
A Phase in Managing Refinery Wastes Polluting Streams

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Wastes from the drilling, pumping, and refining operations in the oil industry are frequently dumped into streams without much thought to the effect on the communities, industries, agriculture, and fish and wild-life that use the water downstream. Dumping practices are carried on commonly because of their expediency and fish are frequently affected. So one phase of the problems of pollution abatement is to develop a procedure of maximum disposal with minimum harm to fish.

Various aspects of the manner in which waste products of the oil industry can act on the fish population have been mentioned by Roberts (10), Gutsell (9), Eldridge (4), Gardiner (8), Fry (6), and Gabrielson (7). Oil on the surface of the water eliminates oxygen exchange between the air and the water (10), and fish without oxygen suffocate; oil in the water may clog the gills to the point where they are ineffective respiratory organs (9, 10). Wastes may lower the dissolved oxygen in water to the point where fish suffocate. Various chemical ingredients of the wastes may be present in sufficient quantities to exert an osmotic effect which fish cannot tolerate. Some of the ingredients may act as poisons and irritants (4)—they may interfere with metabolism, they may destroy the fish's appetite (6), or the food of the fish (6, 7), they may be harmless to the older fish but kill the eggs or fry(8). These are some of the more obvious effects of wastes on fish.

In refining crude oil there are a number of wastes which may be dumped together or kept separate. In the main part of this investigation, emulsion wastes taken from API separators were used, and caustic and acid wastes as well as the water from the cooling towers were not included.

The handling of refinery wastes in a stream abatement program has two general approaches. Wastes can be treated chemically or they may be diluted sufficiently to render little or no harm to fish, when dumped into a stream. A biologist leaves the first problem primarily to the chemists but undertakes the solution of the second problem, that of dilution.

METHODS

All wastes were collected full strength as they entered the stream, and stored in glass containers. When these wastes were discovered to change at room temperature, the capped glass containers, full of wastes were stored in a cold room at 6°C. Wastes kept at this temperature did not change perceptibly over a period of a month, after which tests were not made. Chemical composition of the wastes is shown in Table I.

TABLE I

Chemical Analyses of the Wastes Immediately After They Entered the Stream. Analyses by Doris Beck, Oklahoma Geological Survey, December 16, 1951.)

*p*H—7.5

N. C. hardness	1360 ppm	Na and K	44.0 ppm
Total hardness	1560 ppm		
Dissolved solids	2340 ppm	CO_3	0
S. conductance	. 2340 ppm	HCO_3	236.0 ppm
Ca	585 ppm	SO_4	1390 0 ppm
Mg	24 ppm	Chloride	8.0 ppm
		NO_3	2.4 ppm

A bioassay method for the evaluation of the toxicity of oil refinery wastes was followed according to Doudoroff, *et al* (3), except where indicated.

Wastes were diluted with non-chorinated tap water (the chemical nature of which is given in Table VI) since it was too far to transport water from the unpolluted portion of the stream receiving the refinery wastes. A series of nine dilutions in decreasing concentrations was prepared as described by Anderson (2) with the exception that 1000 ml. were used instead of 100 ml. A tenth bottle containing the diluent served as a control. Wide mouthed jars were used and 500 ml. of the mixture was placed in each jar. Two fish were placed in each jar. In instances where the fish were three to four inches long only one was put in a jar. All experiments were run at room temperature which was in the neighborhood of 25°C. Although the wastes were devoid of oxygen the dissolved oxygen values in the diluted wastes were always above 4 ppm in any of the test concentrations. This eliminated any hope of correlating oxygen demand with the toxicity of the wastes.

Observations were made every twenty-four hours and experiments terminated at forty-eight hours since it was found that the results would stabilize at this time and did not change when tests were prolonged to ninety-six hours.

The concentration at which just 50 per cent of the test animals are able to survive for the specified period of exposure is known as the standard median toxicity threshold (M.T.T.). This was calculated by the graph method described by Doudoroff, *et al* (3).

