

Job Report

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Project Name: Pollution Abatement in Regions M-4 through M-9.

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Investigation of the Existence of Oilfield Pollution in the Mission River

Abstract: The main source of pollution in the Mission River is oilfield waste. The fields are old resulting in excessive salt water disposal. The gravity separation of oil and water is inadequate and excessive amounts of oil are dumped into the river. This pollution has limited the river to rough fish having no sports or commercial fishing value and has helped deplete the oyster population in Mission Bay.

Objective: To determine the damage done to the river by the oilfield waste and its effect on aquatic life.

Procedure: Nine stations were established previously (Figure I) from the head of the river to its mouth. Bi-monthly samples were collected and a chemical analysis made to detect any pollution present and any physical or chemical change occurring from the preceding year.

The stations were selected to represent the changing conditions occurring from tidal fluctuations and tributary flow. The samples were collected during all weather conditions (wet and dry) to obtain a close simulation of the river in its annual cycle. Sampling gear and methods are explained in the chemical data.

Data was obtained from the Railroad Commission office on well location and waste disposal.

Findings: The Mission River is fed by the Medio and Blanco Creeks connecting approximately three miles above Refugio. The two creeks water shed covers an area of 643 square miles, and the drainage keeps the river flowing about 90% of the time. There are seven fields and twenty-nine companies producing oil in the Mission River drainage area. There are over 200 wells with Refugio field and Bonnieview field having 76% of the wells and producing 52% of the waste. Attempts to predict waste flow is impossible and even difficult to estimate. The longer a well pumps oil, the more salt water is produced; so the amount of salt water production will vary from one year to the next and possibly one day to the next. A working value of waste flow may be obtained by a ratio of proportions using the annual average salinity of the river, annual average flow of the river, and average salinity of the bleedwater. The annual average second foot flow of the river less the waste flow would relate to the brine as the average salinity of the field would relate to the average salinity of the river. Thus, the annual average flow of the river (Table 2) was 86.9 cubic feet per second per day. The annual average salinity of the river (Table 1) was 22.5 parts per thousand. The average salinity from ten wells was 69.9 parts per thousand. From this the flow of the waste is calculated to be 21.0 cubic feet per second or 323,158 barrels per day. This may be verified by checking the salinity that this volume of waste would give the river. If 21.0 cfs of water average 69.9 parts per thousand salinity were added to a river averaging 86.9 cfs water flow (including

waste discharge) the annual salinity average would be 23.4 parts per thousand. The observed annual average salinity was 22.5 o/oo so the precision of the results is 97%. If the waste flow is 21.0 cfs, the total dilution water or river flow necessary for freshwater fish to live in the Mission River is as follows:

$$\frac{100 - 48 \text{ hr median tolerance limit}}{48 \text{ hr TLM}} \times \text{effluent flow} = \text{Dilution Volume}$$

$$\frac{100 - 14.1}{14.1 \text{ (from 1959 report)}} \times 21.0 \text{ cfs} = 127.89 \text{ cfs}$$

The river has not obtained this flow in the last ten years (Table 2).

The upper eight miles of the river is composed of bleed water diluted with the natural drainage of Medio and Blanco Creeks up to the point where it reaches the head of the standing water or end of tidal influence (station 3). Below this point the waste is diluted heavily with Copano and Mission Bay water, and the salinity is reduced rapidly to the mouth. Since 70% of the river is affected by the tide, it wouldn't seem feasible to declare that the river would be important to fresh water fishes. However, at this point the river could be dammed off to retain some good freshwater fishing areas upstream.

Methods of Disposal

The wells in the Refugio area are conveniently located close enough to the river or a tributary of the river to dispose of bleedwater via a separator pit. The well pumps into a gun barrel which partially separates the oil from the high saline water. The oil is pumped into storage tanks and the water into a pit (of varying dimensions throughout the field). These pits have four inch bottom lines to drain the water by gravity flow and leave the oil. This water then flow to the river. The retention time in the pits is probably less than six hours but because of the pit size and the amount of water flow it is not adequate to retain the waste oil. Hence, the river contains oil 67% of the time (Table 1). A ten acre pond is necessary to successfully retain the oil from every 1000 barrels of waste disposed per day.

