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THE EFFECT OF CHLORINATION ON BIOCHEMICAL OXYGEN DEMAND

Reduction of BOD is a commonly used measure of wastewater treatment effectiveness. Traditionally chlorine has been applied at wastewater treatment plants for odor control, reduction of oxygen demand and disinfection. This study reports the effect of the addition of chlorine at 5 different concentrations, before and after the breakpoint, on the BOD level in the wastewaters treated. In general, chlorination up to the breakpoint showed a tendency to increase the BOD.

1. INTRODUCTION

The biochemical oxygen demand (BOD) test has been a fundamental measurement in wastewater treatment for more than 50 years. This test measures the oxygen consumption by microorganisms during aerobic decomposition of organic pollutants. Waste treatment plant effectiveness is measured by the reduction of BOD through the treatment processes. Although national standards for sewage effluent are 30 mg/dm^3 of BOD, standards may be as low as 5 mg/dm^3 for some discharges [1].

Traditionally chlorine has been used at wastewater treatment plants for odor control, reduction of oxygen demand and disinfection. Chlorine has also been used for control of activated sludge bulking, as well as for problems encountered with trickling filters, sludge thickening, digester supernatant treatment and digester gas scrubbing. A considerable amount of research on the reduction of BOD by chlorine was done in the late 1920s and early 1930s. Reduction in 5-day BOD (BOD_5) levels by chlorination was reported to approach 40% [2], [3]. The mechanism of the BOD_5 reduction was investigated in order to provide additional

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information on chlorination as a potential treatment process [4]. However, this study did not allow accurate prediction of BOD_5 reduction by chlorination.

More recently it was concluded that chlorination of filtered final effluents does not bring about a reduction of BOD [5]. In a study primarily designed to assess the effect of chlorine on nitrogenous BOD, it was shown that as the chlorine dose was increased from 1.3 to 5.3 mg Cl_2/dm^3, the carbonaceous BOD decreased [6]. This study concluded that although the rate of oxygen uptake was not affected, the ultimate BOD was reduced as chlorine concentration increased.

Several reasons may account for the variability of the data and its interpretation. First, except for the latter study [5], very little consideration has been given to the level of effluent chlorination and more specifically, whether or not chlorine was added at a concentration sufficient to satisfy the demand primarily due to the presence of ammonia and to a lesser extent other inorganic species. Another possibility for apparent BOD_5 reduction could have been the formation of less biodegradable or even toxic compounds, such as chlorinated phenols (e.g., [7]). Whether or not chlorination reduces and/or retards the BOD is, in itself, open to question. However, coupled with the concomitant production of chlorinated organics and residual chlorine species this practice may adversely affect the environment.

This study reports the effect of the addition of chlorine at 5 different concentrations, before and after the break point, on BOD.

2. RESEARCH APPROACH

The overall approach used in this research was to determine a breakpoint curve for each composited wastewater sample. Once the breakpoint curve was experimentally characterized, the effect of the chlorination on biochemical oxygen demand (BOD) was determined at several sample points on the breakpoint curve.

Three wastewater treatment plants were chosen for the study. One plant, Goulds–Perrine, receives mostly domestic waste and is located several miles inland. The second treatment plant, Virginia Key, is located on an island and receives wastewater via a pipeline located under Biscayne Bay. At the time of the study one half of the plant used pure oxygen for the activated sludge process, and the other half (the old plant) used air. Thus, these were treated as 2 different plants. Each treatment plant was sampled 3 times over 10 months for a total of 9 samples.

The wastewater was collected from each plant before chlorination and either refrigerated at 4° C or brought to the laboratory as soon as possible and processed. The samples were collected between 6:00 A. M. and 12:00 P. M. at each plant. A composite sample of 30 114 dm^3 was obtained consisting of 6–19 dm^3 gallon samples over a 6 hour period. The 19 dm^3 samples were mixed together in a 40151 dm^3 container and kept aerobic through gentle aeration until the analyses were made. Chemical characterization of each sample was performed and a portion of the composited sample was then divided into an appropriate number of samples and chlorinated. The samples were allowed to stand in the dark for 2 hours and the breakpoint determined. From this breakpoint curve, sample points were chosen for study (fig. 1).

