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Environment Canada

Conservation and Protection Comparison of U.S. EPA Effluent Limitations with Ontario Refineries Performance



TD 899 P4 G68 1989



Prepared by: M. H. Goulet April, 1989 Revised Nov., 1989



Environment Canada Environnement Canada

Conservation and Protection Conservation et Protection

DATE: 20/11/81



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Please find enclosed a new haft of the above - mentioned report. I hope we have answered most of your questions on the potto pren droft.

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Oil, Gas and Energy Division Industrial Programs Branch Environmental Protection Directorate Conservation and Protection Environment Canada

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ACKNOWLEDGEMENT

I wish to thank all refineries which were very cooperative in supplying the necessary information and helpful in answering my many questions. Without their help this undertaking would not have been possible.

I also wish to thank Bernard Made and Marie Louise Geadah for initiating the gathering of information.

SUMMARY

This report studies the potential impact of applying the U.S. EPA procedures for the calculation of effluent limitations in the petroleum industry to Ontario refineries.

The limit calculation equation, a step by step description of the calculation process and an example are provided. A graphical analysis of global and individual short term and global long term performances of Ontario refineries according to U.S. limitations is presented and discussed. The "Environmental Status Report of the Canadian Petroleum Refining Industry 1987" was examined to verify the level of compliance with Canadian regulations and guidelines for the Ontario region.

It was concluded that long term performance was essentially better than the short term performance. No seasonal variations occur on effluent discharge quality based on the five parameters monitored. There is good biological treatment performance based on phenol concentrations found in the effluents. The inclusion of process factors and size factors into the monthly limit calculations has the impact of greatly varying the discharge allocations under these procedures. Compliance with Canadian regulations was very good overall for the Ontario region.

The level of compliance of U.S. refineries to their own limitations should be reviewed by analyzing reports published by the U.S. EPA.

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CONCLUSIONS

In comparing Ontario refinery performances with U.S. EPA limitations it was discovered that long term averages of pollutants discharged by Ontario refineries are comparable to expected performance in the U.S.

Short term performance (daily and monthly average discharges) do not meet the expected level of compliance when all refineries are taken into consideration. However, when the lowest performers are excluded for each of the parameters studied, the remaining refineries meet the calculated limits with the exception of those for total suspended solids.

The inclusion of process factors and size factors in the limit calculation equation has a definite impact in that they vary the discharge allocations when calculated based on real production.

Compliance with Canadian regulations was very good overall in the Ontario region.

No seasonal variations could be detected on effluent discharge quality for the parameters studied.

The biological treatment performance was acceptable based on phenol concentrations found in the final effluent.

RECOMMENDATIONS

Sources of the variability of discharge loadings on a daily and monthly basis should be identified.

The level of compliance of U.S. refineries with their own limitations should be analyzed by reviewing "Quarterly Noncompliance Reports" and "Semi Annual Statistical Summary Reports" published by the EPA. This would allow a comparison of how stringent these limits are with what was expected at the time of their promulgation.

I) - INTRODUCTION

U.S. petroleum refinery effluents are regulated by the Environmental Protection Agency (EPA) under the authority of the Federal Water Pollution Control Act. Canadian petroleum refinery effluents are regulated by Environment Canada (EC) Petroleum Refinery Liquid Effluent Regulations and Guidelines promulgated under the Fisheries act in 1973. It is recognized that American requirements are the more stringent ones. In this report, U.S. limitations are applied to Ontario refinery discharges to establish how well they would currently perform under the U.S. regulations. The EC limitations are based on crude oil throughput whereas EPA limitations take into consideration the throughput of all process units. The importance of such considerations is analyzed and the EPA's established long-term expected performance is also compared to the Ontario refineries annual averages for 1987.

The history of the development of U.S. BAT and BPT/BCT regulations, and of the mechanisms involved in calculating permissible discharges is beyond the scope of this report. For more information on these topics refer to the referenced materials.

The report only deals with process wastewater limits. Additional effluent discharge allocations are provided for contaminated storm water and ballast water by BPT guidelines. It was however impossible to obtain the relevant data to consider these additional allocations. Once through cooling water is regulated separately from process, ballast or storm waters.

II) - AMERICAN PROCEDURES FOR THE CALCULATION OF EFFLUENT LIMITATIONS

This section presents some background information necessary to the understanding of U.S. limitations. A step by step description of the procedures including a detailed example is also presented below.

II-A) BACKGROUND

Best Available Control Technology Economically Achievable (BAT) limitations control the discharge of toxic (priority) pollutants (chromium and phenols) and non-conventional pollutants (COD, ammonia and sulphides) in the effluents of existing direct discharges in the petroleum refining industry. Conventional pollutants (BOD, oil & grease AND T.S.S.) are considered under Best Conventional Treatment Economically Available (BCT).

II-B) SUBCATEGORIZATION:

The petroleum refineries have been divided into five subcategories for the purpose of the EPA guidelines applications:

i) TOPPING:

-Includes those refineries who use topping (initial distillation) and catalytic reforming.

-Excludes those refineries who use cracking and coking processes.

ii) CRACKING:

-Includes those refineries who use topping and cracking processes.

-Excludes those refineries who use any of the petrochemical, lube or integrated subcategory processes.

iii) PETROCHEMICAL:

-Includes those refineries who use topping, cracking and petrochemical operations. ("petrochemical"= production of 1st generation petrochemicals and isomeration products (i.e. BTX, olefin, cyclohexane, etc...), or production of 2nd generation petrochemicals (alcohols, ketones, cumene, styrene, etc...), when they represent 15% or more of total refinery production.) -Excludes those refineries who use any of the lube and integrated subcategory processes.

iv) LUBE

-Includes those refineries who use topping, cracking and lube oil manufacturing processes.

-Excludes those refineries who use any of the petrochemical or integrated subcategory processes.

v) INTEGRATED

-Includes those refineries who use topping, cracking, lube oil manufacturing and petrochemical operation processes.

