THE SELF-PURIFICATION RATES OF POLLUTED STREAMS
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by R. Muñoz,[a] M. Martínez,[b] A. Rodríguez,[a] M. Pedraja,[a] R. Seda,[b] and C.M. Chan.[b]

WATER RESOURCES RESEARCH INSTITUTE
UNIVERSITY OF PUERTO RICO
MAYAGUEZ, PUERTO RICO

a) Department of Chemical Engineering, University of Puerto Rico.

b) Department of Biology, University of Puerto Rico.

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INTRODUCTION

Stream sanitation attains ever increasing importance as a country's population grows and as industrial and agricultural operations expand to improve nation's economies. The ability of a stream to recover from pollutional loads under natural forces determines not only the degree of treatment required for the wastes it receives but also the total permissible contamination reaching it from all sources. A quantitative knowledge of the natural assimilative capacity of streams is therefore essential to define the extent to which it can be used by man as a sink for wastes.

At the present time no definite answer can be given to the question of how long a time period is required for a river in a tropical country such as Puerto Rico to recover from a sudden pollutional load imposed on it. This knowledge would be of great value in determining location sites for new industries and for waste treatment plants, in regulating properly the volume of waste waters which could be safely discharged into receiving streams and in establishing guide lines for adequate legislation on pollution control of the island's streams. It would thus contribute to a better utilization of the available water resources.

This study was undertaken with the purpose of measuring quantitatively the self-purification rates of polluted natural waters in Puerto Rico, and to correlate these rates with the conditions prevailing in the streams. The biological indexes of pollution were also characterized during the course of this work, and appear discussed in another publication [18].

PERTINENT THEORY AND PREVIOUS WORK

If a clean, saturated stream receives a sudden organic pollutional load, deoxygenation occurs through the bacterial oxidation of the wastes, while at the same time oxygen from the atmosphere dissolves in the water tending to bring it back to saturation. The relative rates at which deoxygenation and reaeration proceed define the time which will be required to bring back the stream to its original clean condition through self-purification.

Laboratory and field tests have shown that the rate at which deoxygenation occurs through the bacterial oxidation of organic matter follows that of a first order reaction, being therefore dependent on the concentration of oxidizable material present [5,15], and that it is also dependent on temperature [11]. Reaeration, or the absorption of oxygen from the atmosphere, occurs at a rate which is proportional to the degree of unsaturation of the aborbing liquid, and once absorbed at the surface the oxygen spreads throughout the mass of water by molecular diffusion and by mechanical mixing of the layers of the fluid. The fundamental sag curve equation that defines the combined effects of deoxygenation and reaeration is [5]

$$\frac{dD}{dt} = k_1 L - k_2 D \qquad (1)$$

in which

$\frac{dD}{dt}$ = rate of change of the oxygen deficit (D)

$k_1 L$ = rate of increase in the oxygen deficit due to the removal of organic matter (k_1 = organic matter removal constant and L = concentration of organic matter)

$k_2 D$ = rate of decrease in the oxygen deficit due to reaeration (k_2 = reaeration constant)

Integration of equation (1) between the limits D_o at a reference point $x = o$ and $L = L_o$, and D at a point distant a time of flow t from the reference point yields

$$D = \frac{k_1 L_o}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \not+ D_o e^{-k_2 t} \qquad (2)$$

In general, when organic matter is removed by oxidation only, it may be assumed that the rate of deoxygenation is equal to the rate of B.O. D. removal.

The rates at which bacterial self-purification occur can be expressed for all practical purposes by a first order reaction [2], which corresponds to a condition of uniformity of the rate of purification [5].

The results of carefully controlled laboratory experiments have been found to be too refined to apply with any exactness to a gross subject as the bacterial oxidation of organic matter of all kinds in actual streams. The rate of oxidation of organic matter has been found to be influenced by the existing type of bacteriological population and its metabolic activity [2], and to depend on the composition of the wastes involved [7,10]. Organic matter may also be removed by settling and by volatilization. Reaeration rate, in turn, is also dependent on a number of factors which cannot be accounted for in generalized expressions. Among these are included the roughness, depth, surface velocity, and turbulence of the streams [13]; reaeration due to the presence of green plants [3,14]; temperature [17]; the presence of sewage [8]; and the shape of the area available for flow [15].