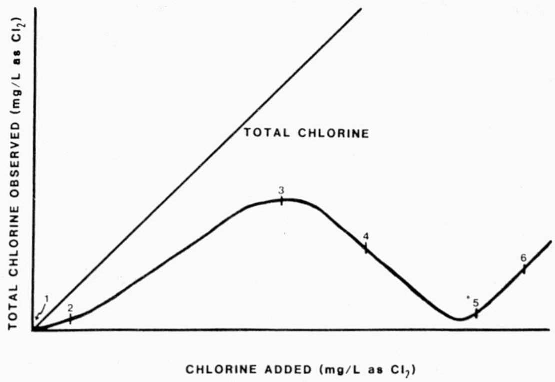

Fig. 1. Generalized breakpoint curve and sample points for studying the effect of chlorination on BOD

Sample point 1 was the effluent with no chlorine added. This sample point served as a control throughout the experiment. Sample point 2 was chosen in order to provide approximately 0.5 mg/dm^3 total chlorine residual. Sample point 3 was at the peak at the highest chlorine concentration, while sample point 4 was chosen when total chlorine decreased. At point 3 it was assumed that most ($>90\%$) of the chlorine residual was NH_2Cl. At point 4 disproportionation of the $NHCl_2$ occurred with the resultant evolution of N_2. The chlorine residual at this point was both NH_2Cl and $NHCl_2$. Sample points 5 and 6 corresponded to chlorine concentration that resulted in a free residual of about 1 and 10 mg/dm^3 as Cl_2 after a 2-hour contact time.

For each composited wastewater sample a 5-day BOD was determined at all 6 chlorine concentrations. To simulate operational BOD determinations, at every chlorine concentration $Na_2S_2O_3$ was added after 15 minutes contact time (it was added at stoichiometric concentration to the total chlorine at every sample point). One sample from each plant was used to determine the 20-day BOD (BOD_{20}). Samples 3 and 6 were run with and without seeding of the sample, with unchlorinated wastewater to provide information on regrowth of bacteria [8].

In addition to the BOD data, the formation and distribution of organohalogen compounds were determined at each sample point [9].

3. METHODS AND MATERIALS

3.1. BREAKPOINT CURVES

To 1 dm^3 aliquots of effluent a solution of NaOCl was added, with stirring, in increments of 5 ng/dm^3 as Cl_2. The container was capped and allowed to stand in the dark for 2 hours. After 2 hours, aliquots were tested for free chlorine using the FACTS test procedure. This provided the immediate screening necessary to locate the breakpoint. From the screening, a number of samples were measured for total chlorine using the iodometric titration to more thoroughly characterize the breakpoint curve.

3.1.1. FACTS. The colorimetric procedure, Free Available Chlorine Test with Syringaldazine (FACTS) was used as a qualitative tool to differentiate free chlorine in the presence of mono- and dichloramine [10].

3.1.2. Iodometric titration. The titrimetric method was the Iodometric Method 1, 409A of the 15th edition of *Standard Methods* [8].

3.1.3. Chlorine. To minimize the addition of unknown chemicals to the wastewater samples, NaOCl reagent grade 5% was used as the source of chlorine. The pH of the solutions was adjusted to 8–8.5, then the solution was standardized using iodometric titration.

3.2. BOD

In this study, the modified 20-day procedure known as "the single-dilution technique" was utilized [11]. In this technique 2 containers were used for each test instead of large numbers of BOD bottles. Each container was filled with aerated sample or with an aerated mixture of sample and dilution water. The primary container was kept full and properly stoppered to exclude air. Samples for determining dissolved oxygen content were siphoned from the primary container and the volume of sample taken was replaced from the reservoir. When the dissolved oxygen in the sample container declined to about 2 mg/dm^3, its contents were reaerated. After reaeration, a new sample was taken for determination of dissolved oxygen.

The single dilution technique offers several advantages: a) all BOD measurements are made from the same bottle, which assures uniformity of the sample and avoids concentration variability on biological activity; b) additional subsamples from the same sample can be taken for other analyses; c) as all analyses are made on the same sample, all observations are interrelated and errors are minimized; d) the large volume of sample used is a more representative sample; e) less incubator space is required than for the multiple dilution technique.

In this investigation, the volume of the primary container was 9.5 dm^3 and the reservoir was 2 dm^3. Both were incubated at 20° C and the contents of the primary container mixed thoroughly with a magnetic stirring bar before withdrawing the samples. Dissolved oxygen determinations were made on 17 cm^3 samples, siphoned into modified BOD bottles, using a Yellow Springs Instrument dissolved oxygen meter Model 54A. A rotating magnet in the bottle created the required velocity across the probe tip. The first sample volume siphoned into the BOD bottle was discarded to flush the siphon before obtaining the sample for the oxygen measurement.

4. RESULTS AND DISCUSSION

4.1. CHEMICAL CHARACTERIZATION OF WASTEWATER SAMPLES

Three wastewater effluents were sampled 3 times during the course of this study. The results of the chemical characterization of all 9 of the composited samples are shown in tab. 1.