The Palestine oil field in east Texas had a similar problem. Bleedwater from the entire field was pumped into a 20 acre pond. The oil was skimmed, burned and the contents were drained into another 20 acre pond. Water from this pond is then drained through a series of baffles into a third 20 acre pond. From it water is discharged into a river at high water stage. This method has proven successful in keeping the oil at a minimum and reducing the salt content of the river by maximum dilution.

Problems of Waste Disposal

The major problem concerned in oil production is the disposal of the salt water or "bleed water". The oil developments in this area are located on salt domes, and consequently the production of salt water greatly exceeds the oil production. The reinjection method of disposing of the brine has been considered too expensive by many of the independent operators; so the nearest stream or body of water is used as the route of disposal. As mentioned previously, there are some attempts to separate the oil from the salt water, but in most cases it is futile. Also during a torrential rain the pits are subject to overflow and spill the skimmed oil into the river.

In a previous report a study was made on oyster mortality in Mission Bay caused by bleed water. There was some indication that the crude oil was damaging

the oyster reefs in Mission Bay. An experiment carried out by Gowanloch on crude oil damage to oysters in Louisiana proved the oysters that came in contact with crude oil showed an average mortality of 71% against 2% mortality in the control. The mortality rate of three trays of oysters in the Mission River (1959 report) indicated 100% mortality. However, a suspensoid analysis at the mouth was 6.0 grams/liter. Four grams/liter is considered to be harmful.

The previous survey also found twenty-five oyster reefs with 1" to 12" of silt covering them. The current survey located only 15 reefs with over 3" of silt cover and the others with over 8". The mouth of the river was also silted enough to make it impassable by boat. The rainfall the last three years (Table 4) has been higher causing a greater flow and a heavier silt load.

With the river carrying heavy concentrations of oil 67% of the time and a silt load in excess of the tolerance of oysters, 4 grams/liter (Figure V) Mission Bay could not be considered an ideal location for oyster production. However, the siltation is not the problem in Copano Bay that it is in Mission Bay; since the Mission Bay acts as a settling basin for the silt and retains it. The oil is carried through Mission Bay into Copano Bay where it disperses and eventually gets to the bottom resulting in imparting the taste or destroying the reef. Oil has been noticed coming out of Mission Bay and extending approximately three miles into Copano Bay.

Chemical Characteristics of Effluent and Receiving Waters

Chemical analysis was restricted to the components that would most alter the physical or chemical characteristics; pH, dissolved oxygen, total dissolved solids, and hydrocarbons. A mineral analysis (Table 3) indicates there is a reverse ion effect in calcium and magnesium in the bleedwater and bay water. There are indications that this may provide a block for some marine fishes since a toxicity study on a marine index showed a salinity tolerance well above the average salinity of the river, yet few marine fishes were found from station 1 to 6 (Flury). However, the alteration is not considered a serious pollution threat other than increasing the salinity higher than that tolerated by marine or freshwater organisms.

Hydrogen ion concentration: pH readings were taken with a model M Beckman meter with a glass and calomel electrode. The bleedwaters had a 90% range from 6.0 to 6.9 (Figure IV). This acidic waste is lower than the tolerance range of marine organisms (7.0-8.5) but could not be considered a lethal factor. Adequate buffering is provided by the waters and the pH ranges from 7.0 to 8.7 80% of the time.

Dissolved oxygen: The modified Winkler, Rideal-Stewart Method was preferred since significant errors occur in water containing appreciable quantities of nitrates, iron salts, or certain organic compounds. Samples were taken with a 2000 ml. Kemmerer sampler and drained without aeration into a 250 ml. B.O.D. bottle. The sample was fixed and determined within thirty minutes. Seventy-four per cent of the samples had a range from 5 to 7 mg/l (Figure III). None of the samples taken fell below the 4.0 mg/l level, well above the minimum survival limit of 3.0 mg/l.

