relationships in refinery operations, determination of the best method of characterizing of refinery discharges will enhance the interpretation of the industry water pollution profile. If unit raw waste loads could be developed for each production process, then the current effluent waste water profile could be obtained by simply adding the components, and future profiles by projecting the types and sizes of refineries. However, the information required for such an approach is not available. Essentially all of the available data on refinery waste waters apply to total API separator effluent, rather than to effluents from specific processes.

Another factor detracting from the application of a summation of direct subprocess unit raw waste loads, is the frequent practice of combining specific waste water streams discharging from several units for treatment and/or reuse. Thus, such streams as sour waters, caustic washes, etc., in actual practice are generally not traceable to a specific unit, but only to a stripping tower or treatment unit handling wastes from several units. The size, sequence, and combination of contributing processes are so involved that a breakdown by units would be extremely difficult to achieve.

In view of the limitations imposed by the summation of waste water data from specific production process, the evaluation of refinery waste loads was based on total refinery effluents discharged through the API (Oil) separator, which is considered an integral part of refinery process operations for product/raw material recovery prior to final waste water treatment.

Raw Waste Loads

The information on raw waste loading was compiled from the 1972 National Petroleum Refining Waste Water Characterization Studies and plant visits. The data are considered primary source data, i.e., they are derived from field sampling and operating records. The raw waste data for each subcategory of the petroleum refining industry, as subcategorized in Section IV, have been analyzed to determine the probability of occurrence of mass loadings for each considered parameter in the subcategory. These frequency distributions are summarized in Tables 18 through 22 for each subcategory.

Waste water Flows

As shown in Table 18 through 22, the waste water flows associated with raw waste loads can vary significantly. However, the

TABLE 18

TOPPING SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M³ (LB/1000 BBLs) OF FEEDSTOCK
THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50% (MEDIAN)	90%
BOD ₅	1.29(0.45)	3.43(1.2)	217.36(76)
COD	3.43(1.2)	37.18(13)	486.2(170)
TOC	1.09(0.38)	8.01(2.8)	65.78(23)
TSS	0.74(0.26)	11.73(4.1)	286(100)
O&G	1.03(0.36)	8.29(2.9)	88.66(31)
PHENOLS	0.001(0.0004)	0.034(0.012)	1.06(0.37)
AMMONIA	0.077(0.027)	1.20(0.42)	19.45(6.8)
SULFIDES	0.002(0.00065)	0.054(0.019)	1.52(0.53)
CHROMIUM	0.0002(0.00007)	0.007(0.0025)	0.29(0.1)
FLOW*	8.00(2.8)	66.64(23.3)	557.7(195)

* 1000 cubic meters/1000 m³ Feedstock Throughput (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 19

CRACKING SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M³ (LB/1000 BBLs) OF FEEDSTOCK
THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50% (MEDIAN)	90%
BOD ₅	14.3(5.0)	72.93(25.5)	466.18(163)
COD	27.74(9.7)	217.36(76.0)	2516.8(880)
TOC	5.43(1.9)	41.47(14.5)	320.32(112)
O&G	2.86(1.0)	31.17(10.9)	364.65(127.5)
PHENOLS	0.19(0.068)	4.00(1.4)	80.08(28.0)
TSS	0.94(0.33)	18.16(6.35)	360.36(126.0)
SULPHUR	0.01(0.0035)	0.94(0.33)	39.47(13.8)
CHROMIUM	0.0008(0.00028)	0.25(0.088)	4.15(1.45)
AMMONIA	2.35(0.82)	28.31(9.9)	174.46(61.0)
FLOW*	3.29(1.15)	92.95(32.5)	2745.6(960.0)

* 1000 cubic meters/1000 m³ Feedstock Throughput (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 20

PETROCHEMICAL SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M³ (LB/1000 BBL) OF FEEDSTOCK
THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50% (MEDIAN)	90%
BOD ₅	40.90(14.3)	171.6(60)	715(250)
COD	200.2(70)	463.32(162)	1086.8(380)
TOC	48.62(17)	148.72(52)	457.6(160)
TSS	6.29(2.2)	48.62(17)	371.8(130)
O&G	12.01(4.2)	52.91(18.5)	234.52(82)
PHENOLS	2.55(0.89)	7.72(2.7)	23.74(8.3)
AMMONIA	5.43(1.9)	34.32(12)	205.92(72)
SULFIDES	0.009(0.003)	0.86(0.3)	91.52(32)
CHROMIUM	0.014(0.005)	0.234(0.085)	3.86(1.35)
FLOW*	26.60(9.3)	108.68(38)	443.3(155)

* 1000 cubic meters/1000 m³ Feedstock Throughout (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 21

LUBE SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M³ (LB/1000 BBL) OF FEEDSTOCK
THROUGHPUT