Equations to predict the rate of recovery of a stream have been presented on the basis of generalized parameters describing the physical characteristics of the streams. They provide results which are only approximate because of the underlying approximations and assumptions involved. Langbeim and Durum [9] correlate the reaeration coefficients obtained by various investigators in laboratory and river studies by the equation

$$k_2 = 3.3\ v/H^{1.33} \qquad (3)$$

where

k_2 = reaeration constant base e, in days $^{-1}$

v = stream velocity, ft/sec.

H = depth, ft.

From fluid mechanics considerations O' Connor [4] suggests the following equation to define stream aeration:

$$k_2 = \frac{(D_L v)^{\frac{1}{2}}}{H^{3/2}} \qquad (4)$$

in which D_L = diffusivity of oxygen in water, ft^2/hr, and Phelps [13] uses the empirical formula

$$k_2 = \frac{c\,v^n}{H^2} \qquad (5)$$

in which the values of the constant c and n depend primarily upon physical stream conditions which influence turbulence. Fair [5] proposes the use of a self-purification factor defined by the proportion between the reaeration and the deoxygenation constants.

Stream microbiology has been extensively studied in many non-tropical countries. Phelps reviews these works and discussed those organisms which are characteristic of polluted waters. More recent studies have been specifying biological indicators of contamination and pollution in streams [1, 6, 16].

PROCEDURES & METHODOLOGY

The selection of the rivers considered in this study was based on the criteria that they represented as wide a variety as possible of types of contamination while also including only streams of approximately constant flow, with no tributaries reaching the river sections being examined for recovery. Very few river sections in Puerto Rico met these criteria, since not only is the island criss-crossed by small creeks that join the larger rivers, but also the streams are very short in length and are usually bordered by heavily populated zones and industrial sites. Out of six sections of streams finally chosen, three represented sewage polluted waters, two were contaminated with wastes from the cane sugar industry, while the last one received wastes from both a cane sugar mill and from a paper mill which produced paper from sugar cane bagasse via its alkaline chemical digestion. As shown in Table I, in each river, the first sampling station was chosen upstream from the point at which the pollutional load entered it, while two other stations were located downstream from this point of contamination and as far apart as possible from each other. Samples for chemical and bacteriologic tests were gathered one a day at each station during fifteen consecutive days, and physical measurements were simultaneously made. These included the daily measuring of depth, cross-sectional area of flow, and average superficial velocities. Distances were determined by direct measurements in topographic maps.

Collections for biota studies included bottom material, plankton, aquatic plants, and semi-aquatics. Most of the identifications were made in the laboratory, while the organisms were still alive, using a light microscope.

All chemical, physical, and bacteriologic characteristics of the samples collected were determined in accordance with the procedures specified in "Standard Methods for the Examination of Water and Wastewaters", Twelfth Edition.

DISCUSSION OF RESULTS

Table 2 summarizes the data gathered in this study. The chemical and bacteriologic results shown represent 15-day averages for each station, whereas the data corresponding to stream velocity, depth, and flow cross-sectional area represent the average values determined for all stations in each stream during the 15-day testing period.

The data corresponding to the last two rivers (Grande de Añasco and Grande de Arecibo) show that anaerobic conditions were reached in them. The breakdown of oxygen resources arising from the high initial demand of the wastes introduced in them produced septic conditions in the zones under study. The proximity of the sea precluded the possibility of moving the test zones further downstream from the sources of pollution. Since anaerobic decomposition of organic wastes utilizes the oxygen of the organic matter itself, the mechanism and equations previously presented for self-purification of the waters no longer hold. Accordingly, the data gathered in these two rivers could not be used for evaluation of the reaction constants.

Organic matter removal was assumed to occur solely through aerobic bacterial oxidation in each of the other four streams, as the shallowness of their beds and the swiftness and turbulency of their currents made sedimentation very unlikely. The organic matter removal constants thus became equal to the B.O.D. reaction constants, and were calculated in the zones included between stations number 2 and 3 in each river by using the equation arising from the assumption of a first order oxidative reaction:

$$\frac{L}{L_o} = e^{-k_1 t} \tag{6}$$

The values thus obtained were substituted in equation 2 to obtain the corresponding reaeration constants. Table 3 summarizes the results obtained.