A striking feature of the results was the difference in the Cl^- values between the Goulds–Perrine and Virginia Key plants. The increased Cl^- is probably due to infiltration of salt water into the gravity collection systems.

Table 1

Chemical characterization of wastewater samples

Parameters (mg/dm^3)	Goulds–Perrine			Virginia Key (new)			Virginia Key (old)		
	30/1/81	10/4/81	1/5/81	12/12/80	17/2/81	16/4/81	5/1/81	12/3/81	2/4/81
Alkalinity (as $CaCO_3$)	95	104	173	191	189	114	126	188	195
Hardness (as $CaCO_3$)	151	157	170	426	465	391	384	416	330
pH	7.35	–	–	–	6.90	6.75	7.3	–	7.40
Total residue at 103° C	0.20	0.41	0.38	–	2.7	1.7	0.50	3.5	1.3
Total residue at 550° C	0.13	–	–	–	2.6	–	–	3.8	0
Total filterable residue at 103° C	0.20	0.38	0.39	–	2.8	1.8	0.46	3.9	1.2
Total filterable residue at 550° C	0.15	–	–	–	2.7	–	–	3.0	–
Chloride	–	76.7	73.8	–	1145	936	–	835	631
Sulfate	79.4	34.5	47.4	–	157	129	99.2	108	92.1
NH_3–N	6.0	5.0	3.2	5.0	8.0	12.0	7.2	8.0	8.0
NO_2/NO_3–N	–	9.1	5.3	0.07	–	0.07	0.04	–	0.02
Kjeldahl–N	–	5.6	–	–	16.5	–	22.0	–	18.5
PO_4 (undigested)	–	0.69	0.89	–	1.7	1.8	0.35	1.6	0.75
PO_4 (digested)	–	0.87	1.1	–	2.0	2.2	0.96	1.6	1.0
Total organic carbon (filtered)	8.0	7.8	8.6	9.3	7.4	14.9	19.3	36.2	38.4

It should also be noted that the Virginia Key – new plant (using pure oxygen) – has lower TOC levels as compared to the old plant (using only air). This may reflect increased efficiency resulting from the use of O_2.

4.2. BREAKPOINT CHLORINATION

4.2.1. Introduction. A detailed discussion of the breakpoint phenomenon is beyond the scope of this paper and readers are reffered to References [12]–[14] or [15].

4.2.2. Goulds–Perrine plant. Three composite samples were obtained from the Goulds–Perrine wastewater treatment plant. These samples were obtained on (30/1/81), (10/4/81), and (2/5/81). The breakpoint chlorination curves and sample point are shown in fig. 2.

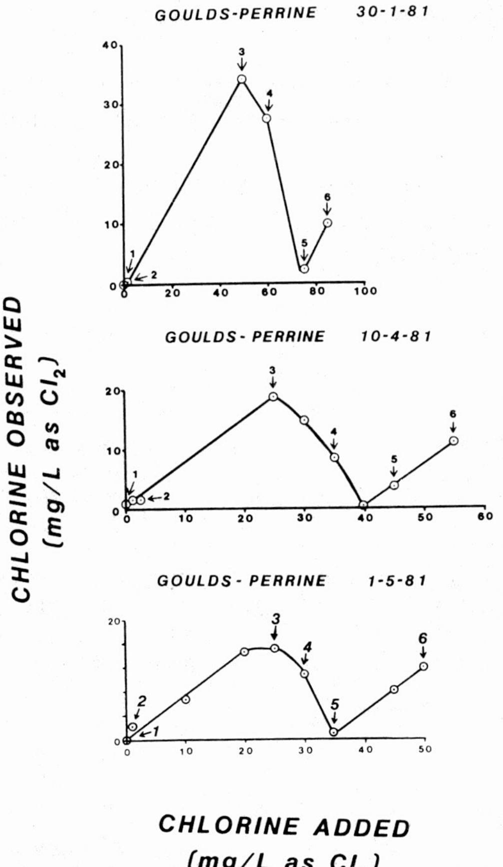

Fig. 2. Chlorination breakpoint curves of the wastewater collected at the Goulds–Perrine treatment plant. The sample points used for this study are shown on the respective curves

