

EFFECTS OF TREATMENT AND FLOW ON THE DEOXYGENATION RATE CONSTANT

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Abstract. The laboratory bench-scale experiments were conducted to investigate the effects of varying degrees of waste treatment and the flow conditions in the receiving waters on the deoxygenation rate constant (k), and ultimate biochemical oxygen demand (L), and the total O_2 utilisation of the receiving waters. Industrial wastewaters were collected from 10 major industrial plants located along the Houston Ship Channel in Texas. Two different degrees of treatment for industrial wastewaters were studied. Three different flow conditions studied were the high, the average and the low flow in the Houston Ship Channel. The k values increased for both further treatment and decreased flow in the reactor runs. The L values were higher for the average flow conditions than for the low flow conditions. The total O_2 utilization was found to increase with a decrease in the flow of the receiving waters.

1. Introduction

Dissolved oxygen (DO) is an important parameter in determining stream sanitation conditions. The Streeter and Phelps equation has been widely used for predicting the DO profile of a river subjected to organic pollution (Streeter and Phelps, 1925). Two major factors influencing the DO profile are: (1) deoxygenation by organic pollutants introduced into the river from point sources and non-point sources, and (2) reoxygenation by mass transfer of O_2 from the atmosphere. Although other factors such as benthic demand, algal respiration, and photosynthesis will also affect the DO sag curve in a river (Streeter and Phelps, 1925; Camp, 1963; Dobbins, 1964), in most cases the DO profile is largely controlled by the two factors cited above. The Streeter-Phelps equation may be expressed as

$$\frac{dD}{dt} = -k_1L + k_2D. \quad (1)$$

The sag equation resulting from the integration of Equation (1) is

$$D = \frac{k_1L_0}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t}) + D_0e^{-k_2t} \quad (2)$$

D and D_0 are the DO deficits at any time t and at time zero, respectively; k_1 and k_2 are the deoxygenation rate and the reaeration rate constant, respectively; L and L_0 are the ultimate carbonaceous biochemical oxygen demand (BOD) of river water at any time t and at time zero, respectively. In this paper the deoxygenation rate constant is represented by the symbol k .

The 1985 Zero Pollutant Discharge goal stipulates that no liquid effluents will be allowed to discharge to receiving waters. This will necessitate expensive waste treatment methods beyond the tertiary stage. It is doubtful whether all waste treatment plants in this country can meet this requirement by 1985, especially those plants in small municipalities of limited resources. In addition, the non-point source pollution such as agricultural and forest land runoff and strip-mine drainage will continue to contribute pollutants to receiving waters. The prediction of the DO profile in rivers and the determination of the deoxygenation rate constant will still be necessary in the foreseeable future.

The purpose of this paper is to determine the effects of treatment and flow on the deoxygenation rate constant k under the simulated laboratory conditions.

2. Method

Industrial wastewaters collected from ten major industrial plants located along the Houston Ship Channel were used in the deoxygenation rate study. Table I shows the locations of these plants and their symbols used in this paper. Several 12-gallon drums were used for the experiment. A total of six reactor runs was made under two different degrees of treatment and three different flow conditions. The six combinations were: (1) the less treatment, high flow conditions, (2) the more treatment, high flow condition, (3) the less treatment, average flow condition, (4) the more treatment, average flow condition, (5) the less treatment, low flow condition, and (6) the more treatment, low flow condition. Three flow conditions studied consisted of high

TABLE I
Ten industrial plant wastewaters

Industrial plants	Symbol	Location of plants mile station (mile)
Humble Oil -- Baytown	B	1
Enjay Chemical	BE	1
Diamond Alkali	A	11
Rohn & Hass	E	11
Schell Chemical	D	12
Ethyl Corporation	I	15
Southland Paper	C	15
Phillips Chemical	F	16
Champion Paper	G	18
Sinclair Refinery	H	18

