Job Report

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Project No. MP-2-R-3 Date March 16, 1962

Project Name: Pollution Abatement in Region V

Period Covered: September 1, 1960 to September 1, 1961 Job No. F-5

Bio-assay of Pontiac Refinery's Effluent and Determination of Its Effects on the Marine Environment in Corpus Christi Bay

Abstract: Pontiac Refinery has a toxic waste that empties into Corpus Christi Harbor at a rate of 500 gallons per minute. The most toxic substance present in this waste is a phenolic compound that has a direct toxic effect on aquatic life. Beds of oil sludge formed by the waste settling on the bay bottom are indirectly toxic, since they reduce the dissolved oxygen content below the survival level of 4.0 parts per million, a level below which many vertebrates and invertebrates cannot survive. Natural purification and dilution of the waste by harbor water reduces the toxic level of the pollution load, restricts the contaminated area within the cove to 300 feet beyond the outfall and minimizes damage to the marine environment.

Objective: The previous study indicated waste from Pontiac Refinery was capable of causing pollution and damaging the marine environment in Corpus Christi Bay. Recommendations were made to plant personnel that would reduce the toxic level of the waste by dilution with bay water at a 1:9 ratio, or by holding the waste in retention and then releasing into an open ditch for excess aeration. The investigation was continued to determine any change in the toxic components of the effluent.

Procedure: Six stations were established within the disposal area to get representative samples of the effluent and evaluate the quality of harbor water. The stations were set up as indicated in Figure 1 to eliminate sampling errors from deposition of settable solids from the weir and accumulation of oil downstream. Grab samples were made to avoid skimming the water surface.

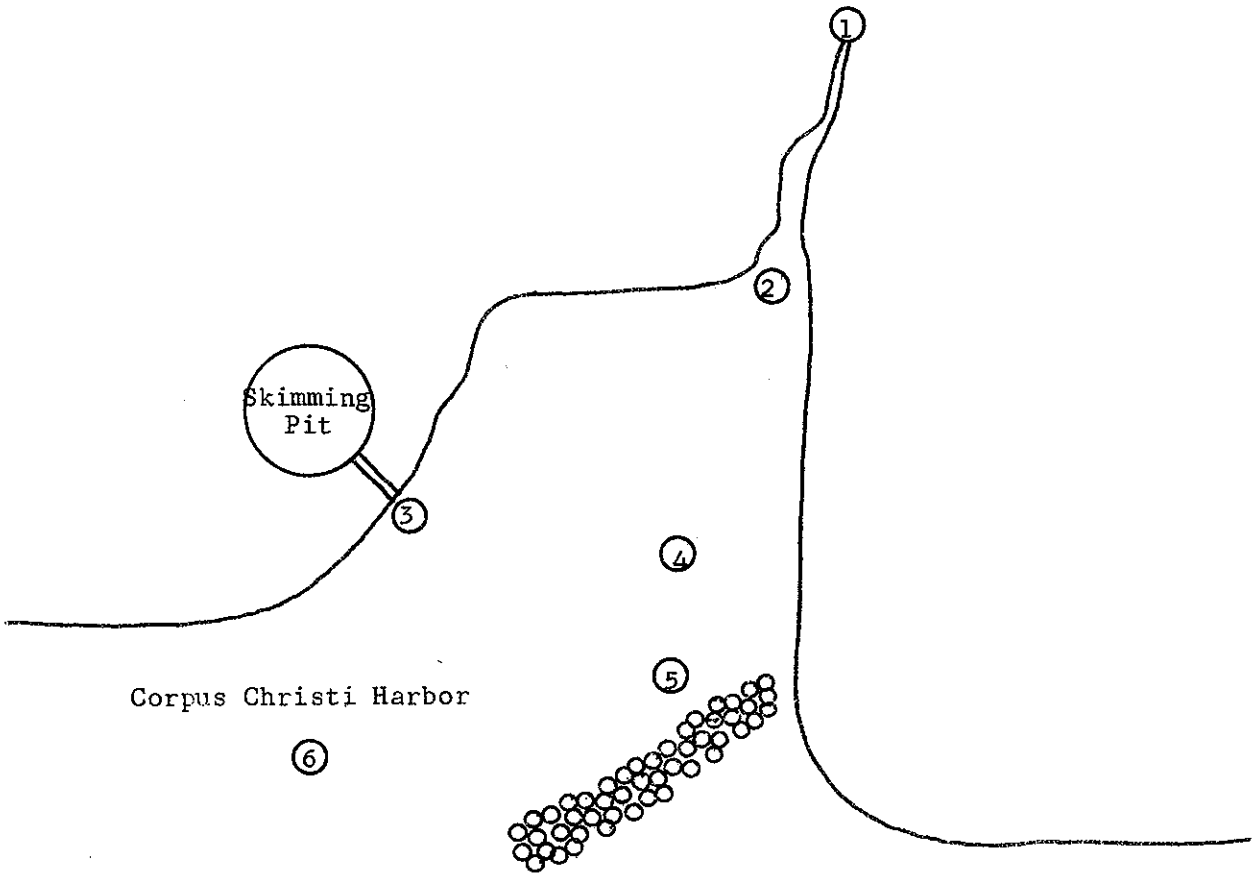
Samples were taken monthly and a chemical analysis was made. Analysis, such as dissolved oxygen and pH, were made in the field. Samples collected for other analyses of phenols, sulfides, and oil were preserved by chemical treatment and tested at the laboratory according to Standard Methods, Tenth Edition, within a 24-hour period. Dissolved oxygen analysis was determined by the Rideal-Stewart modification of the Winkler Method. This method was preferred because significant errors may occur if the water contains appreciable quantities of nitrates, iron salts, or certain organic compounds. pH measurements were made by a Beckman Model G glass electrode meter.