An analysis of the resulting data shows that the reaction rate constants are best expressed as functions of the hydraulic properties of the streams through equations of the type $k_2 = a\, v^b/H^c$, where a, b, and c are constants. The reaeration constants at 20°C were correlated with an average deviation of 33% by the following version of O'Connor's equation:

$$k_2 = 0.0163 \frac{D_L \; v}{H^3} \qquad (7)$$

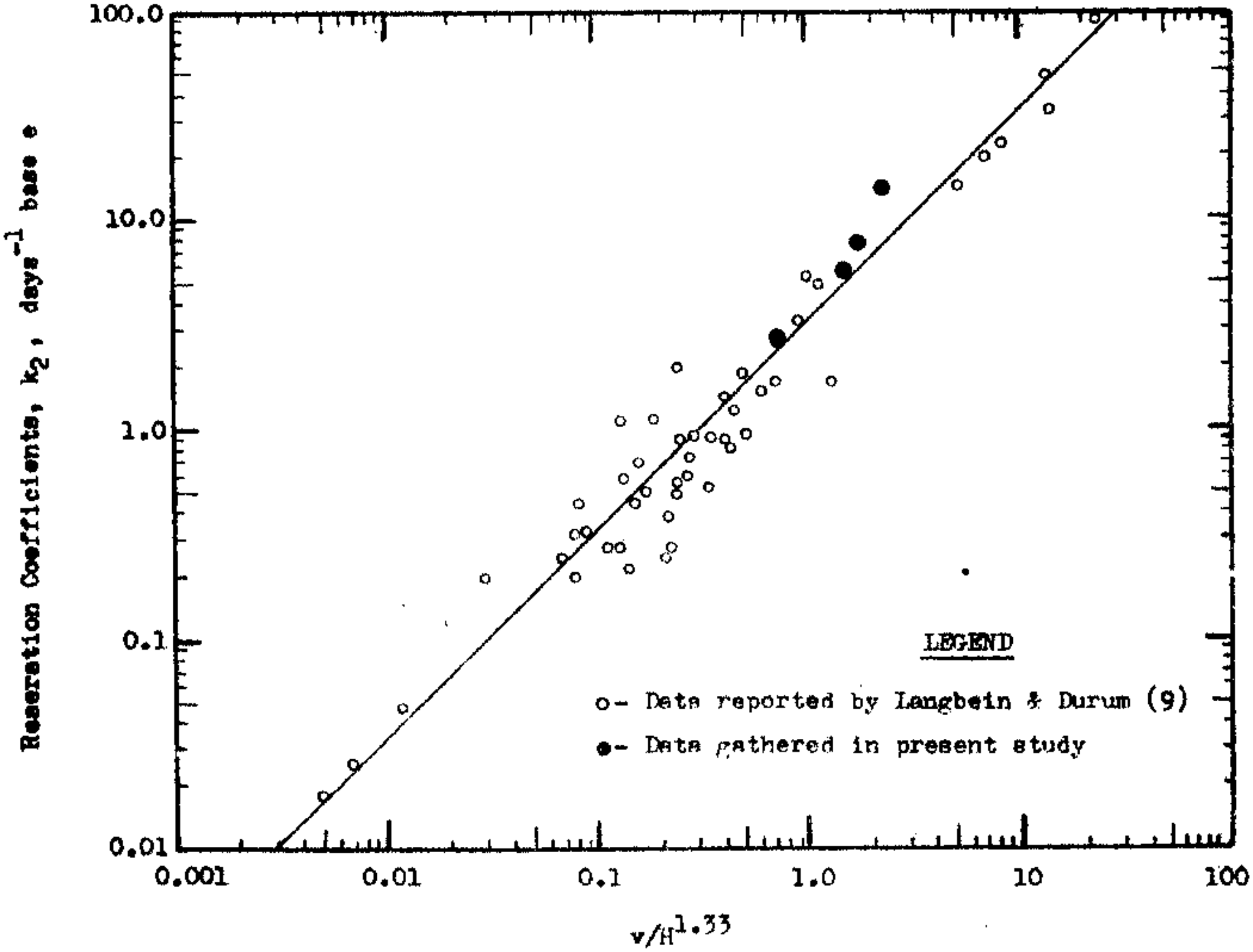

FIGURE 1 - CORRELATION OF REAERATION COEFFICIENTS WITH HYDRAULIC PARAMETERS

They could also be expressed by equation (3) with only 40% mean deviation, this being of the same order of magnitude as the average deviation of the data included in Langbeim and Durum's original correlation. The values of the reaeration constants determined in this study thus agree with those observed under nontropical conditions for streams of equivalent hydraulic parameters. Figure I illustrates this consistency.