Total Dissolved solids: Samples were collected in 250 ml. self sealing, magnesium citrate bottles at each station bi-monthly and at ten wells each month to determine the average salinity value of the river and the well brine. The annual average of 22.5 o/oo was compared to the toxicity limit studies on fresh-

water species from the previous annual survey. This value of 22.5 o/oo is well above the tolerance of freshwater species and is an indication that they could not survive under the present conditions. However, since the river is intermittently fed by rainfall and run off and there is a tidal influence extending approximately 17 miles up the river, the river has very little value as a natural habitat for fresh water species. During wet years (above 35.0 inches of rainfall per year) there is enough freshwater drainage to sufficiently dilute the high saline waters and not substantially increase the salinity of the bays, but during dry years the bay salinity is increased above 35.0 o/oo. This increases oyster mortality as well as diseases and predators. The high salinity ruins the area for shrimp nursery ground since small shrimp prefer brackish or fresh water.

Hydrocarbons: Oil analyses were determined by the method found in "Standard Methods" tenth edition. Concentrations ranging from less than 1.0 o/ooo to 600 o/ooo (Table 1) have occurred. Oil pools usually collect at the head of the standing waters, about 17 miles from the mouth, where the incoming tide and flow of the river meet. The oil spreads into a mono-molecular layer draining out the mouth and dispersing into Mission Bay, North winds or heavy river flow will occasionally carry the oil into Copano Bay. It then clings to clay particles settling to the bottom or is washed on the beach. Bio-assays conducted by agitating 25 ml. of crude oil with 10 liters of salt water (20 o/oo salinity) showed signs of clogging the gills of marine indicies with a soluble substance and eventually causing death. Experiments performed by Galstoff et al, 1935, shows that the rate of feeding of the oyster decreases in direct proportion to the concentration of oil. He also proved that the toxic action of oil is due to the organic constituents of the oil and not the mineral salts. From these experiments he concluded that oil held by the mud and deposited on the bottom continues for a long time to yield substances injurious to aquatic life and that the disappearing of visible oil does not mean the end of pollution.

Comments: The pollution problems on the Mission River are involved. The unsightly conditions have been encountered so long they have become accepted by the general public. Also, the revenue provided by the companies to the local people is enough to discourage local concern and interest. However, the damage by the wastes to the sports and commercial fisheries should be considered also. By having a better understanding of the problems in the river and lethal conditions of the waste, the conditions could be remedied. Since salt water injection has been considered economically unfeasible by the majority of the operators, it may be possible for the companies to construct community pits, 10 acres/1000 barrels of waste released per day and release the brine at high water stage.

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Table 1
Chemical Data on the Mission River

Station	Date	Salinity (o/oo)	Dissolved Oxygen (mg/l)	Oil (mg/l)	pH
A	September	.8	---	0.0	7.5
1	"	40.1	4.1	82.3	7.3
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	32.0	---	24.1	7.8
6	"	31.5	5.2	----	7.7
7	"	20.3	---	----	7.7
8	"	18.2	---	----	7.6
A	October	.8	5.5	0.0	7.3
1	"	35.1	4.8	102.0	6.9
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	24.4	---	----	---
6	"	22.4	6.1	95.0	7.1
7	"	18.9	---	----	7.3
8	"	16.1	---	----	7.6
A	November	.9	5.8	0.0	7.2
1	"	61.0	---	41.3	6.8
2	"	60.3	---	----	---
3	"	61.5	---	----	---
4	"	43.5	---	----	---
5	"	31.2	---	----	---
6	"	23.4	6.7	35.4	7.0
7	"	25.1	---	----	---
8	"	21.0	---	----	---