Toxicity tests were made in the laboratory to determine a median tolerance limit (TLm) concentration in which 50 percent of a marine index, pinfish, can survive for a 24-hour period. The tests were made in 10-liter containers with five fish per test. The dilutions were increased until the median tolerance factor was obtained.

Findings: Pontiac Refinery produces gas oil, aviation gasoline, and

Figure 1

Effluent Disposal Area



natural gasoline. Phenolic compounds are produced in the waste by decomposition of napthenic acids in the catalytic cracker. Caustic washes are used to remove most of the phenols from the cracked gasoline, and the resulting extract is reclaimed. All of the plant's wastes are separated into two discharges flowing through three API separator units. One discharge drains from a separator that handles 250 gallons per minute of boiler blowdown and cooling tower waste. This discharge flows through a 36-inch line, through a weir, and into a ditch that flows for 100 feet before emptying into the harbor. Two other API separator units form the second discharge. One unit handles 40 gallons per minute of boiler blowdown and cooling water waste, and the other separator handles 190 gallons per minute. These two smaller units' wastes combine with a pump house waste that flows into a gravity separator skimming pit located at the edge of the harbor.

Previously, ballast water taken from ships was processed through the large API separator. At times this increased discharge overloaded the separator unit, so a tank was constructed to receive ballast water from the ships. The waste flows from the tank into two skimming pits prior to emptying into the channel. The skimmed oil is siphoned off by vacuum trucks and burned.

The combined waste empties into an area that is recessed from the harbor approximately 300 feet. This recessed cove is blocked off on the west side by a rock wall which prevents most of the waste from being washed into the harbor by prevailing southeast winds.

The largest concentration of toxic components from the waste occurs at Station 1. This effluent was derived directly from the large separator and flowed through a weir. Phenols reached a high of 49.0 parts per million. The pH was alkaline at 9.2, and sulfides had a mean of .46 parts per million. Oil concentration ranged from 20.0 to 100.0 parts per million. After the waste emptied into the ditch and was aerated for approximately 100 feet (Station 2), the sulfides were reduced to .40 parts per million. Dilution by the harbor water reduced the phenols to an average of 30.0 parts per million with a high of 41.0 parts per million. The pH was reduced to 8.3 by dilution from the 7.6 bay water. The oil concentration remained the same.

Station 3 had a less toxic waste, averaging 21.0 parts per million phenols, 15.0 parts per million oil, and 0.0 parts per million sulfides. This effluent flow was a composite of the two smaller API units flowing through a gravity separator pit allowing for some retention time, thus reducing the toxic components.

Stations 4 and 5 were collection points for contaminants in the area. A rock wall retained the flow of water and prevailing winds pushed the waste in the vicinity. Dilution reduced the phenol content to less than 5.0 parts per million in all samples. However, the oil concentration increased to 50 to 150 parts per million. This was a result of the oil cumulating and does not necessarily mean an increase in concentration from the effluent.