The equation

$$k_1 = 0.0006 \frac{(D_L \quad v)^{3/2}}{H^{9/2}} \qquad (8)$$

in which the units of k_1 are days $^{-1}$ base e at 20°C, correlates with negligible deviation the B.O.D. reaction constants obtained for all the aerobic streams studied with the exception of the Maricao River. These observed B.O.D. reaction rates are also of the same order of magnitude as those reported elsewhere for non-tropical environments. As examples, Fair (Ref. 5 , page 525) cites k_1 ranges from 0.16 to 0.70 days $^{-1}$, while O'Connor (Ref. 4, page 129) reports values as high as 3.0 days $^{-1}$ at 12°C for a shallow, rocky bed stream, which would be hydraulically similar to those considered in this study. The abnormally high value for k_1 of 10.0 days $^{-1}$ at 20°C observed for the Guanajibo River may have been caused by green algae in the bed of the stream. As expected from the fact that anaerobic oxidation proceeds at a slower rate than that at which the aerobic process occurs, the lower B.O.D. rate constants among those observed corresponded to the Grande de Añasco and Grande de Arecibo rivers if calculated assuming that equation (6) applied to their cases. This is not vigorously true, as oxygen concentrations must be larger than about 4 mg./l. for the first-order relationship to hold.

The observed coliform die-off rates calculated on the basis of the applicability of Chick's first order law range from 0.8 to 2.9 days $^{-1}$ base e at 20°C, thus agreeing in order of magnitude with those reported for non-tropical streams under assumed uniformity of removal [5] , and with the 0.5 to 3.5 ranges of coefficients cited by O'Connor [12] for fresh-water streams. With the exception of the coefficient obtained for the Guajataca River, the coliform die-off rates determined for the other three aerobic streams could be correlated with negligible deviation by the equation.

$$k_{coliform} = 0.00126 {\frac{(D_L\ v)^{1/2}}{H^{3/2}}}^{2.3} \qquad (9)$$

The rate at which coliform bacteria removal occurred in waters polluted with cane sugar wastes was much lower than the removal rates observed in the streams polluted with sewage. The coliform density rose sharply with time in the two streams in which anaerobic conditions prevailed, even though the concentration of chlorides in them was higher than those in the four streams. In both of them cane sugar wastes were also present.

The observed self-purification factors, calculated as per Fair's definition, fall within the range of those considered to be characteristic of swift streams by other investigators [5] .

CONCLUSIONS

Polluted fresh-water streams in Puerto Rico undergo natural purification at rates equivalent to those which have been observed elsewhere under non-tropical environments.

Correlations previously established to relate the reoxygenation rates of polluted streams with their hydraulic properties are found to hold equally well for Puerto Rico's rivers. Expressions for the rate of removal of organic matter and of coliform organisms in terms of hydraulic parameters are presented. Reaction rates appear to be unaffected by the composition of the wastes involved, although the rate of coliform bacteria removal is slowed down by the presence of cane sugar wastes.

The ability of polluted rivers in Puerto Rico to recover deficiencies of oxygen and to assimilate wastes as they flow downstream, may be predicted from a knowledge of their depths and velocities by using the correlations developed in this study.