Table 1. - Continued

Station	Date	Salinity (o/oo)	Dissolved Oxygen (mg/l)	Oil (mg/l)	pH
A	December	.7	---	0.0	7.3
1	"	52.5	---	97.0	6.8
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	41.3	---	----	7.1
6	"	29.1	6.1	31.2	7.2
7	"	25.4	---	----	7.4
8	"	21.0	---	----	7.4
A	January	.8	5.5	0.0	7.1
1	"	52.0	4.7	35.0	6.9
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	25.1	---	----	7.5
6	"	21.0	6.1	19.3	7.5
7	"	19.2	---	----	8.1
8	"	18.0	---	----	8.2
A	February	.8	7.5	0.0	7.4
1	"	38.1	---	19.3	7.1
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	21.0	---	----	---
6	"	16.2	6.5	21.2	7.3
7	"	14.5	---	----	7.4
8	"	12.1	---	----	7.4
A	March	.9	---	0.0	7.1
1	"	53.0	---	87.0	7.0
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	38.1	---	600.0	8.1
6	"	21.2	---	38.0	7.8
7	"	20.4	---	----	7.3
8	"	19.1	---	----	7.3
A	April	.7	7.1	0.0	6.8
1	"	41.1	5.4	29.4	6.5
2	"	----	---	----	---
3	"	----	---	----	---
4	"	----	---	----	---
5	"	----	---	----	---
6	"	21.0	6.2	18.1	7.3
7	"	16.2	---	----	7.3
8	"	14.1	---	----	7.3

Table 1 - Continued

Station	Date	Salinity (o/oo)	Dissolved Oxygen (mg/l)	Oil (mg/l)	pH
A	May	.3	5.8	0.0	7.1
1	"	34.1	---	92.4	5.5
2	"	----	----	----	----
3	"	----	----	----	----
4	"	29.3	----	----	----
5	"	24.5	----	----	----
6	"	15.2	7.1	21.3	8.2
7	"	12.1	----	----	7.6
8	"	10.5	----	----	7.6
A	June	.8	6.1	0.0	7.1
1	"	25.4	6.3	34.0	6.7
2	"	----	----	----	----
3	"	----	----	----	----
4	"	----	----	----	----
5	"	9.2	----	----	7.6
6	"	8.5	----	0.0	7.5
7	"	10.1	----	----	7.6
8	"	11.1	----	----	7.6
A	July	.7	6.5	0.0	8.0
1	"	51.5	5.8	84.0	7.1
2	"	49.3	6.1	----	7.3
3	"	47.2	5.8	----	7.3
4	"	38.3	6.5	93.4	7.4
5	"	35.1	----	----	7.5
6	"	25.1	----	----	7.5
7	"	23.2	----	----	7.5
8	"	18.4	----	----	7.6
A	August	.8	8.1	0.0	6.9
1	"	29.3	----	87.0	6.3
2	"	28.5	----	----	6.8
3	"	27.6	----	----	6.8
4	"	23.4	----	----	7.1
5	"	20.5	----	----	7.3
6	"	14.2	6.8	53.4	7.3
7	"	10.1	----	----	7.5
8	"	10.1	----	----	7.5

Table 2

Mission River Discharge for Ten Year Period
in cubic feet per second

Year	Maximum discharge	Minimum discharge	Annual Average
1950	45.0	.8	4.23
1951	4380.0	1.0	38.20
1952	14400.0	2.3	98.50
1953	2540.0	2.8	41.50
1954	1670.0	2.4	19.50
1955	244.0	2.0	6.97
1956	525.0	1.6	7.99
1957	3470.0	1.2	105.00
1958	17600.0	2.0	146.00
1960	5760.0	3.6	86.90

Table 3

Chemical Analysis of Bleedwater, Mission River and Copano Bay
in parts per million