For these experiments several kinds of fish were utilized: red shiner (*Notropis lutrensis*), golden shiner (*Notemigonus crysoleucas*), green sunfish (*Lepomis cyanellus*), fathead minnow (*Pimephales promelas*), and goldfish (*Carassius auratus*). Preliminary experiments utilizing the bluegill (*Lepomis macrochirus*), the redear sunfish, (*Lepomis microlophus*) and the largemouth bass (*Micropterus salmoides*) were made. These fish were selected for a number of reasons: (1) many of them inhabited the polluted and unpolluted parts of the stream into which the studied wastes were dumped; (2) they were readily available; (3) it was felt that these fish might possibly cover a range of tolerance in that the notropid minnow would represent a rather susceptible group while the goldfish would represent a more resistant group. The fish were secured from streams and ponds in the vicinity of the laboratory. They were not taken from the stream receiving the pollution since this source was too far away.

Toxicity of Wastes With Respect to the Time of Collection

The toxicity of the effluent was measured according to its effect on a standard organism which in this case was the red shiner, a minnow readily available and found in the stream receiving the studied wastes. The median toxicity thresholds of the red shiner through the months from January to May ranged from 5 to 21 per cent (Table II). In other words, fifty per cent of the fish could tolerate solutions containing 5 to 21 per cent wastes. This suggests a considerable variation in the toxicity of the wastes from time to time.

TABLE II

Variations in the Median Toxicity Thresholds of the Red Shiner and the Hydrogen Ion Concentration for Each Date of Collection, January to May, 1952.

Date of Collection	Date of Experiment	No. of Fish	M. T. T. Per Cent	pH at Time of Collection	pH at Time of Experiment
Jan. 29	Feb. 2	12x10	18.8	9.15	——
Feb. 9	Feb. 14	4x10	15.8	——	——
Mar. 5	Mar. 11	8x10	6.2	——	——
Mar. 23	Mar. 25	12x10	5.0	10.1	10.1
April 6	April 24	12x10	21.1	10.4	19.4
April 20	April 29	12x10	18.4	9.8	9.8
May 4	May 5	12x10	18.9	10.0	10.0

Toxicity of Wastes With Respect to pH

The *p*H of undiluted wastes at the time of experimentation did not seem to be correlated with the median toxicity thresholds of the red shiner (Table II). For instance, the *p*H of wastes on April 6, was 10.4 while the toxicity threshold was 21.1 per cent. With wastes with a similar *p*H of 10.1 on March 23, the threshold was 5.0 per cent. Even though the *p*H and the toxicity of the wastes dropped at the same time, there was no apparent correlation.

The *p*H was found to change with aeration (Table III). The *p*H of wastes exposed to the air at room temperature dropped from 10.3 to 9.7 in one day, and kept dropping for six more days until it reached 7.9 where it remained. When air was bubbled through wastes, the *p*H dropped from 10.3 to 8.4 in one day and remained there. The fall in *p*H to 7.9 in the unaerated sample and only to 8.4 in the aerated wastes was not explained, but it is possible that the active aeration facilitated the escape into the air of carbon dioxide or some other volatile substance that lowered the *p*H. Such a change in *p*H did not occur in stoppered bottles at 6° C. This change in *p*H indicated chemical changes were occurring in the wastes which meant that the wastes could also be changing in their ability to kill fish.

TABLE III

Changes in pH in Aerated and Non-aerated Refinery Wastes at Room Temperature.

Date 1951	*p*H of aerated wastes	*p*H of non-aerated wastes
April 16	10.3	10.3
April 16 (8 Hr. later)	9.8	10.1
April 17	8.4	9.7
April 18	8.4	8.7
April 19	8.4	8.2
April 20	8.4	8.0
April 21	8.4	8.0
April 22	8.4	7.9
April 23	8.4	7.9
April 24	8.4	7.9
April 28	8.4	7.9
April 29	8.4	7.9
April 30	8.4	7.9
May 1	8.4	7.9
May 2	8.4	7.9

Toxicity of Wastes With Respect to Temperature

The question was raised, does the toxicity of the effluents change? Wastes collected on March 6 were stored in a constant temperature room at 22°C., and on March 11 the median toxicity threshold was 5.8 per cent. A week later it was 14.8 per cent. This variation may mean either that wastes became less toxic with age, or that the fish used in the second experiment were less susceptible to the wastes than those used in the first.

