JOB REPORT

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Bio-Assay of the Pontiac Refinery Final Effluent and Its Effects on Aquatic Life in Corpus Christi Harbor

Abstract: The Pontiac Refinery has a waste emptying into the Corpus Christi Harbor that carries toxic chemicals, an oil waste and a high chemical oxygen demand waste that is detrimental to aquatic life. This should be remedied by a dilution process, retention ponds, or enlargement of present separators.

Objective: To determine the toxicity of Pontiac's effluent and control additional pollution in the harbor.

Procedure: Stations were established as follows: (1) at the outfall; (2) in ditch prior to disposal in harbor; (3) 100 yards from outfall; (4) 200 yards from outfall.

Samples were taken once a month and analized for toxic components. Toxicities were made to determine the concentration in which 50% of the species could survive. This is the median tolerance limit (TLm) and tests were made for a 24 hour, 48 hour and 96 hour period. Dilution ratios were determined for a 100% survival.

Findings: Field studies were established previously to determine the possible effects of Pontiac Refinery's waste to aquatic life in Corpus Christi harbor. This is a continued study to determine any chemical or physical change of the receiving waters.

Pontiac Refinery produces gas oil, aviation gasoline, and natural gasoline. In the process phenolic compounds are produced by decomposition of napthenic acids in the catalytic cracking process. Caustic washes are used to remove the phenols from the cracked gasoline and the resulting extract is sold for reclamation. All of the process effluents from this plant are combined into one waste stream (final effluent) that empties into a 36 inch sewer line and is discharged into a ditch emptying into Corpus Christi harbor.

A general description of the chemical characteristics of the final effluent is given in Table 1.

Samples collected at the outfall had a phenolic odor and with a general appearance of a brown, turbid, oily waste. The waste was normally very alkaline with pH values ranging from 8.9 to 9.8. Phenols ranged from 20.0 to 44.0 ppm and sulfides ranged from 0.1 to 8.1 ppm. A mean 48 hour TLm was 7.9%.

There was very little change of the concentration of chemical components at station 2 (Table 2). This occurs since there is very little tidal exchange in the area resulting in no dilution to decrease the concentration.

Station 3 showed some signs of self-purification. There were no signs of phenols and the pH was reduced to a mean of 8.8. The dissolved oxygen was below the survival limit of aquatic organisms indicating a high chemical oxygen demand waste.

Station 4 indicated the water to be better qualified for aquatic organisms since the water depth and wind agitation allowed the water to be better mixed thus reducing any signs of a toxic pollutant present.

As evidenced by analysis, the area from station 1 to station 3 was a polluted area unfit for aquatic organisms - so the bulk of the work was limited to this area.

It is believed that the principal effects of a refinery effluent is the depletion of oxygen. This was found true by dissolved oxygen analysis from station 1 to 4. The mean concentration of dissolved oxygen at station 1 was 0.0 ppm. There was a slight increase up to 3.0 ppm to station 3. However, the dissolved oxygen content did not reach the point satisfactory for aquatic life (above 4.0 ppm) until the water depth increased. This allowed for better mixing and dilution.

Ludzack, et al (1957) reported that the principal effects of a refinery effluent in Ohio was the formation of beds of oil sludge which depleted oxygen when disturbed by high winds. Water was collected in the middle of the harbor when a 48 TLm value proved to be 100%. Sludge samples were collected at station 3 and one gram/liter was added to the water and physical effects were noted. After <u>five</u> grams/liter were added the fish became very excited and swam around vigorously. An oil sheen developed and after 15 minutes of agitation 10 ppm of oil was formed, A dissolved oxygen was not taken since the tank was aerated with air stones.

A ten liter jar was filled with bay water and aerated for ten minutes to obtain oxygen saturation. A dissolved oxygen was taken before any addition of sludge. .5 g/l of bottom sludge was added and a dissolved oxygen was taken every 15 minutes there after until there was no indication of a decrease in oxygen. When 1.5 g/l of bottom sludge was added the dissolved oxygen decreased 39.3% (Table 4).

A decrease of 44.9% was found as compared to the harbor water away from contamination and in the area of disposal. This would account for the low dissolved oxygen readings at stations 1, 2, and 3 (Table 2).

Phenols were always above the optimum of 10.0 ppm at the outfall. However, dilution was great enough to reduce the concentration to less than 1.0 ppm at station 3.

Bio-assays were used to evaluate the toxicity of the waste stream. A summary of the results showing the direct toxicity of all final effluent is shown in Table 3.

Median tolerance limit tests were conducted for 24, 48 and 96 hour periods until 50% of the species survived. A dilution ratio, unit volume of effluent to dilution water, was determined to produce a 50% survival. This ratio multiplied by the effluent flow gives the amount of water needed for 50% of the fish to survive. An application factor of 10 was used to determine survival of 100% of the specimens. The final effluent had a mean median tolerance value of 6.5 as indicated by taking the 100% survival value of 3.5% and the 100% death value of 12.0 and interporating by a straight line graph (Figure I). The mean

48 hour TLm value of the combination of toxicities is 7.9 (Table 3). From these two values the mean is 7.2% so the dilution volume is calculated as follows:

$$\frac{100-TLm}{TLm} \text{ X Effluent Flow = Dilution Volume}$$

Dilution Volume X Application Factor (10) = 31,750 gallons or 73.5 cfs. of purified water would have to be injected in the final effluent outfall to be safe for aquatic life. However, this would not be satisfactory for the heavy concentration of oil. The present API separator is not sufficient to handle the oily materials in the waste.