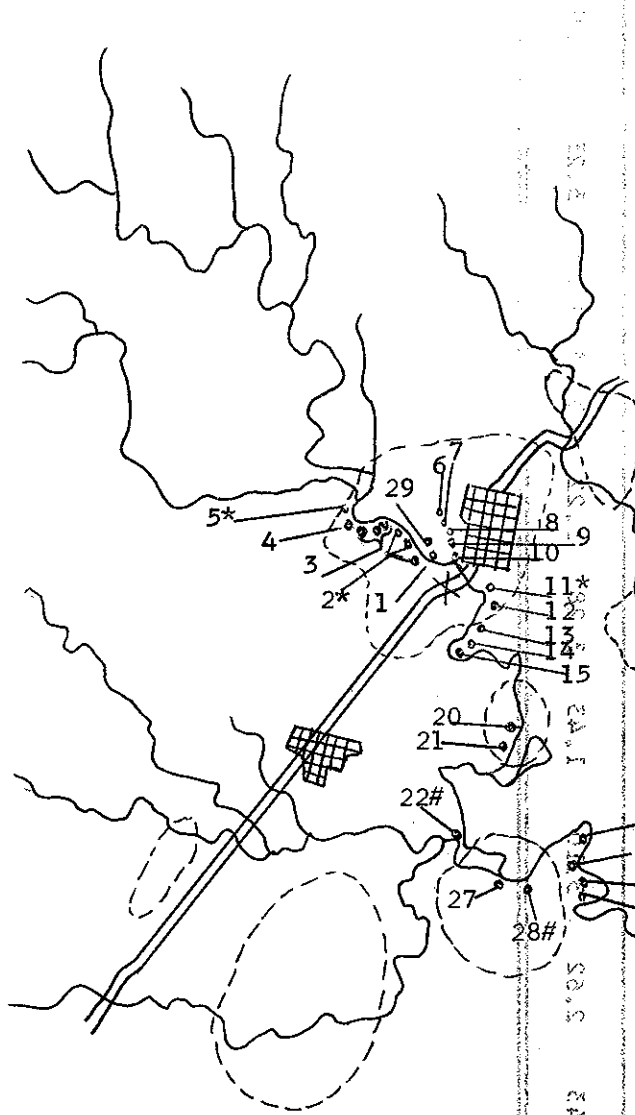
Ions	Copano	Mission River	Bleedwater
bicarbonate	71.0	171.0	387.0
sulfates	825.0	526.0	15.0
chlorides	5509.0	18213.0	42535.0
calcium	135.0	725.0	1039.0
magnesium	321.0	621.0	221.0
sodium	3305.0	10928.0	25453.0
silica	14.0	25.0	45.0
aluminum oxide	2.0	9.0	12.0
iron	1.0	91.0	185.0
Total solids	10183.0	31309.0	69892.0

Table 4

Rainfall in Refugio County for Seven Year Period
(in inches)

Year	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Total
1960	7.13	1.58	2.29	1.48	3.93	2.66	1.68	2.50	10.02	2.03	5.86	.95	42.11
1959	8.11	.76	2.59	.85	4.88	.38	3.19	4.38	5.66	1.90	8.44	5.58	46.72
1958	1.14	6.20	.62	8.63	7.63	1.19	.66	3.26	.57	.62	1.01	16.08	47.61
1957	2.30	1.01	1.61	.38	2.79	3.72	9.15	4.78	4.98	.0	.80	6.99	38.51
1956	1.06	.97	.56	5.14	.76	1.79	4.46	2.76	.16	.21	3.54	2.28	23.69
1955	4.31	1.10	.62	1.12	1.54	.05	.39	1.65	.83	2.14	2.42	9.06	25.23
1954	8.06	.76	1.74	.73	.18	.21	3.44	3.21	1.80	1.13	.56	2.18	24.00
Average	4.58	1.77	1.43	2.62	3.10	1.43	3.28	3.22	3.43	1.34	3.23	6.16	35.41