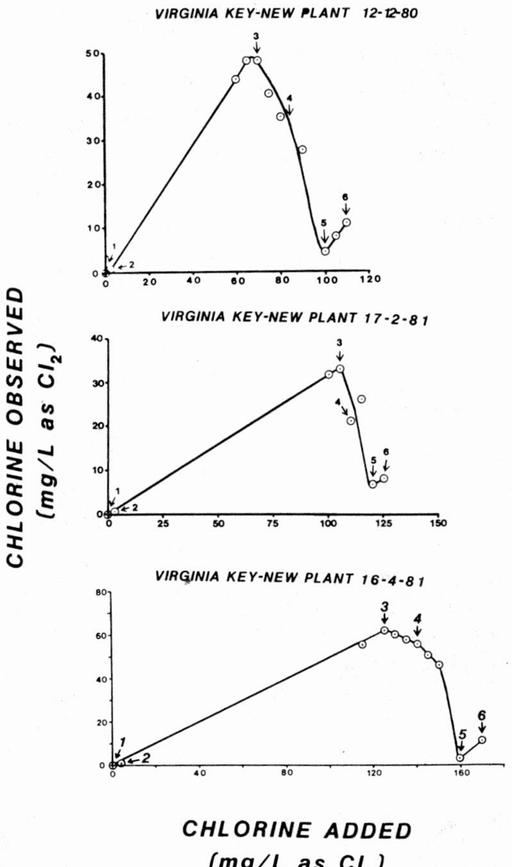

Fig. 3. Chlorination breakpoint curves of the wastewater collected at the Virginia Key – New Plant. The sample points used for this study are shown on the respective curves

Chlorination of the Goulds–Perrine plant effluent resulted in classical breakpoint curves. It was apparent in sample point 2 of the (10/4/81) sample that an error was made in the total chlorine measurement because 0.98 mg/dm^3 as Cl_2 was added and 2.2 mg/dm^3 observed. This could have been due to the presence of iron in the effluent, as ferric chloride is used as a coagulant aid and alum ($Al_2(SO_4)_3$) for phosphate removal.

The weight ratios of $Cl_2:NH_3$–N were 12.2, 6.8, and 12.5 for the (30/1/81), (10/4/81), and (2/5/81) samples, respectively. The low ratio for the 10/4/84 sample presumably reflects an incorrect NH_3–N value. The breakpoint curve for the 10/4/81 sample indicates that the chlorine residual values are accurate. Thus, if one were to average the other 2 $Cl_2:NH_3$–N ratios, using the breakpoint value of 34 mg/dm^3 as Cl_2, then a more realistic NH_3–N value of 2.75 mg/dm^3 NH_3 as N would be obtained for the 10/4/81 sample.

4.2.3. Virginia Key – New Plant. Three composite samples were collected from the Virginia Key wastewater treatment plant that uses pure O_2 in the activated sludge process. These samples were collected on (12/12/80), (17/2/81), and (16/4/81). The breakpoint chlorination curves and sample points are shown in fig. 3.

Table 2

BOD values at different levels of chlorination for 3 effluent samples from Goulds–Perrine

		1	2	3	4	5	6	7	8
30/1/81	BOD_5 (mg/dm^3)	14.0	7.4	7.0	6.9	6.9	5.9	5.7	3.4
TOC = 8.0 mg/dm^3	Level	3S	5	6S	6	3	2	1	4
NH_3–N = 6.0 mg/dm^3									
K–N = n/a	Chlorine added	50	75	85	85	50	0.95	0	60
NO_2+NO_3 = n/a	(mg/dm^3)								
10/4/81	BOD_5 (mg/dm^3)	14.5	12.7	6.2	5.8	4.4	4.3	3.4	1.9
TOC = 7.8 mg/dm^3	Level	3S	3	6	6S	2	4	1	5
NH_3–N = 5.0 mg/dm^3									
K–N = 5.0 mg/dm^3	Chlorine added	25.0	25	50	50	0.98	30	0	35
NO_2+NO_3 = 9.1	(mg/dm^3)								
1/5/81	BOD_5 (mg/dm^3)	17.6	9.7	6.4	6.4	4.8	4.3	3.8	2.6
TOC = 8.6 mg/dm^3	Level	3S	6S	3	4	2	6	1	5
NH_3–N = 3.2 mg/dm^3									
K–N = n/a	Chlorine added	25	55	25	35	1.15	55	0	45
NO_2+NO_3	(mg/dm^3)								
= 5.3 mg/dm^3									
	BOD_{20} (mg/dm^3)	28.2	27.4	21.4	20.1	19.8	19.4	14.7	11.3
	Level	3	3S	1	6S	2	6	4	5

n/a – not analyzed.

The $Cl_2:NH_3$–N weight ratios for the 3 samples, (12/12/80), (17/2/81), and (16/4/81), were 20.0, 15.0, and 13.3, respectively. The NH_3–N value for the (12/12/80) sample was probably low and was probably about 7 mg/dm^3 as N. The absolute value is not critical because the data analysis was based on the breakpoint curves obtained.