II-C AMERICAN PROCEDURE FOR CALCULATING EFFLUENT LIMITATIONS:

American calculations are based on specific formulas tacking into account calculated size factors and process factors, the rationale being that refinery B that has twice as many units or producing twice as much as refinery A does not necessarily discharge twice the amount of pollutants.

The main equation is:

effluent limit (lb/d) =

effluent limitation factor (lb/1000 bbl) * size factor * process factor * refinery feedstock rate (1000 bbl/d)

Table 1 lists the pre-established effluent limitation factors.

STEP 1: DETERMINATION OF SIZE FACTOR

The size factor is based on the refinery feedstock (throughput) rate. The refinery feedstock rate is the largest of the crude process rates (atmospheric distillation or vacuum distillation). Table 2 gives feedstock rate ranges and their respective size factors.

STEP 2: DETERMINATION OF PROCESS FACTOR

The process factor is based on the process configuration. A process configuration number is a process feedstock divided by the

TABLE 1 EPPLUENT LIMITATION PACTORS

		B/	T				BA	Ť	
Pollutant/ Pollutant Property	maximum for any 1 day		avg of sball n	30 days ot exceed	Pollutant/ Pollutant Property	maxi any	nun for 1 day	avg of shall no	30 days ot exceed
	Netric	Baglish	Metric	Baglish	· roperej	Hetric	Baglish	Metric	Bnglish
TOPPING					LUBB				
4-AAP	0.1680	0.0600	0.0760	0.0270	4-AAP	0.3800	0.1330	0.1840	0.0650
Total Cr	0.3450	0.1220	0.2000	0.0710	Total Cr	0.7700	0.2730	0.4500	0.1690
Cr+6	0.0280	0.0100	0.0120	0.0044	Cr+6	0.0680	0.0240	0.0300	0.0110
COD	117.0000	41.2000	60.3000	21.3000	COD	360.0000	127.0000	187.0000	66.0000
8	2.8100	0.9900	1.2700	0.4500	ji -	23.4000	8.3000	10.6000	3.8000
Sulfide	0.1490	0.0530	0.0680	0.0240	Sulfide	0.3300	0.1180	0.1500	0.0530
BODS	22.7000	8.0009	12.0000	4.2500	BOD5	50.6000	17.9000	25.8000	9.1000
TSS	15.8000	5.6000	10.1000	3.6000	TSS	35.6000	12.5000	22.7000	8.0000
04G	6.9000	2.5000	3.7000	1.3000	04G	16.2000	5,7000	8.5000	3.0000
pH	(3)	(3)	(3)	(3)	pB	(3)	(3)	(3)	(3)
CRACKING					INTEGRATED				
4-22b	0.2100	0.0740	0.1000	0.0360	4-AAP	8.4000	0.1400	8,1920	8,0618
Total Cr	0.4300	0.1500	0.2500	0.0880	Total Cr	0.8200	0.2900	8,4808	8.1788
Cr+6	0.0350	0.0120	0.0160	0.0056	Cr+6	0.0680	0.0250	0.0320	0.0110
COD	210.0000	74.0000	109.0000	38.4000	COD	388.0000	136.0000	198.0000	70.0000
l	18.8000	6.6000	8.5000	3.0000	J J	23.4080	8.3000	10.6000	3.8000
Sulfide	0.1800	0.0650	0.0820	0.0290	Sulfide	0.3500	0.1240	8,1580	0.0560
BOD5	28.2000	9.9000	15.6000	5.5000	BOD5	54.4000	19.2000	28,9000	10.2000
285	19.5000	6.9000	12.6000	4.4000	TSS	37.3000	13.2000	23.7000	8.4008
D&G	8.4000	3.0000	4.5000	1.6000	OFC	17,1000	6.0000	9,1000	3.2000
p8	(3)	(3)	(3)	(3)	ρĦ	(3)	(3)	(3)	(3)
PETROCHENICA	L								
-AAP	0.2500	0.0880	0.1200	0.0425					
lotal Cr	0.5200	0.1830	0.3000	0.1070					
lr+6	0.0450	0.0160	0.0200	0.0072					
:0D	210.0000	74.0000	109.0000	38.4000					
l	23.4000	8.2500	10.6000	3.8000					
alfide	0.2200	0.0780	0.0990	0.0350					
IOD5	34.6000	12.1000	18.4000	6.5000					
35	23.4000	8.3000	14.8000	5.2500					
ÆG	11.1000	3.9000	5.9000	2.1000					
H	(3)	(3)	(3)	(3)					

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1) All Metric units are in Kg/1000 cu metres of feedstock

2) All English units are in pounds/1000 bbl of feedstock

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3) Within the range of 6.0 to 9.0

4) When the chloride ion concentration in the effluent exceeds 1000 mg/l (1000ppm), TOC may be substituted as a parameter in lieu of COD. A TOC effluent limitation shall be based on effluent data from the particular refinery which correlates TOC to BOD5. If adequate data is not available, the effluent limitations for TOC shall be established at a ratio of 2.2 to 1 to the applicable effluent limitations for BOD5. REFERENCE (2,5,6)

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TABLE 2 BIZE FACTOR					
1000bbl of feedstock per stream day	TOPPING	size f Cracking	actor by subc PETROCHEM	ategory LUBE	INTEGRATED
LESS THAN 24.9	1.02		0.73	0.71	0.73
25.0 TO 49.9	1.06	0.95	0.76	0.71	0.73
50.0 TO 74.9	1.16	1.04	0.83	0.74	0.73
75.0 TO 99.9	1.26	1.13	10.01	0.81	0.73
100.0 TO 124.9	1.38	1.23	0.99	0.88	0.73
125.0 TO 149.9	1.50	1.35	1.08	0.97	0.76
150.0 TO 174.9	1.57	1.41	1.13	1.05	0.83
175.0 TO 199.9	1.57	1.41	1.13	1.14	16.0
200.0 TO 224.9	1.57	1.41	1.13	1.19	0.99
225.0 OR GREATER	1.57	1.41	1.13	1.19	1.04

REFERENCE (2,5,6)

8

total refinery feedstock multiplied by a weighting factor. Weighting factors are used to take into account that certain processes produce more pollutants than others. They therefore deserve higher discharge allocations. Crude processes have a weight factor of 1, cracking processes have a weight factor of 6, lube processes have a weight factor of 13, and asphalt processes have a weight factor of 12. Process configuration numbers from all processes (Table 3) are summed to yield a total refinery process configuration. Table 4 lists the process configuration ranges and their respective process factors.