Figure I
Oil Lease Locations in the Mission River Watershed



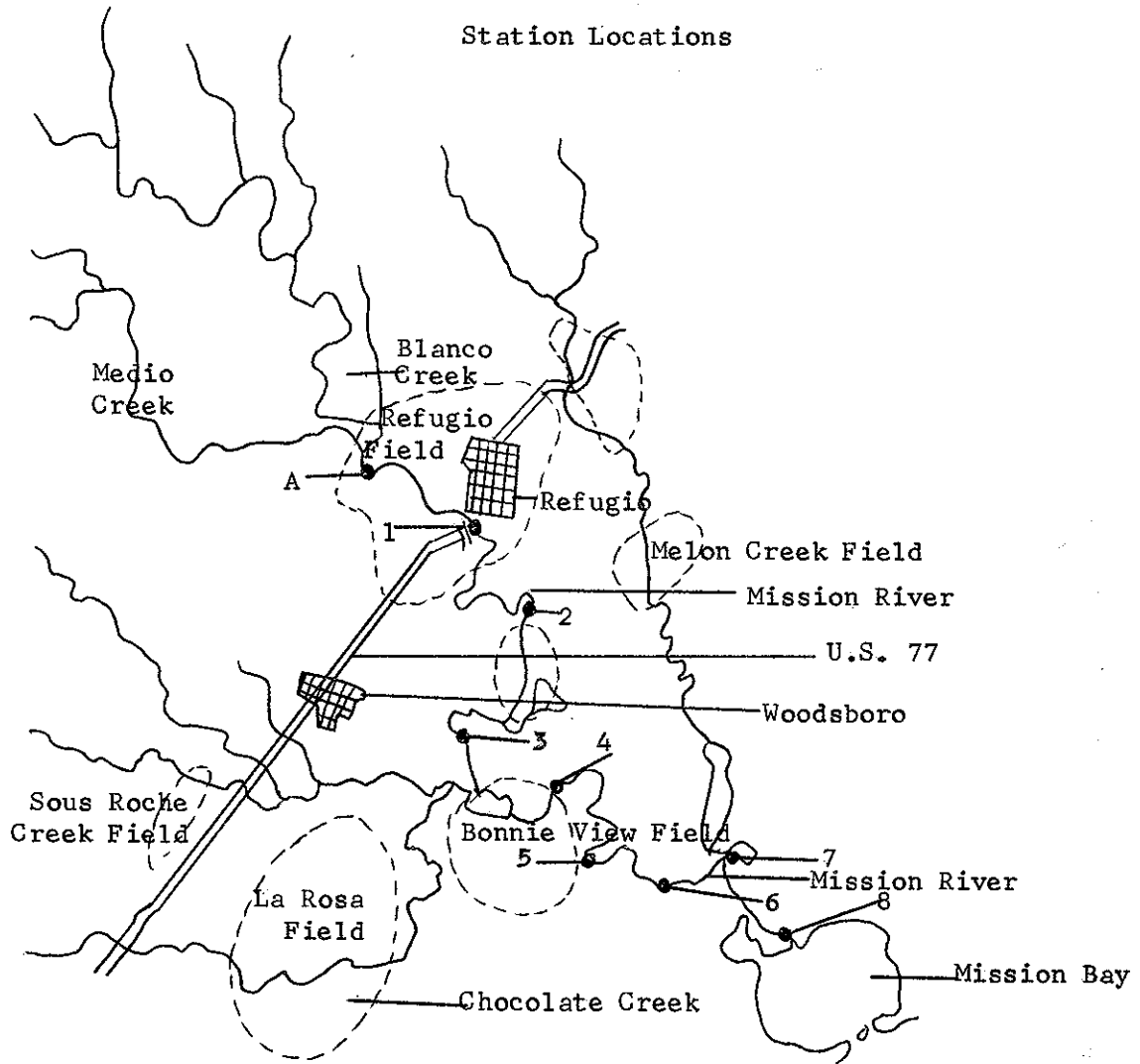
1. Wyrick & Hughs Corp.
- *2. Union Sulphur & Oil Corp.
3. Union Producing
4. C.E. Starrick
- *5. Atlantic Refining Co.
6. American Petrofina
7. Brown and Trall
8. National Drilling Corp.
9. E.Q. LaQuay
10. National Drilling Corp.
- *11. Humble Oil Corp.
12. Chicago Corp.
13. Republic Nat. Gas
14. C.E. Starrick
15. Sun Ray Mid-Continent
16. C.E. Starrick
17. Republic Gas Co.
18. Union Oil of Calif.
19. J.M.C. Drilling Co.
20. Southern Minerals
21. Southwestern Oil & Ref.
- #22. Kirkwood & Morgan
- #23. W.G. Seegar
24. Sun Ray Mid-Continent
- #25. George Taggart
- #26. United Producing
27. Phillips Petroleum Co.
- #28. P.R. Rutherford
29. Papalote Oil Corp.