TABLE I

SAMPLING STATIONS AND TYPES OF WASTES IN RIVERS INCLUDED IN REAERATION STUDY

Name of River	Type and Origin of Contamination	SELECTION INCLUDED IN STUDY		
		Station Number	Distance from Source of Contamination	Flow Pattern
Rosario River	Sewage from Maricao's municipal treatment plant (septic tank)	1	1,200 feet upstream	Swift, shallow, riffles
		2	2,500 feet downstream	
		3	73,750 feet downstream	
Guajataca River	Sewage from Lare's municipal treatment plant (trickline filter)	1	300 feet upstream	Swift, shallow, riffles
		2	500 feet downstream	
		3	33,900 feet downstream	
Culebrinas River	Cane sugar wastes from Plata sugar mill	1	500 feet upstream	Swift, shallow, riffles
		2	6,750 feet downstream	
		3	52,650 feet downstream	
Guanajibo River	Sewage from San Germán's municipal treatment plant (septic tank)	1	1,000 feet upstream	Swift, shallow, riffles
		2	500 feet downstream	
		3	7,900 feet downstream	
Grande de Añasco River	Sugar cane wastes from Igualdad sugar mill	1	500 feet upstream	Sluggish, pools
		2	600 feet downstream	
		3	9,000 feet downstream	
Grande de Arecibo River	Combined wastes from Cambalache sugar mill and from Int'l. Paper Co., paper mill	1	800 feet upstream	Sluggish, pools
		2	200 feet downstream	
		3	5,000 feet downstream	

TABLE 2

SUMMARY OF EXPERIMENTAL DATA

River	Hydraulic Data (15-day averages for the two stations involved)				Analytical Results (15-day averages for each station)										
	Depth ft.	Speed ft./sec.	Flow area ft.^{2}	Rate M.G.D.	Station	Temp. °C	D.O. p.p.m.	B.O.D. p.p.m.	Coliform M.P.N./ 100 ml.	pH	Color	Turbidity	Chlorides p.p.m.	Alkalinity p.p.m. $CaCO_3$
Rosario	0.75	1.063	7.5	5.15	1	24.2	7.9	0.7	3,500	7.6	7	5	17.5	114
					2	25.5	7.0	3.2	35,000	6.7	9	10	21.8	125
					3	25.5	8.0	0.8	9,400	7.5	7	5	21.2	119
Guajataca	1.05	0.74	20.5	9.8	1	23.0	7.7	1.0	14,800	7.3	10	34	12	98
					2	25.6	4.8	5.1	110,000	6.9	15	42	15	110
					3	25.4	6.8	3.1	15,000	7.1	15	48	13	128
Culebrinas	0.93	1.351	20.0	17.46	1	26.4	8.2	1.1	24,000	7.2	20	12	13	106
					2	28.1	5.8	8.5	17,500	6.7	22	18	15	113
					3	28.1	6.8	1.3	11,000	7.1	20	14	15	107
Guanajibo	0.72	1.345	9.28	8.1	1	28.1	7.6	1.0	3,500	7.4	5	10	18	237
					2	29.0	5.8	4.1	92,000	7.0	29	45	20	243
					3	28.0	6.2	1.6	7,600	6.9	30	70	20	241
Grande de Añasco	5.2	0.57	96.7	35.6	1	28.7	7.9	1.5	1,300	8.1	6	15	10	116
					2	32.0	2.7	102.3	54,000	7.4	13	20	26	130
					3	31.0	0.0	91.5	350,000	6.5	24	30	115	140
Grande de Arecibo	3.0	0.50	90.6	29.3	1	25.8	8.5	1.5	2,200	7.9	5	10	15	141
					2	28.0	1.4	130.0	240,000	6.9	15	95	64	175
					3	29.0	0.0	121.5	1,300,000	6.7	20	115	402	211

TABLE 3

SUMMARY OF RESULTS

River	Time of Flow, Station 2 to Station 3, days	Dissolved oxygen deficit, p.p.m.		Rate Constants, days $^{-1}$ base e						Self-purification constant at 20°C, $f = k_2/k_1$
				At temperature of river			At 20° C			
		Sta. 2	Sta. 3	Reaeration, k_2	B.O.D. reaction, k_1	Coliform die-off, k_c	Reaeration, k_2	E.O.D. reaction k_1	Coliform die-off, k_c	
Rosario	0.775	1.3	0.3	6.7	1.79	1.7	5.2	1.39	1.3	3.74
Guajataca	0.522	3.5	1.5	3.1	0.95	3.8	2.4	0.74	2.9	3.24
Culebrinas	0.393	2.1	1.1	9.9	4.78	1.2	6.8	3.3	0.83	2.06
Guanajibo	0.0635	2.0	1.7	22.2	14.8	3.0	15.0	10.0	2.0	1.5
Grande de Añasco	0.170	4.7		Anaerobic conditions were reached at Station No. 3 in each of these two streams.						
Grande de Arecibo	0.111	6.4								

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