The second possibility was considered unlikely since the same trend occurred in all subsequent experiments with newly collected wastes but with fish from the same aquarium; also when the wastes were kept in a cold room at 6°C., toxicity thresholds remained the same. This suggested that the susceptibility of the fish did not appreciably change, or that it changed in direct accordance with the toxicity of the wastes, which is unlikely. On this basis the toxicity of the wastes were said to decrease at room temperature.

As previously mentioned, the toxicity thresholds remained relatively the same when wastes were stored at 6°C. This was based on an experiment involving 480 red shiners for a period of twenty days (Table IV). Such an observation suggests that wastes probably become detoxified faster during the summer than the winter.

TABLE IV

Median Toxicity Thresholds for the Red Shiner of Wastes Collected on May 4th, and Stored at 6°C. in Glass Stoppered Bottles for Twenty Days.

Date of Experiment	Number of Fish	pH	M. T. T.
May 5	12x10	10.0	18.9
May 12	12x10	10.0	18.8
May 15	12x10	10.0	18.5
May 24	12x10	10.0	19.0

Toxicity of Wastes With Respect to Aeration

Aeration was found to have an effect on the median toxicity threshold and the following data, though meager, tend to bear this out. In each of the experiments in Table V, aerated wastes had a slightly lower toxicity, meaning that more wastes were required to kill fish and consequently that the wastes were less toxic.

These observations suggest a possible application of retaining the wastes in ponds and thus exposing them to the air and reducing their toxicity. Retaining wastes in ponds is nothing new and the refinery supplying the wastes used in this study employed this practice to achieve another end—that of reclaiming the oil that would accumulate on the surface. A field observation tends to corroborate the possibility of reduced toxicity in holding ponds. Toxicity thresholds of wastes (Table II), show values from 15.8 to 21.1 per cent except during the month of March when they dropped to 6.2 and 5.0 per cent which means that the wastes were more toxic. During the month of March, wastes were not retained in the pond but allowed to flow right on into the stream. Of course the possibility that stronger effluents came from the plant in March cannot be eliminated.

TABLE V

Toxicity of Wastes with Respect to Aeration.

Date of Collection	Date of Experimentation	Number of Fish	M. T. T. in Aerated Wastes	M. T. T. in Non-Aerated Wastes
March 5	March 11	4x10	6.7	5.8
March 5	March 15	4x10	15.8	11.9
March 5	March 18	4x10	16.6	14.8

The Effect of Different Diluents on the Median Toxicity Threshold

It was thought that different diluents might alter the median toxicity threshold of fish. The diluent in the experiments throughout this paper was unchlorinated tap water, and since it was relatively high in dissolved salts (Table VI) it is conceivable that such water might affect the killing power of the wastes. Simultaneous experiments where comparable data were sought on the toxicity threshold of the green sunfish, first in tap water, then in lake water, revealed that the diluents had little effect. The median toxicity threshold of these sunfish was 25.1 per cent when tap water was used, and 22.5 per cent when lake water was the diluent. For all practical purposes the values are similar and lie near the threshold (23.3 per cent) obtained from all experiments where green sunfish were used. Greater variation might be obtained with a greater variety of diluents.

TABLE VI

Chemical Composition of the Diluents. Tapwater—City of Norman, By A. C. Shead, December 28, 1939.[1]

Na, sodium ion	240 ppm	SO_4 sulfate ion	130.0 ppm
Cl, chloride ion	18.0 ppm	SiO_3 metasilicate ion	2.0 ppm
HCO_3, bicarbonate ion	425.0 ppm	AlO_3 aluminate ion	3.0 ppm
CO_3 carbonate ion	3.0 ppm	pH	8.3
Total dissolved solids	603 ppm		
Hardness	0		

Toxicity of Wastes to Various Species of Fish

Since the toxicity of the wastes was never the same and the experiments were made at different times, it was difficult to obtain median toxicity thresholds that were comparable from species to species. To do this, the red shiner was used as a standard and the median toxicity threshold for each species was expressed in relation to that of the standard on January 29. Thus no matter how the wastes varied, the median toxicity threshold for the red shiner was assumed to vary likewise. For example, if the median toxicity threshold dropped from 18.8 to 9.4 per cent between experiments then it would be necessary to double the threshold for other fish run at the time of the second experiment to provide a threshold comparable to that for the red shiner on January 29.