<u>PARAMETERS</u>	<u>PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO</u>		
	<u>10%</u>	<u>50% (MEDIAN)</u>	<u>90%</u>
BOD ₅	62.92(22)	217.36(76)	757.9(265)
COD	165.88(58)	543.4(190)	2288(800)
TOC	31.46(11)	108.68(38)	386.1(135)
TSS	17.16(6)	71.5(25)	311.74(109)
O&G	23.74(8.3)	120.12(42)	600.6(210)
PHENOLS	4.58(1.6)	8.29(2.9)	52.91(18.5)
AMMONIA	6.5(2.3)	24.1(8.5)	96.2(34)
SULFIDES	0.00001(0.000005)	0.014(0.005)	20.02(7.0)
CHROMIUM	0.002(0.0006)	0.046(0.016)	1.23(0.43)
FLOW*	68.64(24)	117.26(41)	772.2(270)

* 1000 cubic meters/1000 m³ Feedstock Throughput (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 22

INTEGRATED SUBCATEGORY RAW WASTE LOAD**
 EFFLUENT FROM REFINERY API SEPARATOR
 NET KILOGRAMS/1000 M³ (LB/1000 BBLs) OF FEEDSTOCK
 THROUGHPUT

<u>PARAMETERS-</u>	<u>PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO</u>		
	<u>10%</u>	<u>50%(MEDIAN)</u>	<u>90%</u>
BOD ₅	63.49(22.2)	197.34(69.0)	614.9(215)
COD	72.93(25.5)	328.9(115)	1487.2(520)
TOC	28.6(10.0)	139.0(48.6)	677.82(237)
O&G	20.88(7.3)	74.93(26.2)	268.84(94.0)
PHENOL	0.61(0.215)	3.78(132)	22.60(7.9)
TSS	15.16(5.3)	58.06(20.3)	225.94(79.0)
SULPHUR	0.52(.182)	2.00(.70)	7.87(2.75)
CHROMIUM	0.12(0.043)	0.49(0.17)	1.92(0.67)
AMMONIA	3.43(1.20)	20.50(7.15)	121.55(42.5)
FLOW*	40.04(14.0)	234.52(82.0)	1372.8(480)

* 1000 cubic meters/1000 m³ Feedstock Throughput (gallons/bbl)

** Probability plots are contained in Supplement B

loadings of pollutants tend to vary within fairly narrow limits, independent of flow.

Since the inter-refinery data suggest that the pollutant loading to be expected from a refinery is relatively constant in concentration, an examination of water use practices was made. The waste water flow frequencies reported in Tables 18 through 22 are dry-weather flows, and in many cases include large amounts of once-through cooling water. Refineries with more exemplary waste water treatment systems are probably making a greater effort to control waste loads and flows. Conversely, refineries with very high water usages and/or raw waste loads either do not have identifiable waste water treatment plants, or have them under construction.

The primary methods for reduction of the waste water flows to the API separator are either segregation of once-through cooling waters, or by installation of recycle cooling towers and/or air coolers. In order to estimate the flows that should be attainable in refineries with good water practices, a statistical analysis was made of flows from refineries in which 3 percent or less of the total heat removal load is accomplished by once-through cooling water. Data for this analysis were obtained from the tabulation of refinery cooling practices contained in the 1972 National Petroleum Refining Waste Water Characterization Studies. These frequency distributions are summarized in Table 23.

Basis for Effluent Limitations

The 50 percent probability-of-occurrence raw waste loads outlined in Tables 18 through 22 are reflective of the performance of median refineries within each subcategory. At the same time, attainable process waste water flows, as reflected by the median water usage for refineries in which 3 percent or less of the total heat removal load is accomplished by once-through cooling water, are indicative of equitable process waste water loadings which require waste water treatment.

Consequently, these 50 percent probability-of-occurrence waste water loadings and estimated process waste water flows were selected as one basis for developing effluent limitations, and are used in subsequent sections to define these effluent limitations.

TABLE 23

WASTE WATER FLOW FROM PETROLEUM REFINERIES USING
3% OR LESS ONCE-THROUGH COOLING WATER FOR HEAT REMOVAL*

KILOGRAMS/1000 M³ (LB/1000 BBLS) OF FEEDSTOCK
THROUGHPUT

(gal/ bbl feedstock)
w/water

SUBCATEGORY	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50% (MEDIAN) ^{req.}	90%
TOPPING	8.01(2.8)	57.2(20)	314.6(110)
CRACKING	16.59(5.8)	71.5(25)	148.72(52)
PETROCHEMICAL	40.04(14)	85.8(30)	183.04(64)
LUBE	65.78(23)	128.7(45)	243.1(85)
INTEGRATED	91.52(32)	137.28(48)	1287(450)

* Probability plots are contained in Supplement B