flow, the average flow and the low flow condition. The flow data of the Houston Ship Channel of June 22, June 12 and August 19, 1968 were selected for the high, the average, and the low flow condition, respectively, in the laboratory study. It gives duration of reactor runs of 2 days, 34 days, and 76 days for the high, the average, and the low flow study, respectively. The durations are corresponding to the flow time of the ship channel water from Mile 24 to Mile 0 of the Houston Ship Channel for the respective flow condition. Two degrees of waste treatment are the less treatment and the more treatment condition. The less treatment condition refers to the waste treatment employed by the ten major industrial plants in 1968, which used either a primary treatment or inadequate secondary treatment system. The effluents for less treatment condition were obtained from the ten industrial plant's waste treatment facilities. The more treatment condition refers to the secondary treatment. The effluents for the more treatment condition were obtained from the laboratory bench-scale activated sludge reactors. Laboratory reactors were only set up for seven larger plants, H, G, C, I, D, E, and B to produce effluents used in the more treatment study. For wastes F, A, and BE only effluents of the less treatment condition were available from the industrial plants, and were used in both treatment conditions for the experiment runs.

Tables II, III, and IV list the amount of industrial waste and fresh water added to the 12-gallon drums at varying time intervals corresponding to the flow time of the Houston Ship Channel from the Turning Basin (Mile 24), to the discharge points of the fresh waters and industrial waste effluents. To simulate fresh water dilution in

TABLE II
Wastewater addition at high flow condition

Time (h)	Fresh water added (ml)	Industrial wastes added		Total amount of water in drum (ml)	Mile station* (mile)
		Industrial plant	ml		
0	2876	—	0	2876	24
11.15	3153	—	0	6029	22
16.35	2954	—	0	8893	20
18.15	501	—	0	9484	19
20.0	0	G	78.0	9562	18
	0	H	8.9	9571	
22.0	739	—	0	10 310	17
24.05	0	F	4.2	10 314	16
26.25	1539	I	36.9	11 890	15
	0	C	13.3	11 903	
32.3	0	D	14.7	11 918	12
34.55	0	E	3.6	11 922	11
	0	A	212.0	12 134	
36.95	2128	—	0	14 262	10
39.0	14 856	—	0	29 118	9
46.9	845	B	24.7	29 988	
	0	BE	12.3	30 000	
47.75	0	—	0	30 000	0

*Mile station along the Houston Ship Channel for the corresponding flow time.

TABLE III
Wastewater addition at average flow condition

Time (h)	Fresh water added (ml)	Industrial wastes added		Total amount of water in (ml)	Mile station (mile)
		Industrial plant	ml		
0	2195	—	0	2195	24
135.5	729	—	0	2924	22
235.0	361	—	0	3285	20
280.5	61	—	0	3346	19
330.0	0	G	718	4064	18
	0	H	81.9	4146	
372.2	49	—	—	4195	17
419.2	0	F	39	4234	16
468.6	204	I	340	4778	15
	0	C	122	4900	
605.1	0	D	136	5036	12
654.1	0	E	33	5069	11
	0	A	1956	7025	10
692.7	282	—	0	7307	10
729.7	0	—	0	7307	9
802.8	22 249	B	227	29 670	1
	0	BE	114	29 897	
810.75	103	—	0	30 000	0

TABLE IV
Wastewater addition at low flow condition

Time (h)	Fresh water added (ml)	Industrial wastes added		Total amount of water in (ml)	Mile station (mile)
		Industrial plant	ml		
0	6650	—	—	6650	24
14.25	4655	—	—	11 305	22
24.0	2382	—	—	13 687	20
29.9	731	G	4827	19 245	18
	0	H	550	19 795	
31.9	0	F	262	20 057	16
35.1	-944*	I	2282	21 395	15
	0	C	821	22 216	
42.3	722	—	—	22 938	13
45.0	0	D	912	23 850	12
47.9	-11 157*	E	221	12 914	11
	0	A	13 136	26 050	
53.3	1067	—	—	27 117	10
	0	—	—	27 117	9
73.9	592	B	1527	29 236	1
	0	BE	764	30 000	
75.9	0	—	—	30 000	0

*Fresh water removed from channel for plant uses.