Of the five species of fish used, goldfish, green sunfish, red shiners, golden shiners, and fathead minnows, the median toxicity thresholds were respectively 33.1, 23.3, 18.8, 18.7, and 17.0 per cent (Table VII). Four of the five species were chosen because they were found commonly in the drainage system where the pollution occured. Goldfish were selected as a more tolerant species. Preliminary experiments on bluegill, redear, sunfish and largemouth bass seemed to indicate that these species may be more susceptible than any of the previously mentioned fish, but they were not found in the drainage system.

TABLE VII

The Median Toxicity Thresholds (M. T. T.) for Five Species of Fish. Preliminary Runs on Bluegill, Redear, Sunfish and Largemouth Black Bass Indicated that These Three Species May Be More Susceptible.

Species	M. T.T.	No fish	Size of fish
Goldfish	33.1	6x10	3.0-4.0
Green sunfish	23.3	24x10	1.5-2.5
Red shiner	18.8	12x10	1.5-2.5
Golden shiner	18.7	6x10	1.5-2.5
Fathead minnow	17.0	22x10	2.0-3.0

Field Evaluation of the Median Toxicity Threshold

In order to evaluate the median toxicity thresholds obtained in the laboratory, field studies were set up to obtain comparable data. To facilitate these studies, stations were laid out as indicated in Figure 1. Station 1 was the source of the pollution and Stations 2, 3, 4, and 5 were on AP Creek which flowed into the Little Washita. Station 6 was one and one-half miles downstream from the confluence of AP Creek and the Little

[1] Norman water comes from several wells and the composition changes according to wells in use. The above analyses are believed to be representative, but since the exact chemical composition (organic and inorganic) of the waste was unknown, the amount of impurities in the water used as a diluent is of relatively small importance.