STEP 3: CALCULATION OF EFFLUENT LIMITS.

Based on the results from step 1 and step 2, and using appropriate effluent limitation factors found in table 1, maximum daily and thirty day BAT limits are calculated for all pollutants using the main equation.

STEP 4: CALCULATION OF NEW BAT LIMITS (FOR PHENOLS, TOTAL CHROMIUM AND HEXAVALENT CHROMIUM)

NBAT limits are based on a revised procedure introduced by the EPA after BAT limits had been set (as a result of a lawsuit settlement). These limits are calculated on the basis of total process feedstock rates for five distinct process categories: crude, cracking and coking, asphalt, lube, and reforming & alkylation. The total feedstock rate of each is multiplied by another set of effluent limitation factors (table 5) to determine NBAT limits.

STEP 5: COMPARISON OF BAT AND NBAT

NBAT limits for phenol, total chromium and hexavalent chromium are subsequently compared with BAT limits and the most stringent values are retained as the appropriate limits.

II-D) EXAMPLE:

Example calculation for a hypothetical refinery in the lube subcategory with a crude oil feedstock rate of 125 000 bbl/sd (sd = stream day).

With a through put of 125 000 bbl/sd we obtain from table 2 the value 0.97 for the size factor. With a global process configuration of 7.27 as calculated in figure 1, we obtain from table 2 the value of 0.88 for the process factor. Table 1 contains the BAT limitation factors, and using the main equation we obtain the BAT limitations in figure 2.

TABLE 3	PROCESS CONFIGURATION
Process Category	Processes Included
Crude	desalting atmospheric distillation vacuum distillation
Cracking and Coking	fluid cat cracking vis-breaking Thermal cracking Moving bed cat cracking hydrocracking fluid coking delayed coking hydrotreating
Asphalt	asphalt production 200f soft. pt. unfluxed asphalt asphalt oxidizing asphalt emulsifying
Lube	<pre>lube hydrofining, hydrofining, hydrofinishing white oil manufacturing propane - dewaxing,deasphalting fractioning,deresining duosol,duotreating, solvent - treating, extraction ,dewaxing ,deasphalt lube vac twr, oil fractionation, batch still (naphta strip), bright stock treating centrifuge and chilling MEK dewaxing, ketone dewaxing MEK-Toluene dewaxing deoiling (wax) naphtenic lubes production so2 extraction wax pressing wax plant (with neutral separation) furfural extracting clay contacting-percolation wax sweating acid treating phenol extraction</pre>
Reforming, Alkylation	H2SO4 Alkylation Cat Reforming

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REFERENCE 2

Process Configuration	TOPPING	process f CRACKING	actor by sub PETROCHEM	category LUBE	INTEGRATED
LESS THAN 2.49	 N K2	 _ 58	0 73	 ח גו	 Λ 7κ
2.5 TO 3.49	0.67	0.63	0.73	0.81	0.75
3.5 TO 4.49	0.80	0.74	0.73	0.81	0.75
4.5 TO 5.49	0.95	0.88	0.80	0.81	0.75
5.5 TO 5.99	1.07	1.00	0.91	0.81	0.75
6.0 TO 6.49	1.17	1.09	0.99	0.81	0.75
6.5 TO 6.99	1.27	1.19	1.08	0.88	0.82
7.0 TO 7.49	1.39	1.29	1.17	0.88	0.82
7.5 TO 7.99	1.51	1.41	1.28	1.00	0.92
8.0 TO 8.49	1.64	1.53	1.39	1.09	1.00
8.5 TO 8.99	1.79	1.67	1.51	1.19	1.10
9.0 TO 9.49	1.95	1.82	1.65	1.29	1.20
9.5 TO 9.99	2.12	1.89	1.72	1.41	1.30
10.0 TO 10.49	2.31	1.89	1.72	1.53	1.42
	2.51	1.89	1.72	1.67	1.54
11.0 TO 11.49 11 5 mo 11 99	2.13	1.89	1.72	1.82	1.68
12.0 TO 12 49	2.70 2.71	1.07 1 00	1 72	T.78	1.03
12.5 TO 12.99	J.44 7 57	1 89	1 77	2.10	1.33 2 17
13.0 TO 13.49	3.84	1 89	1 72	2.34	2.17
1 3.5 TO 13.99	4.18	1.89	1 72	2.44	2.20
14.0 OR GREATER	4.36	1.89	1.72	2.44	2.26
REFERENCE (2,5,6) TABLE 5	NEW BAT LIMI	TATIONS			
		ND.	 N1		
Pollutant/ Pollutant property	maxim any	um for 1 day	avg of shall not	30 days t exceed	
	Metric	English	Metric	English	
4-AAP:	0 0370	0 0130	0 0090	0 0030	
Cracking and Coking	0.0370	0.1470	0.1020	0.0360	
Asphalt	0.2260	0.0790	0.0550	0.0190	
Lube	1.0550	0.3690	0.2570	0.0900	
Reforming and Alkyl.	0.3770	0.1320	0.0920	0.0320	
TOTAL Cr:		·	.		
Crude	0.0300	0.0110	0.0110	0.0040	
Cracking and Coking	0.3400	0.1190	0.1180	0.0410	
Asphalt	0.1830	0.0640	0.0640	0.0220	
	0.8550	0.2990	0.2970	0.1040	
Reforming and Alkyl.	0.3050	0.1070	0.1000	0.0370	
$ \begin{array}{c} LI + O \\ \bullet \end{array} \\ \bullet \\ \bullet \\ Cyndo \end{array} $	0 0019	0 0007	0 0009	0.0003	
Cracking and Coking	0.0019	0.0076	0.0098	0.0034	
Agnhalt	0.0210	0.0041	0.0053	0.0019	
Lube	0.0549	0.0192	0.0248	0.0087	
Reforming and Alkyl.	0.0196	0.0069	0.0088	0.0031	
1) Metric units are in 2) English units are i REFERENCE 2	kg/1000 cu n pounds/100	metres of Obbl of fee 11	feedstock edstock		