A toxicity check made at station 3 had a 100% TLm value. This would seem to indicate the water would be safe for aquatic life over the area but the dissolved oxygen values were reduced by the high oxygen demand in the sludge to the point below survival for fish.

Comments: The final effluent from Pontiac Refinery wastes is detrimental to aquatic life in Corpus Christi harbor from the toxic effects of the excess chemicals present in the outfall and a high oxygen demand waste. This could possibly be reduced by a dilution ratio of 1:9.4 cfs, which has been suggested to plant officials, or by holding the waste in retention and then releasing into an open ditch for excess aeration. When effluents are allowed to drain through an open ditch there is usually a decrease shown in phenols, sulfides, pH, immediate oxygen demand and chemical oxygen demand. Also a larger API separator or a series of two is necessary to reduce the oily wastes in the effluent.

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Table 1

Toxicity and Chemical Characteristics of Pontiac Refinery Effluent

Date	48 hr TLm	Phenols (ppm)	Sulfides (ppm)	pH	Oil (ppm)	Dissolved Oxygen (ppm).
9-3	8.5%	31.0	.5	9.8	27.0	0.0
10-7	12.0	20.0	.1	9.1	22.0	0.0
11-24	5.5	35.0	.8	9.3	32.0	0.0
12-7	9.7	31.0	2.5	9.1	21.0	0.0
1-20	9.0	27.0	3.0	8.9	18.0	0.0
2-15	5.0	31.0	.2	9.3	10.0	0.0
4-4	10.0	21.0	8.1	9.1	31.0	0.0
6-21	3.5	44.0	1.0	9.8	25.0	0.0

Table 2

Chemical Characteristics of Station 2 through 4

Date	Station	48 hr TLm	Phenols (ppm)	Sulfides (ppm)	pH	Oil (ppm)	Dissolved Oxygen (ppm)
9-3	2	8.5%	29.0	.5	9.8	27.0	0.0
9-3	3	100.0	2.0	0.0	8.8	15.0	2.4
9-3	4	100.0	0.0	0.0	7.7	0.0	5.1
10-7	2	---	20.0	0.0	9.1	20.0	0.0
10-7	3	---	1.0	0.0	8.5	--	3.0
10-7	4	---	--	---	7.5	--	5.1
11-24	2	---	35.0	---	9.3	--	0.0
11-24	3	---	--	---	---	--	2.5
11-24	4	---	0.0	---	7.5	--	5.6
12-7	2	9.9	30.0	---	9.1	--	0.0
12-7	3	100.0	0.0	---	9.0	10.0	1.8
12-7	4	---	--	---	---	--	---
1-20	2	---	27.0	---	8.9	--	---
1-20	3	---	0.0	---	8.1	--	---
1-20	4	100.0	0.0	0.0	8.0	15.0	4.9
2-15	2	---	31.0	---	9.3	10.0	0.0
2-15	3	---	0.0	---	8.7	--	2.8
2-15	4	---	--	---	7.8	--	---
6-21	2	3.50	42.0	---	9.8	25.0	---
6-21	3	100.0	0.0	---	8.8	15.0	1.8
6-21	4	100.0	0.0	0.0	8.0	--	5.2

Table 3

Toxicity and Dilution Ratios of Pontiac Effluent

Date	Effluent flow (cfs)	Median Tolerance Limit (Per Cent Concentration) 24 hr.	48 hr.	96 hr.	Dilution Ratio	Dilution Volume (cfs)
9-3	.57	9.0	8.5	8.5	1 : 6	61.6
10-7	.57	12.0	12.0	12.0	1 : 4	41.6
11-24	.57	7.0	5.5	5.0	1 : 10	98.0
12-7	.57	9.7	9.7	9.7	1 : 5	53.0
1-20	.57	10.5	9.0	9.0	1 : 6	57.6
2-15	.57	5.0	5.0	5.0	1 : 11	108.3
4-4	.57	12.0	10.0	10.0	1 : 5	51.3
6-21	.57	3.5	3.5	3.5	1 : 28	276.0
Mean	.57	8.6	7.9	7.8	1 : 9.4	93.4

Table 4

Oxygen Consumed by Bottom Sludge

Contents	Concentration	Dissolved Oxygen Reading Before Add.	After Add.	Time
Bottom Sludge	.5 g/1	5.0 ppm	4.9 ppm	15 minutes
Bottom Sludge	.5 g/1	5.0 ppm	4.5 ppm	30 minutes
Bottom Sludge	1.0 g/1	5.0 ppm	4.5 ppm	15 minutes
Bottom Sludge	1.0 g/1	5.0 ppm	4.1 ppm	30 minutes
Bottom Sludge	1.5 g/1	5.0 ppm	4.3 ppm	15 minutes
Bottom Sludge	1.5 g/1	5.0 ppm	3.1 ppm	30 minutes

FIGURE I

Maximum and Minimum 48 hr. TLm