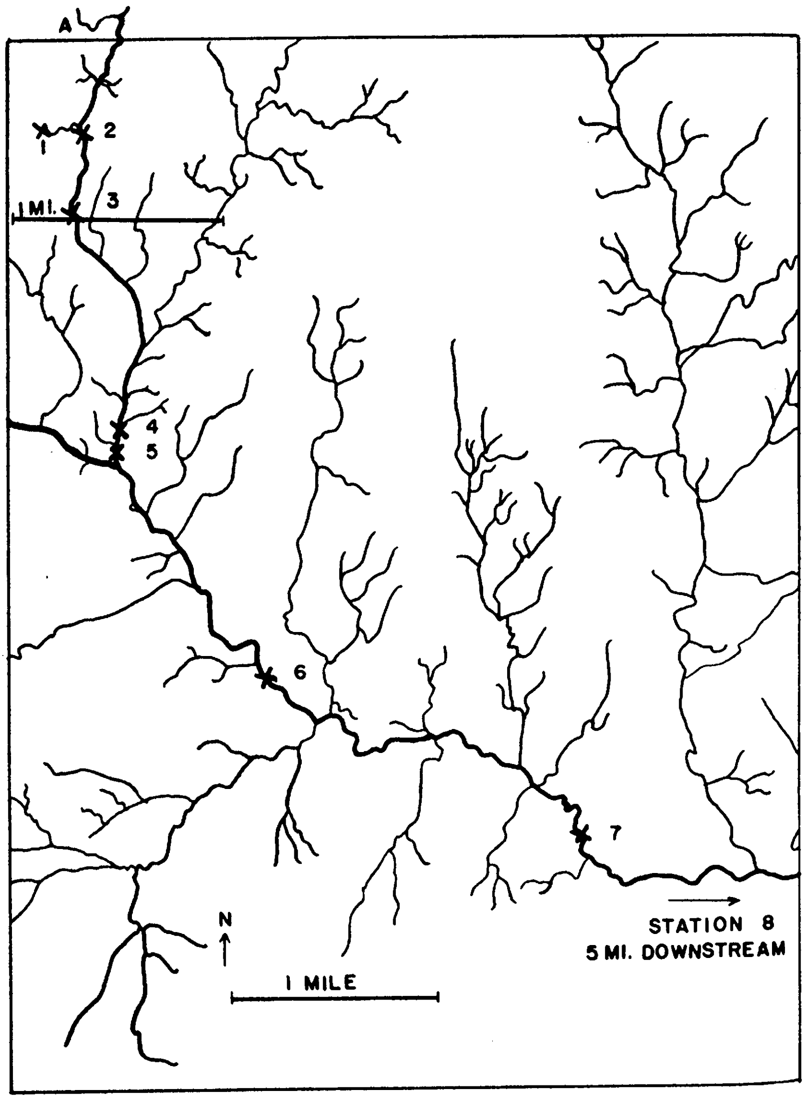

FIGURE 1. Sampling Stations Along AP Creek and the Little Washita River.

Washita. Station 7 was two miles below Station 6, and Station 8 five miles downstream from Station 7.

Field studies first involved finding the percentage volume wastes at each station, which was done by determining flow measurements with a pygmy current meter. At the point of discharge of the effluent, flow measurements were considered to be 100 per cent wastes. Then moving downstream, if the flow measurement was double that of the effluent, the percentage volume wastes was calculated to be fifty per cent and so on. In other words, the effluent discharge was calculated as a percentage of the total flow. These percentages are shown in Table VIII.

Unfortunately, there is another factor to consider. Effluents from the refinery enter AP Creek at point A (Figure 1). This is largely water from the cooling tower but it is flushed through old dried-up holding ponds and here picks up pollutants. Preliminary tests revealed these wastes to have a median toxicity threshold in the neighborhood of 13.8 per cent. In view of the fact that the discharge of this effluent is relatively low (around 30 gallons per minute) these wastes are calculated to make up 14 per cent of the volume of AP Creek just before the other refinery wastes enter at Station 2. Since the new wastes appeared to be 1.36 times as strong as the wastes entering at Station 2, let us assume that forty-one gallons per minute of wastes equal in toxicity are contributed to the main effluent so that the adjusted percentage volume of wastes from Stations 2 to 8 then would be 66.6, 59.0, 34.1, 12.2, 10.3, 8.1, and 4.5 respectively.

These percentage volume wastes were then correlated with field toxicity studies and the distribution of fish along the course of the polluted stream. Field toxicity studies were conducted, using five jars at each station into each of which were placed two red shiners. This was a check as to whether or not diluted wastes would support fish life. All fish died shortly after they were placed in the water collected at the first three stations while all fish lived in the tests made at the last three (Table VIII). Nine fish died at Station 4 where the percentage volume wastes was 34.1, while two fish died at Station 5 where the percentage volume wastes was 12.2. The median toxicity threshold, using these determinations is 21.6 per cent, slightly higher than the laboratory value of 18.8 per cent which was determined using the same wastes the day following the field studies. It should not be forgotten that higher toxicity thresholds mean lower toxicities and weaker wastes.

TABLE VIII

The Percentage Volume of Refinery Wastes for Each Station, as Calculated by Flow Measurements. The capacity for the water at each station to support fish life is roughly estimated on the basis of toxicity tests where two red shiners were placed for one week in a quart jar containing the respective wastes. Five jars, i. e., ten fish were used at each station.

Station	Percentage volume wastes	Adjusted percentage volume wastes	Number fish dead
1	100	100	10
2	54.9	66.6	10
3	49.0	59.0	10
4	17.6	34.1	9
5	10.1	12.2	2
6	9.3	10.3	0
7	6.7	8.1	0
8	3.7	4.5	0
M. T. T.	13.3	21.6	

This lower toxicity is not surprising. What we have been assuming is that the wastes maintain the same degree of toxicity as they pass downstream. This is not true. It has been shown that toxicity decreases with aeration, and the waters are certainly aerated as they pass downstream. In addition, the increased quantities of bluegreen algae seem to indicate utilization of some of the wastes as they pass downstream. The odor of the wastes indicates loss of volatile compounds which may or may not be toxic. Other compounds may be precipitated out, and so on. Thus one might expect wastes to become less toxic, regardless of dilution.