-

FIGURE 1 Process Configuration:

Process Category	Processes Included		Throughput 1000cum/sd	Throughput 1000bb1/sd	Rel. to throughput	wheighting factor	process config.
Crude	desalting		. 19.87	124.98	1.000		
	atm. distill.		. 19.87	124.98	1.000		
	vacuum distill.		9.54	60.01	0.480		
Total	•••••				. 2.480	X 1	2.48
Cracking	fluid cat cracking		6.52	41.01	0.328		
and	vis-breaking		8.08	0.00	0.000		
Coking	Thermal cracking		0.00	0.00	0.000		
	Noving bed cat crackin	Iq	0.00	0.00	0.000		
	hydrocracking		3.18	20.00	0.160		
	fluid coking		0.00	0.00	0.000	•	
	delaved coking		0.00	0.00	0.000		
Total		•••••		• • • • • • • • • • • •	0.488	X 6	2.93
Luhe	Johe hydrofining		0.84	5.28	0.042		
	white oil manu.		0.00	0.00	0.000		
	propane -						
	devaxing,deasphalt	ing	0.00	9.00	0.000		
	duosol, solvent devazio	Ig	0.00	0.00	0.000		
	lube vac tower, wax fr	act	0.00	0.00	0.000		
	centrifuge and chillin	I g .	0.00	0.00	9.000		
	MBK devaxing		0.00	0.00	0.000		
	deoiling		0.00	0.00	0.000		
	naphtenic lubes		0.00	0.00	0.000		
	SO2 extraction		0.00	0.00	0.000		
	wax pressing		0.00	0.00	0.000		
	wax plant		0.00	0.00	0.000	-	
	furfural extraction		0.64	4.03	0.032		
	clay contacting-percol	ation	0.00	0.00	0.000		
	wax sweating		0.00	0.00	0.000		
	acid treating		0.00	0.00	9.000		
	phenol extraction		0.78	4.91	0.039		
	from data		0.00	0.00	0.000		
Total					0.114	I 13	1.48
Asphalt	asphalt production		0.64	4.03	0.032		
	asphalt oxidation		0.00	0.60	0.000		
	asphalt emplsifying		0.00	0.00	0.000		
Total				••••	0.032	X 12	0.39
				GLOBAL	PROCESS COL	IFIGURATION:	1.21

-

process	factor:	0.88
size fac	ctor:	0.97

FIGURE	2	EFFLUENT	LIMITATIONS

_							
Pollutant/ Pollutant Property -	maxim any	um for 1 day	avg of shall no	30 days t exceed			
	Metric	English	Metric	English			
4-AAP Total Cr Cr+6 COD N Sulfide BOD5 TSS O&G PH	0.32 0.66 0.06 307.30 19.97 0.28 43.19 30.39 13.83 (3)	0.11 0.23 0.02 108.41 7.08 0.10 15.28 10.67 4.87 (3)	0.16 0.38 0.03 159.62 9.05 0.13 22.02 19.38 7.26 (3)	0.06 0.14 0.01 56.34 3.24 0.05 7.77 6.83 2.56 (3)			
 Metric units in kg/1000 cu metres of feedstock English units are in lbs/1000bbl of feedstock Within the range of 6.0 to 9.0 							

-

EFFLUENT LIMITATIONS PER DAY

	BAT							
Pollutant/ Pollutant Property -	maxi any	mum for 1 day	avg of 30 days shall not exceed					
	Metric	English	Metric	English				
4-AAP	6.45	14.19	3.12	6.94				
Total Cr	13.06	29.13	7.63	17.07				
Cr+6	1.15	2.56	0.51	1.17				
COD	6107.12	13551.54	3172.31	7042.53				
N	396.96	885.65	179.82	405.48				
Sulfide	5.60	12.59	2.54	5.66				
BOD5	858.39	1910.02	437.68	971.02				
TSS	603.93	1333.81	385.09	853.64				
O&G	274.82	608.22	144.20	320.12				
рH	(3)	(3)	(3)	(3)				

Metric units in kg/day
 English units are in lbs/day
 Within the range of 6.0 to 9.0

The global process total for each process category is then calculated as shown in figure 3 and is multiplied by the effluent limitation factors for NBAT (table 4) to obtain the NBAT effluent limitations in figure 4.

A comparison of BAT vs NBAT for phenols, total chromium and hexavalent chromium reveals that the NBAT limitations are the more stringent ones for total chromium and hexavalent chromium. Therefore limitations for these pollutants would be set at NBAT values.