the channel tap water was added to the drums. Fresh water and industrial wastewater additions to the drums were in proportion to the actual flows in the ship channel at the respective flow conditions. The contents of the drums were aerated to keep the solids in suspension and the DO uniformly distributed in the water. After the fresh water or wastewater additions, water samples were drawn from the drums for the O_2 uptake rate and total organic carbon (TOC) measurements. A similar set-up of open jar reactors for O_2 uptake curve development was reported by Peil and Gaudy (1975) and Gaudy (1975). The O_2 uptake rates were measured for a period of 10 to 14 days. DO and O_2 uptake rate measurements were made with a Precision Scientific Company's Galvanic Cell Oxygen Analyzer. For the O_2 uptake rate determination samples were measured for the DO contents at given time intervals. When the DO level dropped to 1 mg l^{-1} , the samples were re-aerated (Theriault, 1931; Heukelekian, 1947; Kittrell and Kochtitzky, 1947; Orford *et al.*, 1953; Elmore, 1955). The Beckman Carbonaceous Analyzer was used to determine the TOC content in the samples. The deoxygenation rate constant (k) and the ultimate carbonaceous biochemical oxygen demand (L) were determined by the Reed-Theriault method (Theriault, 1927).

3. Results

3.1. HIGH FLOW CONDITION

The k and L values of simulated channel waters at various mile stations for the high flow condition are plotted in Figure 1. Locations of industrial waste additions are also shown in the same graph. Flow times for the corresponding mile stations for all three flow conditions are listed in Table II, III, and IV. The k values for the more treatment condition are higher than those for the less treatment condition, while the L values show an opposite trend. Due to a high degree of dilution associated with the high flow condition, the channel waters at the start of the reactor runs exhibited a maximum L value for both treatment conditions. For the most polluted stretch in the Ship Channel, e.g., the stretch between Mile 18 and Mile 10, the L values for the less treatment condition increase gradually from 4 mg l^{-1} at mile 18 to a peak of 6 mg l^{-1} at Mile 10. The L values for the more treatment condition in the same stretch vary from 1 to 3 mg l^{-1} .

3.2. AVERAGE FLOW CONDITION

The k and L values for the average flow condition are shown in Figure 2. For the more treatment condition the k value is at a maximum at 0.21 day^{-1} , at Mile 18, decreases to 0.06 day^{-1} at Mile 9, and then increases to 0.18 day^{-1} at Mile 1. For the less treatment condition the k value is at a maximum of 0.2 day^{-1} at Mile 15, decreases to a minimum of 0.04 day^{-1} at Mile 11, and then increases to 0.08 day^{-1} at Mile 1. As expected, the L values for the less treatment condition are higher than

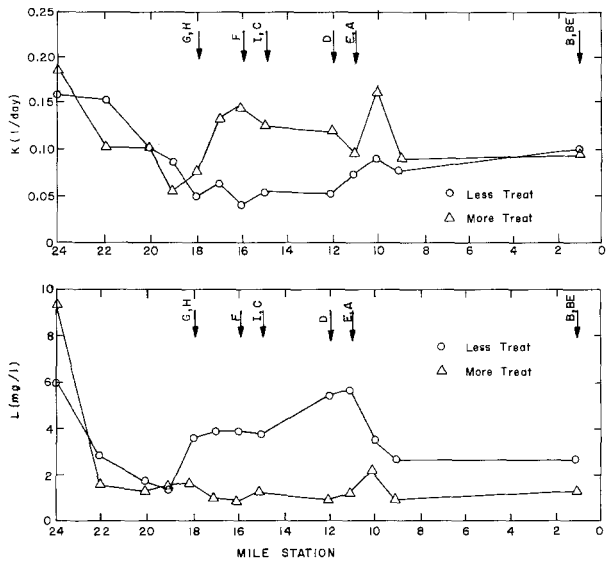


Fig. 1. Deoxygenation rate constant (k) and ultimateBOD(L) for the high flow condition.