The median toxicity threshold for the red shiner in the laboratory (18.8 per cent) corresponded closely to that determined in the field (21.6 per cent) and the actual distribution of the fish during this particular determination indicated that Station 5 was near the critical region. At the time of field evaluation (May 4) no fish were seined at Station 4, plains killifish *Fundulus kansae*, were seined at Station 5, red shiners at Station 6, plains killifish at Station 7, and both shiners and killifish at Station 8. Monthly field studies of the flora and fauna along the stream throughout the year provided further evidence. No fish were ever found at Station 4, while red shiners, fathead minnows, mosquitofish, *Gambusia affinis*, and plains killifish occasionally occurred at Station 5. The presence of these few fish may be misleading since directly above this station is the confluence of an unpolluted tributary. The fish could easily have migrated from the unpolluted waters into those at Station 5, and might not have been there long enough to be affected by the wastes. The more detailed biological examination revealed that the numbers and kinds of organisms increased in a downstream direction to Station 8 where conditions generally conformed to the unpolluted parts of the stream and were considered healthful.

In view of the soundness of applying a factor of safety to the threshold value, the improvement of the biological conditions at Stations 6 and 7 over those at Station 5 seems to indicate that at least 6 to 10 per cent should be used in this particular instance. This means that the amount of wastes tolerated by the red shiner would be from 10 to 13 per cent, and if the red shiner factor could be applied to all species of fish, this refinery might therefore improve the conditions for fish downstream by limiting the discharge of their effluents to 10 to 13 per cent of the receiving waters.

It should be pointed out that all this is based upon only one species of fish, the red shiner, and for the red shiner on a particular day only. It will be remembered that thresholds for the five species of fish used varied from 17.0 to 33.1 per cent, that the strength of wastes during this study varied, and the range of toxicity thresholds for the red shiner was from 5.0 to 21.1 per cent.

However, with more careful consideration of this particular case, the threshold value for the red shiner appears to be a safe selection for the other species of fish involved. The fact that the wastes vary in toxicity from time to time does not appear serious in light of the limited data available. A check on the variations in toxicity in Table II suggests that the only real variation from a practical standpoint was during March when the wastes were allowed to run directly into the stream without being retained for a time.

Other types of refinery wastes not found in the effluent entering AP Creek seem considerably more toxic than the wastes from the API separators that have been used in these studies. Preliminary checks to determine approximately where the threshold values were for the red shiner indicated that acid sludge had to be diluted some three thousand times, and caustic emulsion some fourteen hundred times before fifty per cent of the shiners could live.

RECOMMENDATIONS

The above study is not extensive enough to provide figures that can be applied to the conditions pertaining to any refinery. However, the toxicity of the wastes can readily be checked and when the discharge of the receiving stream is known, calculations can be quickly made to determine whether or not it is practical to attempt to gear waste disposal to the stream discharge. If indications are favorable then further considerations would include a study of kinds of fish involved in the stream and their median toxicity thresholds with respect to the waste that is to be dumped into the stream.

Every practice to reduce the toxicity of the wastes should be made. Although further studies are needed in this respect, it appears now that two recommendations may be made. First, set up a series of detention pools that are long and shallow and which receive maximum wind exposure. This gives the wastes opportunity for aeration as well as exposure to the sun so that the waters can heat and chemical decomposition be promoted. Second, separate the wastes. Some types of wastes appear much more toxic than others. Some of the toxic ones may have small enough outputs so that they can be held in separate ponds.

Chemical treatment of wastes seem to be a valid approach to the disposal of toxic substances, but the actual treatment does not lie within the realm of a biologist. He can only test the effectiveness of such treatment. Satisfactory chemical handling of the refinery wastes is described by Fowler (5). Walker (11) outlines a treatment to be used for disposal of spent and contaminated soluble oil mixtures.

It appears that refinery wastes can be dumped into a stream with minimum damage to the fish life, provided that there is sufficient dilution and that the discharge of the wastes is geared to the discharge of the receiving waters. Whether this is practical or not depends on whether the stream is large enough to receive all the wastes that must be discharged.

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