FIGURE J	PIOCESSES INCLUDED FOI NEW BAT				
Process Category	Processes Included	fedstk rate 1000cum/sd	process total	feðstk rate 1000bbl/sd	process total
Crade	desalting	. 19.87		124.98	
	at n . distill	19.87		124.98	
	vacuum distill	9.54		60.01	
Total		•••••	49.28	•••••	309.97
Cracking	fluid cat cracking	6.52		41.01	
and	vis-hreating	0.00		0.40	
Coting	Thermal cracking	. 8.08		0.00	
ovaray	Noving bed cat cracking	. 0.00		0.09	
	hydrocracking	3.18		20.00	
	fluid coking	A 00		0.00	
	delayed coking	0.00		0.00 0.00	
	hydrotreatian			0.00	
Potal	ularocreacing		9 78	v. vv	61 01
IVCAI		*****	3.10	••••	01.01
Asphalt	asphalt production	. 0.64		4.03	
	soft pt unfluxed	. 0.00		0.00	
	asphalt oxidation	. 0.00		0.00	
	asphalt emulsifying	. 0.00		0.00	
Total		•••••	0.64	•••••	4.03
1-h-	1-6- 6-8-51-1				
Lade	lube hydrofining				
	hydro-fining, finishing	. 0.84		5.28	
	white oil manu	. 0.00		0.00	
	propane -			0.00	
	dewaxing, deasphalting			0.08	
	fractioning, deresining	. 0.00		0.00	
	duosol, duotreating, solvent-			0.00	
	treat, extrac, devax, deasphalt	. 0.00		0.00	
	lube vac tvr, oil fract.			0.00	
	batch still, bright stock	. 0.00		9.00	
	centrifuging and chilling	. 0.00		0.00	
	NBK dewaxing			0.00	
	Ketome, NBK-Tolueme devax	. 0.00		0.00	
	deoiling	. 0.00		0.00	
	naphtenic lubes	. 0.00		0.00	
	SO2 extraction	. 0.00		0.00	
	wax pressing	. 0.00		0.00	
÷	vax plant	. 0.00		0.00	
	furfural extraction	. 0.64		4.03	
	clay contacting-percol	. 0.00		0.00	
	wax sweating	. 0.00		0.00	
	acid treating	. 0.00		0.00	
	phenol extraction	. 0.78		4.91	
•	from data	. 0.00		0.00	
Total			2.26	•••••	14.22
Bafaralas	87604 11501++ia-	A AA		0 00	
ALEIUIBING,	BIJUT AILYICLIUD	. 0.00		U.UU 0 00	
AIKYIGCIOD	Lat RETOTE199	. 0.00	A AA	0.00	
TOTAL	•••••	• • • • • • • • • • • • • •	0.00		¥.VV

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FIGURE 4	I NEW	BAT EFFLU	ENT LIMITAT	IONS (PER	DAY)	
			NBA	 T		
Pollutant/ Pollutant		maxim any	um for 1 day	avg of 30 days shall not exceed		
property		Metric	English	Metric	English	
4-AAP Total Cr Cr+6	:	8.42 6.83 0.44	18.56 15.18 0.97	2.05 2.40 0.20	4.48 5.31 0.43	
1) Metri 2) Engli	c unit sh uni	s in kg/d ts in lb/	 ay day			

III)-COMPARISON OF U.S. EPA GUIDELINES WITH ONTARIO REFINERIES PERFORMANCE:

Monthly process data from Esso Sarnia, Petro-Canada Oakville (PCO), Petro-Canada Clarkson (PCC), Petrosar, Shell Sarnia, Suncor Sarnia and Texaco Nanticoke were entered into a Lotus spreadsheet (produced along with the development of reference 2) in order to calculate monthly process factors, size factors and effluent limitations for each refinery. The results were used to assess the number of potential exceedances occurring in relation to the theoretical EPA limitations.

The EPA limits are based on an expected 99% compliance rate for daily limitations and an expected 95% compliance rate for monthly (30 day) average limitations. Although the regulations stipulate a 30 day moving average rather than a monthly average, monthly averages are most frequently used in the U.S.. The thirty day moving average is not practical since any variation in the feedstock rate demands a new limit be calculated. Therefore a 30 day moving limit would have to be established to go along with the 30 day moving average, which is extremely impractical. It seems that U.S. permits are written by taking the largest feedstock rate of the previous five years of operation to set maximum limits for the duration of the permit, and results compared to monthly average discharges in most cases. No case of a moving average being used has come to our attention. It should also be noted that the EPA enforcement policy expects 100% compliance at all times. However it is our view that 100% compliance cannot be anticipated since there is a natural variability arising from wastewater treatment process capability and accuracy of monitoring so that the 99% and 95% compliance rates are more realistic (the difference between the daily and monthly average compliance rates arises from the fact that the monthly average limitations were chosen to be the more stringent ones).

III-A) GLOBAL PERFORMANCE:

The total number of daily violations were calculated for each of the following pollutants: phenols, oil & grease (O & G), ammonia-nitrogen, total suspended solids (TSS) and sulphides (table 6) and are presented in figure 5. The total number of samples for each pollutant for 1987 (table 8) were multiplied by 1% to yield values for the expected number of exceedances. From figure 5 it can be seen that globally, the allowable number exceedances was surpassed for all pollutants with the exception of phenols with exceedances being more frequent for TSS and sulphides. However if the two lowest performances were removed for each parameter all would fall within or close to "compliance" except TSS (figure 6).

TABLE 6 TOTAL NUMBER OF DAILY EXCEEDANCES PER REFINERY

REFINERY	PHENOLS	AMMONIA	SULPHIDES	0 & G	T.S.S.
ESSO	0	0		0	21
PET-CAN CLARKSON	0	36	5	37	100
PET-CAN OAKVILLE	0	0	194	1	32
PETROSAR	0	0	NR	0	18
SHELL	5	0	41	10	116
SUNCOR	2	5	1	64	133
TEXACO	0	0	0	0	0
TOTAL	7	41	245	112	420
TOTAL EXPECTED EXCEEDANCES	19.0	14.8	9.7	16.8	15.9



EXCEEDANCES EXPECTED EXCEEDANCES

FIGURE 5

TOTAL NUMBER OF DAILY EXCEEDANCES PER POLLUTANT

TABLE 8 TOTAL NUMBER OF SAMPLES PER REFINERY

REFINERY	PHENOLS	AMMONIA	SULPHIDES	0 & G	T.S.S.
ESSO PET-CAN CLARKSON PET-CAN OAKVILLE PETROSAR SHELL SUNCOR	155 357 208 358 241 226	156 360 208 333 47 156	156 360 207 NR 33 44	156 347 208 360 241 201	156 359 208 364 164 158
	358	218	169	171	176
TOTAL	1903	1478	969	1684	1585

200 150 100 50 0 PHENOLS AMMONIA SULPHIDE TSS O & G

EXCEEDANCES EXPECTED EXCEEDANCES

FIGURE 6

TOTAL NUMBER OF DAILY EXCEEDANCES WITHOUT LOWEST PERFORMANCES Total monthly average exceedances were compiled for each pollutant and are presented in table 7 as well as figure 7. The number of expected exceedances was calculated by multiplying the total number of months (12 * 7 refineries) by 5%. Again it is evident that discharges in total, except for phenols, do not meet EPA limitations, but once again without the two lowest performances all parameters fall within "compliance" with the exception of TSS (figure 8).