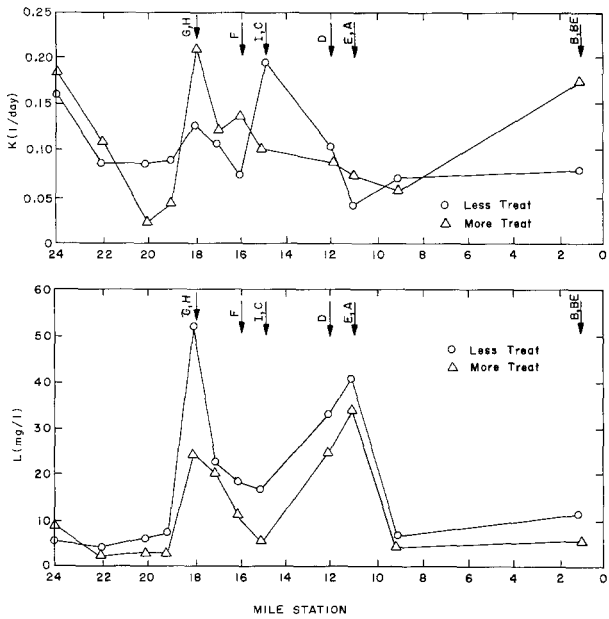


Fig. 2. Deoxygenation rate constant (k) and ultimate BOD (L) for the average flow condition.

those for the more treatment condition. In the most polluted stretch the two high L values are 52 mg l^{-1} and 41 mg l^{-1} at Mile 18 and 11, respectively, for the less treatment condition. For the more treatment condition the high L values are 24 and 35 mg l^{-1} at Mile 18 and 11, respectively.

3.3. LOW FLOW CONDITION

Figure 3 shows the k and L values for the low flow condition. The k values are higher for the low flow condition than those for the high and average flow conditions. the highest k value is 0.85 day^{-1} at Mile 16 and 0.51 day^{-1} at Mile 18 for the less treatment and the more treatment conditions, respectively. The L values for the less treatment condition are higher than those for the more treatment condition. In the most polluted stretch the L values are generally higher than 20 mg l^{-1} , and lower than 10 mg l^{-1} for the less treatment and the more treatment conditions, respectively.

3.4. TOTAL O_2 UTILIZATION

Figures 4 and 5 plot the total O_2 utilization versus mile points for the simulation runs. For high flow condition the total O_2 consumption is 1.1 and 0.9 mg l^{-1} for the less treatment and the more treatment condition, respectively. There is not much

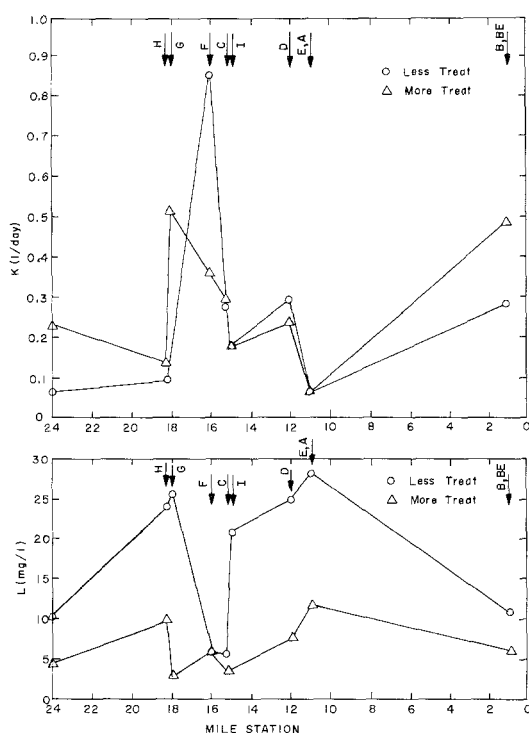


Fig. 3. Deoxygenation rate constant (k) and ultimate BOD (L) for the low flow condition.

difference between O_2 consumption values for the two treatment conditions. The only O_2 consumption was observed between Mile 24 and 22, while it was negligible for the stretch from Mile 22 to Mile 0 due to a high degree of fresh water dilution and a short time of passage from Mile 24 to Mile 0. For the average flow condition the total O_2 utilization value for less treatment condition is roughly twice the value for the more treatment condition. For both treatment conditions nearly 80% of the total O_2 demand is satisfied in the stretch between Mile 18 and Mile 9. Reactor runs for the low flow condition exhibit the highest O_2 consumption values among the three flow conditions studied, which is to be expected due to the low dilution and long flow time experienced in the reactor runs.