Dissolved oxygen tests indicated the water to be unfit for an aquatic environment. The concentration within the disposal area averaged 2.5 parts per million, below the 4.0 parts per million necessary for survival of many species. This area is shallow and retained the oily sludge which results from a refinery waste. As stated in Job No. F-1, 1960 report, 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. Sludge samples collected in the previous job reduced dissolved oxygen 39.3 percent when added to containers of bay water. A decrease of 44.9 percent in dissolved oxygen was found as compared to the harbor water away from contamination and in the area of disposal. The decrease in this investigation indicated a 43.1 percent reduction in dissolved oxygen content at Station 4 and an 18.3 percent reduction at Station 5, as compared to harbor

Table 1

Toxicity and Chemical Characteristics of Pontiac Refinery Effluent and an Analytical Summary of the Previous Investigation

Month	48-hr. TLm	Phenols (ppm)	Sulfides (ppm)	pH	Oil (ppm)	P.O. (ppm)
Sept.	7.6	38.0	.3	9.1	28.2	0.0
Oct.	6.2	41.0	.5	8.9	15.6	---
Nov.	9.5	36.0	1.5	8.7	0.0	---
Dec.	15.2	19.5	.8	9.2	19.4	0.0
Jan.	10.6	21.2	0.0	8.8	28.5	---
Feb.	9.8	33.5	0.0	8.7	21.2	---
March	9.5	30.1	---	9.1	0.0	0.0
April	10.2	29.8	---	9.2	36.3	---
May	9.1	28.2	.2	8.8	0.0	---
June	8.9	26.1	.4	8.9	29.3	---
July	12.1	18.5	.3	9.0	14.6	---
Aug.	8.7	39.2	.6	9.1	10.8	0.0
Summary for 1961	9.8	30.1	.46	8.9	17.0	0.0
Summary for 1960	7.9	30.0	2.0	9.3	23.2	0.0

Table 2

Bi-Monthly Composite Chemical Analysis of Samples From Stations 2 through 6

Date	Station	48-hr. TLm	Phenols (ppm)	Sulfides (ppm)	pH	Oil	DO (ppm)
Sept.-Oct.	2	15.0	29.3	.3	9.1	27.9	0.0
	3	70.0	18.5	0.0	7.9	29.2	3.6
	4	100.0	2.3	0.0	7.8	51.0	2.8
	5	100.0	neg.	0.0	7.7	63.0	4.2
	6	100.0	0.0	0.0	7.5	10.2	5.1
Nov.-Dec.	2	12.0	26.4	1.2	8.9	15.6	0.0
	3	75.0	23.2	0.0	8.1	10.4	4.5
	4	100.0	neg.	0.0	7.9	29.1	3.1
	5	100.0	neg.	0.0	7.8	52.5	4.3
	6	100.0	0.0	0.0	7.4	28.3	5.4
Jan.-Feb.	2	20.0	28.6	0.0	8.9	23.1	0.0
	3	80.0	19.6	0.0	8.0	11.6	
	4	100.0	5.3	0.0	7.9	43.1	2.9
	5	100.0	2.1	0.0	7.8	110.0	3.6
	6	100.0	0.0	0.0	7.4	0.0	5.1
Mar.-Apr.	2	15.0	31.5	---	9.1	19.4	0.0
	3	60.0	20.1	0.0	7.8	0.0	4.9
	4	100.0	0.0	0.0	7.7	0.0	3.5
	5	100.0	0.0	0.0	7.5	9.3	5.1
	6	100.0	0.0	0.0	7.4	0.0	5.9