* Largest producers of salt water.

Conventional pit.

Figure II

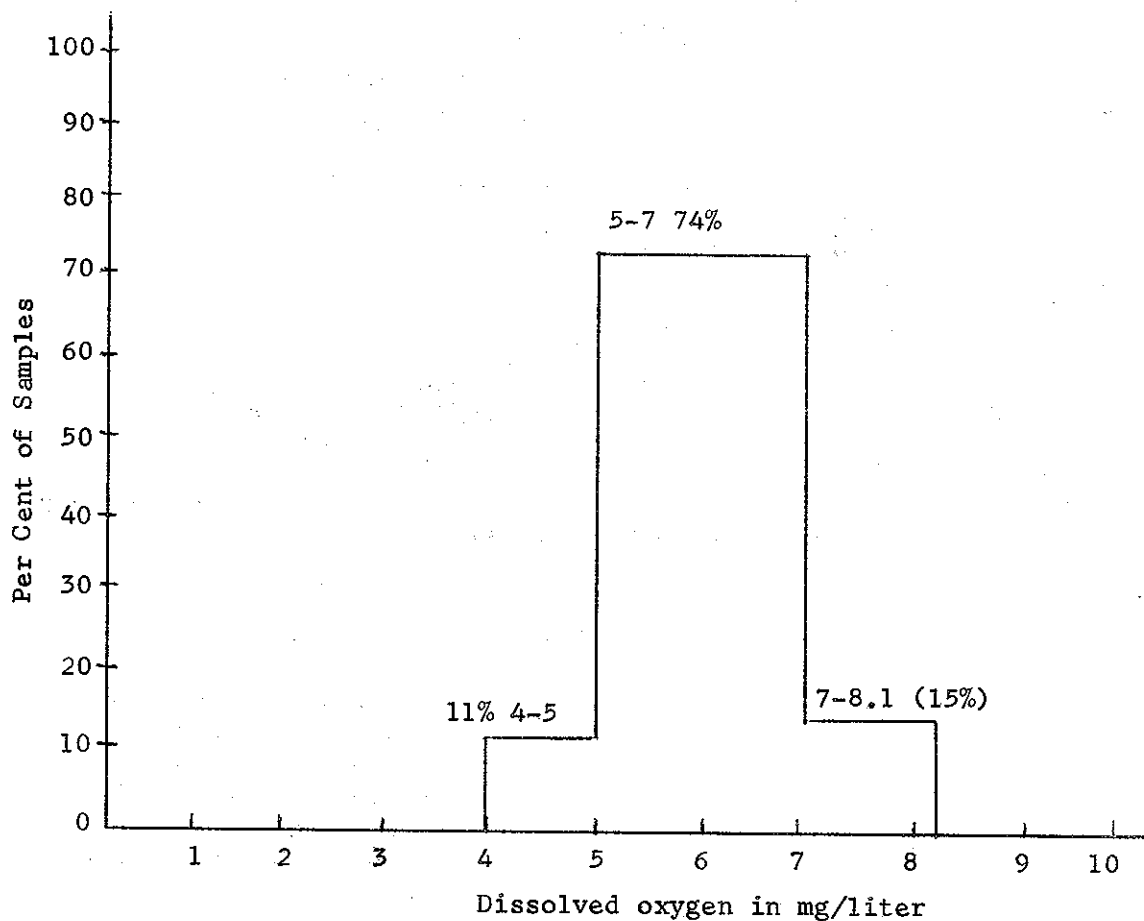
Station Locations



- Station A - head of River
- 1 - Highway 77 bridge
- 2 - Tributary intersection
- 3 - 45 minutes station
- 4 - 25 minutes station
- 5 - 8 minutes station
- 6 - Boat Landing
- 7 - Melon Creek intersection
- 8 - mouth