3.5. TOC

For the high flow and the average flow conditions, TOC values of the reactor contents were measured along with the O_2 utilization determinations. The TOC values at various mile points during the reactor runs are presented in Figure 6. For both flow conditions, the TOC values of channel waters for the less treatment condition are higher than those for the more treatment condition. For the average flow condition, there are two peaks of TOC values of 34 mg l^{-1} at Mile 18 and Mile

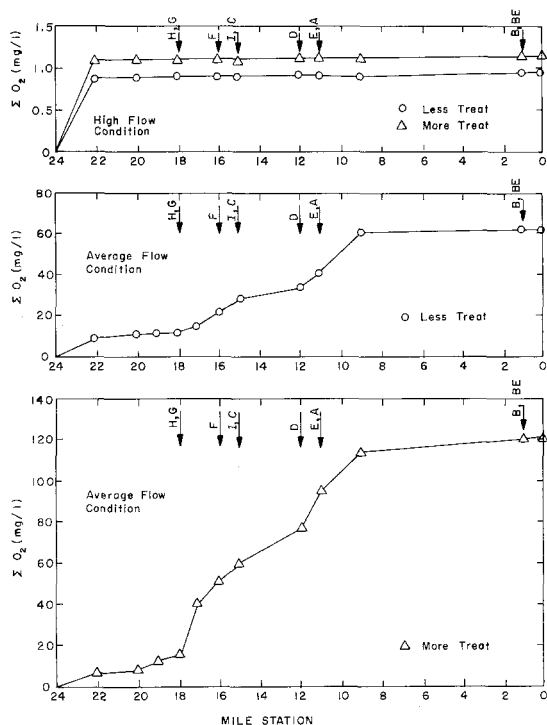


Fig. 4. Total oxygen utilization (ΣO_2) for the high and the average flow conditions.

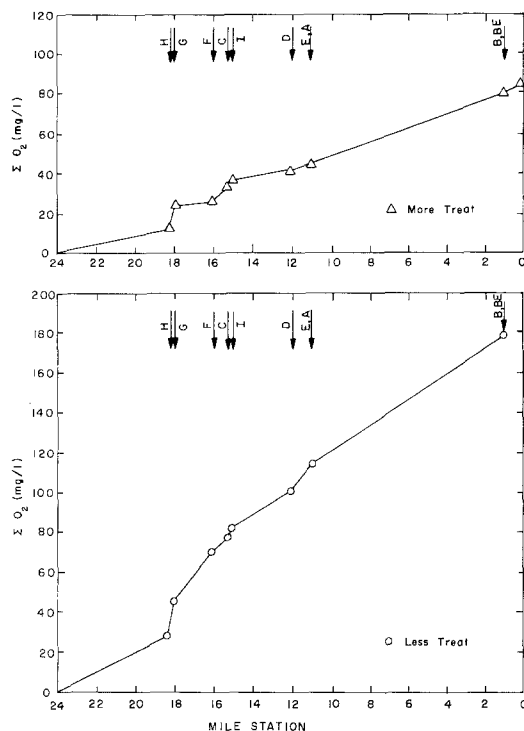


Fig. 5. Total oxygen utilization (ΣO_2) for the low flow condition.

12 for the less treatment condition, while for the more treatment condition a plateau of TOC values of 18 mg l^{-1} extends from Mile 18 to Mile 11. Downstream from Mile 9, the TOC contents of the Channel Waters for both flow conditions were reduced to 12 mg l^{-1} . For the high flow condition, the TOC contents for the less treatment condition are only slightly higher than those for the more treatment condition.

4. Discussion

Table V summarizes the average values of k and L and the total O_2 utilization values for all three flow conditions investigated. For all three flow conditions, the average k values for the more treatment condition were higher than those for the less treatment condition. This is due to the removal of toxic materials present in the wastewaters by further treatment. Consequently the treated wastewaters were rendered more amenable for further biological oxidation at a higher deoxygenation rate.