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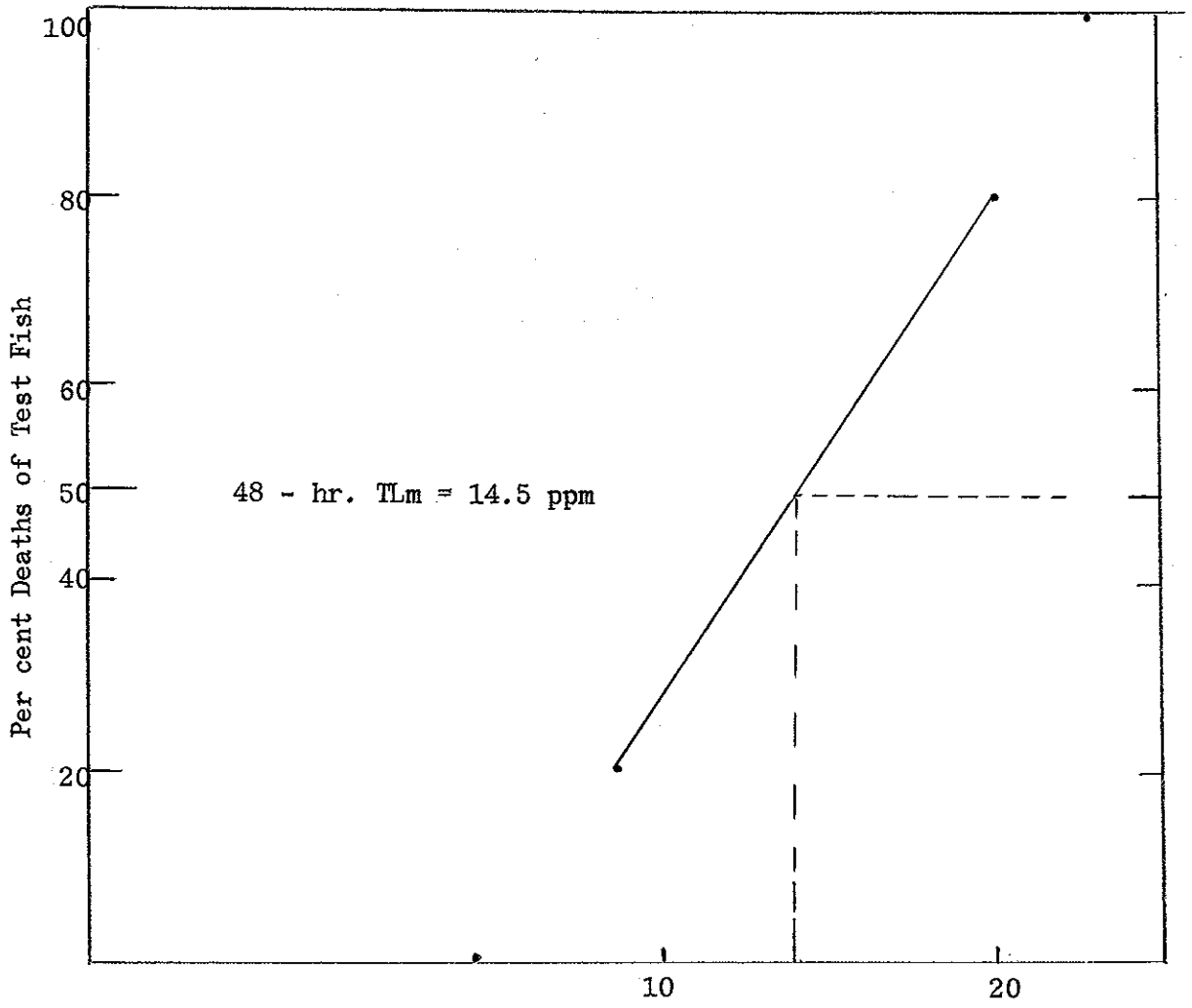
Table 2 - continued

Date	Station	48-hr. TLm	Phenols (ppm)	Sulfides (ppm)	pH	Oil	DO (ppm)
May-June	2	12.0	26.1	.2	8.9	12.2	0.0
	3	90.0	15.3	---	8.0	5.6	4.1
	4	100.0	0.0	0.0	7.8	0.0	2.5
	5	100.0	0.0	0.0	7.8	89.0	3.9
	6	100.0	0.0	0.0	7.7	9.2	5.2
July-Aug.	2	25.0	31.2	.4	9.0	15.1	0.0
	3	75.0	29.6	0.0	7.9	31.5	4.0
	4	100.0	5.6	0.0	7.7	39.6	3.3
	5	100.0	0.0	0.0	7.6	150.0	4.9
	6	100.0	0.0	0.0	7.4	0.0	5.1

Figure 2

Bio-Assay Results of Pin Fish in a Phenol Solution



water away from contamination (Station 6). Since Station 4 is a collection point for oily sludge and the dissolved oxygen reduction was greatest at this point, this would indicate the sludge would cause an oxygen deficiency.

Toxicity studies indicate the toxic condition existing for the first 100 feet is caused by a phenolic compound occuring in the waste. The increase and decrease in the TLm values coincides with the increase and decrease in phenol content (Tables 1 and 2). Some natural purification and dilution by harbor water reduces the phenol content below the safe concentration of 14.5 parts per million (Figure 2). At this point the dispersed oil sludge decreases the dissolved oxygen content below 4.0 parts per million and renders the water unsafe for aquatic organisms as far as Station 6. The water depth increases rapidly to 50 feet, increasing the volume of water and bottom area and reducing harm to the marine environment.

Summary: Using analytical summary data (Table 1) gathered for the last two years at Station 1, there has been very little change in the contaminants. The previous investigation showed an average of 30.1 parts per million in phenols as compared to 30.0 parts per million in this study. The sulfides indicate a slight decrease, with an average of .46 parts per million as compared to 2.00 parts per million from 1960. The oil content appeared in 75 percent of the samples as compared to 100 percent previously. The median tolerance limit remained approximately the same; therefore, the improvements were not effective.

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