Figure III

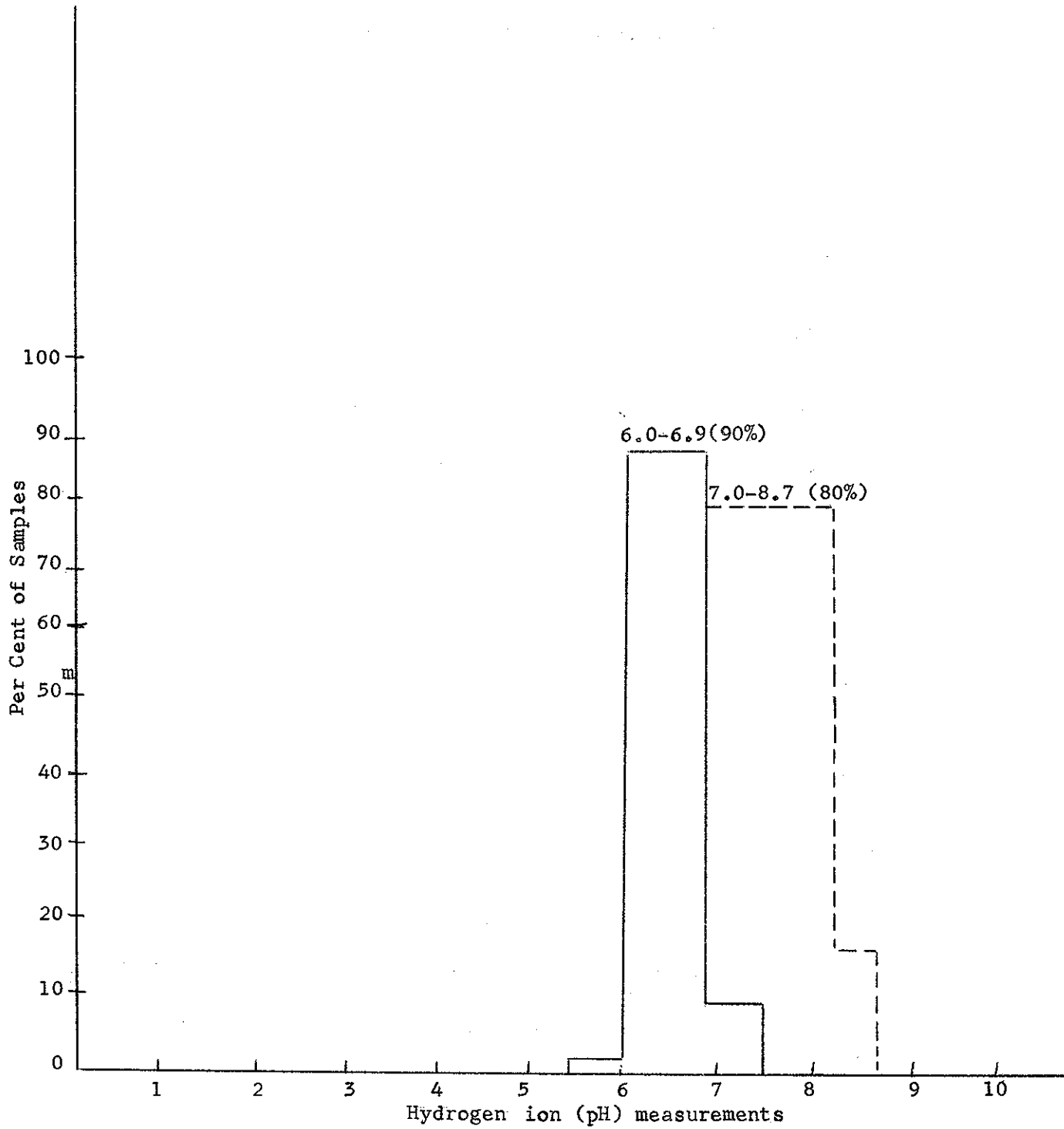
Dissolved Oxygen Measurements in the Mission River



27 samples

Figure IV

Hydrogen ion Measurements in the Mission River



— Bleedwater (35 samples)

- - - Mission River (61 samples)

Figure V

Suspensoids in the Mouth of Mission River