A percentage of "non-compliance" was calculated by dividing the total number of daily exceedances (table 6) by the total number of samples (table 8) times 100, and are given in table 9. The percentage of "non-compliance" for the monthly average was calculated by dividing the total amount of monthly average exceedances (table 7) by the total number of months (12 * 7 refineries) and are also given in table 9. For example sulphide daily discharges are in "non-compliance" 25.28% of the time whereas the expected level would be 1% and monthly average discharges are in "non-compliance" 31.94% of the time whereas the expected level is 5%, only phenol values are within the expectancy. Again if the two lowest performances for each parameter where removed all fall within the acceptable values with the exception of TSS and daily sulphides (table 9).

III-B) INDIVIDUAL REFINERY PERFORMANCES:

Daily exceedances as well as monthly average exceedances per refinery for each pollutant where also analyzed separately to identify specific situations to particular refineries. The number of allowable exceedances were calculated by multiplying the total number of samples for each refinery by 1% (table 6 and figures 9 to 13) for daily exceedances, and by multiplying the number of months (12) by 5% (table 7 and figures 14 to 18) for monthly average exceedances.

Future Ontario limits to be promulgated may be set for gross values except for TSS which may be set for net values. For this reason wherever possible results where compared to gross discharges but when not available (both Petro-Canada's and Suncor) they were compared to net discharges.

ESSO: The crude rates were given in KB (assumed to be Kilo barrels or 1000 bbl) for the entire month. These values were divided by the number of operating days assumed to equal stream days to obtain the feedstock rate in 1000 bbl/sd. Results were compared to the gross BIOX effluent data received to obtain the number of exceedances. As can be seen from figures 9 to 13 Esso has only a small number of exceedances with regards to TSS and

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TABLE 7	TOTAL	NUMBER	OF	MONTHLY	AVERAGE	EXCEEDANCES	PER	REFINERY
---------	-------	--------	----	---------	---------	-------------	-----	----------

REFINERY	PHENOLS	AMMONIA	SULPHIDES	0 & G	T.S.S.
ESSO	0	0	1	0	6
PET-CAN CLARKSON	0	6	0	6	9
PET-CAN OAKVILLE	0	0	12	0	6
PETROSAR	0	0	NR	0	2
SHELL	1	0	9	1	9
SUNCOR	0	1	1	9	12
TEXACO	0	0	· 0	0	0
TOTAL	1	7	23	16	44
TOTAL EXPECTED EXCEEDANCES	4.2	4.2	3.6	4.2	4.2



EXCEEDANCES

EXPECTED EXCEEDANCES

FIGURE 7

TOTAL MONTHLY AVERAGE EXCEEDANCES PER POLLUTANT

TABLE 9 PERCENTAGE OF NON-COMPLIANCE

	ALL RE	VITHOUT !	THE LOVEST PERFORMANCES	
PARAMBTER	DAILY	MONTHLY AVERAGE	DAILY	NONTHLY AVERAGE
PHBNOLS	0.37	1.39	0.00	0.00
ANNONIA	2.77	9.72	0.00	0.00
SULPHIDBS	25.28	31.94	1.03	2.78
0 & G	6.65	22.22	0.59	1.19
T.S.S.	26.50	61.11	10.79	38,10



EXCEEDANCES EXPECTED EXCEEDANCES

FIGURE 8

TOTAL MONTHLY AVERAGE EXCEEDANCES WITHOUT LOWEST PERFORMANCES



FIGURE 9





EXCEEDANCES

EXPECTED EXCEEDANCES

FIGURE 10

NUMBER OF DAILY AMMONIA EXCEEDANCES PER REFINERY



FIGURE 11





FIGURE 12

NUMBER OF DAILY TSS EXCEEDANCES PER REFINERY



FIGURE 13





FIGURE 14

TOTAL MONTHLY AVERAGE PHENOL EXCEEDANCES PER REFINERY



FIGURE 15





FIGURE 16

TOTAL MONTHLY AVERAGE SULPHIDE EXCEEDANCES PER REFINERY



FIGURE 17

TOTAL MONTHLY AVERAGE TSS EXCEEDANCES PER REFINERY



EXCEEDANCES

EXPECTED EXCEEDANCES

FIGURE 18

TOTAL MONTHLY AVERAGE O & G EXCEEDANCES PER REFINERY sulphides. Figures 14 to 18 show that Esso has monthly average exceedances with respect to TSS and only one exceedance with respect to sulphides. It should be noted that 5% of allowed "non compliance" means 0.6 violations per year or one per two years.

PETRO-CANADA CLARKSON: Due to a shutdown, the lube operation from June through year end was not representative of normal operation. Stream days for October and november were reduced due to a maintenance shutdown. Results were compared to final net discharge loadings to obtain exceedance data. As can be seen from figures 9 to 13 this refinery exceeds the theoretical limits for the parameters of TSS, O & G and ammonia as well as slightly surpassing those for sulphides. Figures 14 to 18 show that Petro-Canada Clarkson has several monthly average exceedances with respect to ammonia, O & G and TSS.

PETRO-CANADA OAKVILLE: Crude rates were given in MB/M (assumed to mean 1000 bbl/month). Their values were divided by the number of operational days, assumed to be equal to stream days, to obtain the feedstock rate in 1000 bbl/sd. VSM which stands for volatile suspended matter was assumed to equal TSS (total suspended solids) which usually includes VSM and NVSM (non volatile suspended matter). Results were compared to final net discharge loadings to obtain the number of exceedances. As can be seen from figures 9 to 13 this refinery exceeds the theoretical daily limitations for TSS and sulphides. Figures 14 to 18 show that this refinery has several exceedances of the monthly average theoretical limitations with respect to TSS and sulphides.