The flow condition also had a significant effect on the k values. The results indicated that with a higher flow condition, the k value was lower. The average L values for the average flow condition were higher than those for the low flow condition. Two main factors which affect the L values were: (1) the time of flow

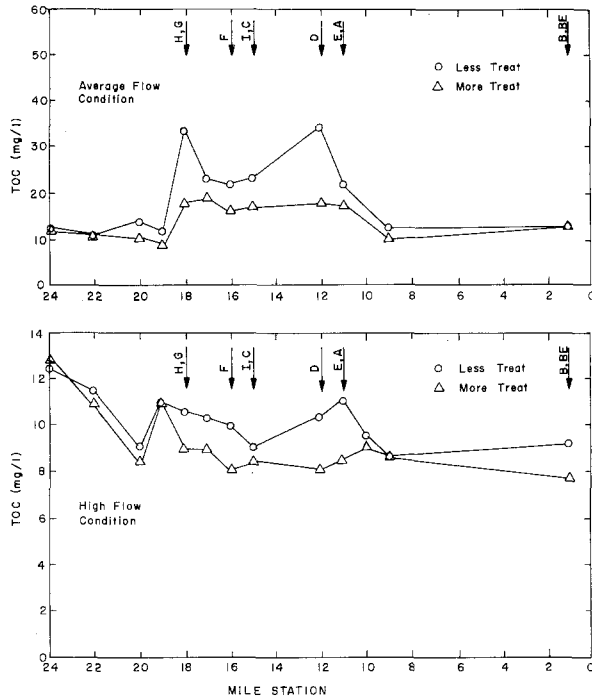


Fig. 6. Total organic carbon (TOC) versus mile stations for the high and the average flow conditions.

between two adjacent mile stations, and (2) the ratio of the wastewater loading to the total channel flow at the specific mile point. For the low flow condition the time of flow between two adjacent mile stations was much longer than that for the average flow condition so that a significant portion of the BOD in the channel water was removed by the time the channel water reached the downstream station. As a result the downstream mile station has better water quality for the low flow condition than that for the average flow condition. On the other hand, the organic pollutant concentrations for the low flow condition were higher than those

TABLE V
Deoxygenation rate constant, ultimate BOD and total oxygen utilization at three flow conditions

Flow condition	k (day ⁻¹)		L (mg l ⁻¹)		Total oxygen utilization (mg l ⁻¹)	
	Less treatment condition	More treatment condition	Less treatment condition	More treatment condition	Less treatment condition	More treatment condition
High flow	0.077	0.124	—	—	1.1	0.9
Average flow	0.113	0.142	25.8	16.4	119	61
Low flow	0.252	0.276	17.1	6.4	185	82

for the average flow condition which caused higher L values. If the effect of organic concentration in channel waters outweighed the effect of time of flow, the L values for the low flow condition would be higher than those for the average flow condition. But in the case of the flow conditions studied the effect of longer travel time on the L values was more important than that due to higher organic concentration. The result of this was a lower L value for the low flow condition than that for the average flow condition. The L values for the high flow condition were not listed, since the reactor runs for the high flow condition lasted only a very short period (less than 2 days).

The data of total O_2 utilization during the reactor runs gave the actual O_2 requirement for the channel stretch from Mile 24 to Mile 0. For all three flow conditions the total O_2 utilization values of the more treatment condition were less than those of the less treatment condition. For both treatment conditions, the lower the flow, the higher the total O_2 utilization value. The high values for the low flow condition were due to the high organic pollution concentration in the reactor and also the long flow time which allowed most of the organic matter to be stabilized.

4. Conclusion

The degrees of treatment and the flow conditions studied were found to have significant effects on the k , L and total O_2 utilization values of the simulated channel waters. Further treatment of industrial wastes increased the k values for all three flow conditions and k values also increased with a decrease in channel flow. For the low flow conditions the channel water exhibited the highest k values. The L values were higher for the average flow conditions than for the low flow conditions. The total O_2 consumption increased with a decrease in channel flow. For the low flow conditions the channel water had the highest values of total O_2 utilization.

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