PETROSAR: Crude throughput rates include a portion of condensate. The results where compared to the daily gross discharge concentrations (mg/L) converted into loadings (Kg/day). No data were submitted for sulphide discharges since Petrosar has been exempted from measuring its sulphide discharges because of an excellent past performance for this parameter. As can be seen in figures 9 to 13 Petrosar only exceeds the theoretical daily TSS limitations. Figures 14 to 18 show that they have no problem meeting monthly average limitations except for two exceedances of TSS.

SHELL: Shell represents a special case since measurements are made at several points during the wastewater treatment process and mixed effluents are discharged. Biotreater data was used to compare O & G and TSS discharges to their theoretical limitations and POW data was used to compare the other parameters to their respective theoretical limitations. These were both assumed to be gross discharges since biotreater discharges consist of treated wastewaters and POW discharges are approximately 10% treated wastewater and 80-90% once through cooling water. However it was difficult to interpret the effluent data: intake concentrations of

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ammonia and sulphides seem to be constantly equal to discharge concentrations i.e. 0.3 ppm. This value could be a limit of detection and entered automatically when these substances are detected at concentrations lower than 0.3 ppm. Figures 9 to 18 show that Shell exceeds all theoretical limits with the exception of ammonia. It has also come to our attention that the wastewater treatment plant receives discharges from two sources, the refinery and an organic chemicals plant. It would therefore fall under the petrochemical subcategory rather than the cracking subcategory, this was not known at the time of original exceedance evaluations and therefore has not been considered.

SUNCOR: Process feedstock rates were given in m^3/d monthly averages assumed to equal m^3/sd . Results were compared to net loadings data. As can be seen in figures 9 to 13 this refinery exceeds the theoretical daily limits for all parameters except phenol. Figures 14 to 18 show that this refinery also exceeds the theoretical monthly average limitations for the same parameters.

TEXACO: No process data was submitted by Texaco but contacts with the refinery lead to the conclusion that this refinery generally runs at full capacity. Therefore capacity crude rates were used and the results compared to gross effluents. This was accomplished by adding intake concentrations to final net concentrations and converting the results to mass loadings. Due to the use of capacity rates the numbers for limitations as well as process factors and size factors are identical throughout the year. Being the most recent of the seven refineries it is not entirely surprising that Texaco has no exceedances. Using capacity rates could lead to artificially high limitations contributing to this seemingly perfect record, However calculations based on 75% capacity would still lead to the same results.

III-C) LONG TERM GLOBAL PERFORMANCE

The EPA has established long term average concentrations to be discharged (table 10) which were compared to the daily discharge averages for 1987 of each pollutant for each refinery (table 11 and figures 19 to 23). Frequency of exceedances with respect to these limits is low (table 11). This leads to the conclusion that the refineries examined can meet these long term averages. However on a short term basis such as daily and monthly average discharges there is a great variability in discharges leading to numerous exceedances. On the other hand there are numerous occasions where the discharges are well below the limitations indicating that "compliance" (during "normal" operation) may be attainable. Exceedances (or % "non compliance") should certainly not be as numerous (as high) as they have been found to be (table 9).

Figures 24 to 26 represent a monthly analysis of exceedances

ABLE 10 LONG TERM AVERAGE CONCENTRATIONS

TSS	10 mg/L
IL & GRBASE	5 mg/L
PHENOLS	0.1 mg/L
SULPHIDES	0.1 mg/L
NHONIY	* 0.5-9.6 mg/L

* DEPENDS UPON THE REFINER SUBCATEGORY

TABLE 11 LONG TERN BICEBDANCES

ARAMBTBR	LINIT (Kg)	1987 AVGERAGE	BICEBDANCE	PARAMETER	LINIT (Kg)	1987 AVGERAGE	BXCBBDABC
BSSO				SHBLL		••••••	
SS	154.10	253.30	YBS	T SS	96.27	503.06	YBS
0 & G	77.05	27.18	N O	0 & G	48.13	27.96	H O
BENOLS	1.54	0.17	N O	PHENOLS	0.96	0.34	1 0
ULPEIDES	1.54	0.30	NO	SULPHIDBS	0.96	19.50	YBS
- THONIA	147.94	14.61	NO	VINORI Y	783.14	12.86	NO
BTRO-CANADA (CLARKSON			SUNCOR			
TSS	101.74	116.97	YBS	TSS	102.95	431.24	VRS
£ G	50.87	34.44	NO	0 # G	51.58	69.17	729
BUOLS	1.02	0.05	10	PHRMOLS	1.03	0.24	100
SULPHIDES	1.02	0.25	NO	SULPHIDRS	1.03	0.21	10
AIRONIY	97.67	19.84	NO	ANNOWIA	97.81	42.66	NO
PETRO-CANADA O)AKVILLB			TEIACO			
5 S	48.29	119.28	YRS	4 68	56 47	27 57	NO
E G	24.15	10.86	NO	0 L C	28 24	11 52	80 80
PHENOLS	0.48	1.00	YRS	DHRWOLS	£V.E4 A 57	B 07	
ULPHI DES	8.48	3.20	YRS	SULPHIORS	A.57	0.02	NO
INONIA	46.36	25.30	NO	AMMONIA	54.21	0.82	NO
DETROSAR							
TSS	61.52	101.85	YRS				
0 & G	30.76	13.63	NO				
BNOLS	0.62	0.04	NO				
LPEIDES	0.62	N.R.	Ϊ.λ.				
ANNONIA	59.06	13.67	10				
AMMONIA MITS WERE CAN	59.06 LCULATED BY NULTIPL	13.67 YING THE LONG TERN	₩0 				

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LINITS BY THE AVERAGE DISCHARGE FLOW FOR 1987 NP = NOT REPORTED

= NOT APPLICABLE



FIGURE 19

T.S.S. LONG TERM AVERAGE 1987



FIGURE 20

O & G LONG TERM AVERAGE 1987



FIGURE 21

PHENOL LONG TERM AVERAGE 1987



SULPHIDE LONG TERM AVERAGE 1987



DISCHARGES EXPECTED DISCHARGES

FIGURE 23

AMMONIA LONG TERM AVERAGE 1987

of the two most often exceeded limits, TSS and sulphides, to determine if there is any seasonal variation. Phenol was also chosen because it is a good indicator of the efficiency of the biological removal techniques. If the lowest performances were removed for TSS and sulphides it could be determined that seasonal variations (such as temperature) are not a factor in the number of exceedances (figures 25 and 26). Since exceedances for phenols are present in very low numbers (figures 5 to 9, 14, 21 and 24) we can conclude that biological removal techniques are very efficient.

III-D) EFFECTS OF PROCESS AND SIZE FACTORS ON LIMIT CALCULATIONS:

The difference between the EC and EPA limitations rests in the inclusion of process factor and size factor in the calculation of the allowable discharges. Table 12 and figures 27 to 32 show the variability that this inclusion brings from month to month for each refinery (Texaco has no variances for reasons discussed in section III-B). Although the size factor does not vary exceedingly the process factor does. This is due to the variability of individual throughputs for each process as well as greater sensitivity of the process configuration factors due to the weighting system, i.e. refineries will seldom vary their monthly average throughput by more than 25 000 bbl per day, whereas the process configuration often varies on a monthly basis. Relative process throughputs are multiplied by the weighting factors which results in the possibility of varying by more than one unit of process configuration. For example for a 1000 000 bbl/day refinery, a change in lube production from 4 000 to 6000 bbl/day would result in a change in the calculated process factor, giving the refinery a supplementary 10% discharge allocation.

The variability in the product of these values leads to the conclusion that the inclusion of the process factor-size factor product in the main limitations formula has a definite impact on effluent limitations. Figures 27 to 32 show that under normal variations of the process configurations with respect to Ontario refineries, EPA limitations if calculated on a monthly basis vary noticeably.

III-E) PERFORMANCE UNDER CANADIAN LIMITATIONS:

The "Environmental Status Report of the Canadian Petroleum Refining Industry 1987" was examined for the Ontario region's performance. The performance was determined to be very good, even without excluding the lowest performances. The status report show that the Ontario region refineries were not in compliance 4.9% of the time for monthly amounts and 0.3% of the time for one day amounts with 84.7% of the required tests reported (figure 33). A





TOTAL DAILY TSS EXCEEDANCES PER MONTH



FIGURE 26



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TABLE 12 PROCESS AND	SIZE FACTORS	PBR RRF1	HBRT									
ref i Hert	JANUARY PI	BRUARY	MARCH	APRIL	HAT	JUNE	110	AUGUST	SEPTENBER	OCTOBER	BOVEMBER	DECEMBER
PROCESS PACTORS:	1 2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		4 6 7 7 6 6									
B 550	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	97 Q	1 42	0 75	1 U
PBT-CAN CLARKSON	2.51	2.12	2.31	1.79	1.79	0.95	0.95	0.95		7 Y	C7 0	
PBT-CAN OAKVILLE	0.74	0.88	1.00	0.88	0.85	0.88	1,00	A.A.A.A.A.A.A.A.A.A.A.A.A.A.A.A.A.A.A.		1 00	70.0	91.7 9 0
PETROSAR	1.39	1.28	1.39	1.28	1.39	1.39	1.51	1.28		1.28	99.9	1 77
Sarl	0.74	0.74	0.74	0.74	0.74	0.88	0.68	0.88	0.88	8.8		
SUNCOR	0.88	0.88	0.88	0.74	0.74	0.74	0.88	0.68	0.74	0.48	0.0 1 1 1	00.0
TBIACO	0.88	0.88	0.88	0.89	0.88	0.88	0.68	0.88	0.88	0.88	0.88	0.80
SIZE PACTORS:												
rsa.	(
	C/ . A	0.13	U.13	0.73	0.73	0.73	0.73	0.73	0.76	0.73	0.73	0.73
PET-CAR CLARKSON	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06
PET-CAN OAKVILLE	1.13	1.04	1.04	0.95	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04
PETROSAR	0.76	0.83	0.76	0.76	0.76	0.83	0.83	0.83	a la	0.83	0.83	16
3887 C	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	
suecor	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.11	1.04
TELACO	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13	1.13
PP t SP;												
B \$\$0	0.55	0.55	0.55	0.55	A. 55	1 55 1	0 55	0 CC	5 0	10.1		7 C C
PBT-CAN CLARKSON	2.66	2.25	2.45	1.90	1.90				7V	50 V		(C.)
PRT-CAN OAKVILLE	0.84	0.92	1.04	0.84	0.92	0.92	1.04	1 G U	() () ()		00.0	(7 .7
PETROSAR	1.06	1.06	1.06	0.97	1.06	1.15	1.25	1.06		1 00	31 1	11.1
SHELL	0.77	0.77	0.17	0.77	0.77	0.92	0.97	0 0	0 0	00.1	1.1.1	1.11
SUNCOR	0.92	0.92	0.92	0.77	0.77	0.77	0.92	1.92	10.77	0 0 0	7C.U	10.72
TBIACO	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	6.0 66.0	0.99
13 14 14 14 14 14 14 14 14 14 14 14 14 14	ry 19 19 19 19 19 19 19 19 19 19	31 61 11 10 10 11	01 71 19 19 19 11 19 11									

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FIGURE 28

PROCESS AND SIZE FACTOR MONTHLY VARIATIONS, SUNCOR



FIGURE 30

PROCESS AND SIZE FACTOR MONTHLY VARIATIONS, PETRO-CANADA CLARKSON



FIGURE 32

PROCESS AND SIZE FACTOR MONTHLY VARIATIONS, PETRO-CANADA OAKVILLE



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FIGURE 33

% OF TIME IN COMPLIANCE WITH CANADIAN REGULATIONS comparison of the two levels of non compliance for this same time period (1987) quickly reveals that, as previously recognized, EPA limitations are the more stringent ones.

IV) REFERENCES

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