4.2.4. Virginia Key – Old Plant. Three composite samples were collected from the Virginia Key wastewater treatment plant that uses air in the activated sludge process. The 3 samples were collected on (5/1/81), (12/3/81), and (2/4/81). The breakpoint chlorination curves and sample points are shown in fig. 4.

The $Cl_2:NH_3$–N ratio for the Virginia Key – Old Plant samples of (5/1/81), (12/3/81), and (2/4/81) were 16.9, 14.4 and 14.4, respectively.

4.2.5. Summary. Classical breakpoint curves were obtained for all samples. The average $Cl:NH_3$–N ratio for all the samples was 13.9 including the high value from the Virginia Key – New Plant sample (12/12/80) and the low value from the Goulds–Perrine plant sample (10/4/80). This value of 13.9 is considerably above the theoretical 7.6 weight, and probably reflects the presence of chlorine demanding compounds other than ammonia.

5. BIOCHEMICAL OXYGEN DEMAND STUDIES

5.1. GOULDS–PERRINE PLANT

The Goulds–Perrine treatment plant has an activated sludge process that includes the addition of aluminum sulfate for the removal of phosphorus. In the 3 samples, the effluents were clear, had a good general appearance, and yielded low BOD test results. One sample from level 3 and one from level 6 were seeded with raw wastewater following the initial treatment, 15-minutes contact time with chlorine subsequent quenching of the Cl_2 with sodium thiosulfate.

5.1.1. Sample (30/1/81). The chemical analysis of the effluent showed a TOC concentration of 8.0 mg/dm^3 and 6.0 mg/dm^3 of ammonia nitrogen. The BOD_5 values range from a maximum of 14.0 mg/dm^3 for level 3S to 3.4 mg/dm^3 for level 4, and can be placed in 3 categories: high (3S); medium (5,6S, 6, 3, 2, and 1); and low (4), (tab. 2). The plots of the BOD's showed a "lag" phase of 1 day for levels 3 and 6 (fig. 5). The curves showed a fairly high rate of demand between days 2 and 5 for levels 3, 3S, 5, 6, and 6S.

The shape of the curves suggested that the comparison of the rate coefficients was not feasible and this was corroborated mathematically by the negative k values obtained [16]. In this sample, the unchlorinated sample was penultimate in low BOD values. The BOD's seem to be stimulated by chlorination, the greatest stimulation being at level 3.

5.1.2. Sample (10/4/81). The effluent obtained on (10/4/81) had a TOC of 7.8 mg/dm^3, 5.0 mg/dm^3 of ammonia nitrogen, 5.6 mg/dm^3 of Kjeldahl nitrogen, and 9.1 mg/dm^3 of nitrite and nitrate nitrogen. These concentrations were very similar to the ones in the effluent obtained on (30/1/81). Levels 3S and 3 exerted the highest BOD (14.5 mg/dm^3 and 12.7 mg/dm^3, respectively) and level 5 showed the lowest BOD (1.9 mg/dm^3). Level 1 was, as in the sample of (30/1/81), the penultimate value with 3.4 mg/dm^3 (tab. 2, fig. 5).

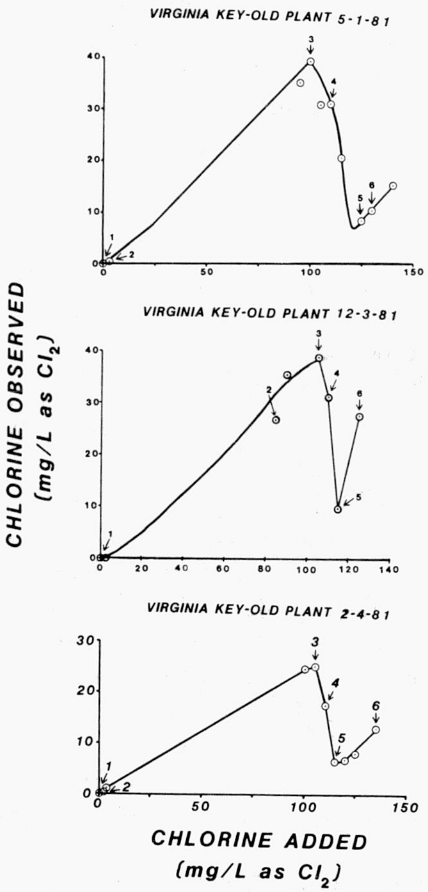

Fig. 4. Chlorination breakpoint curves of the wastewater collected at the Virginia Key – Old Plant. The sample points used for this study are shown on the respective curves

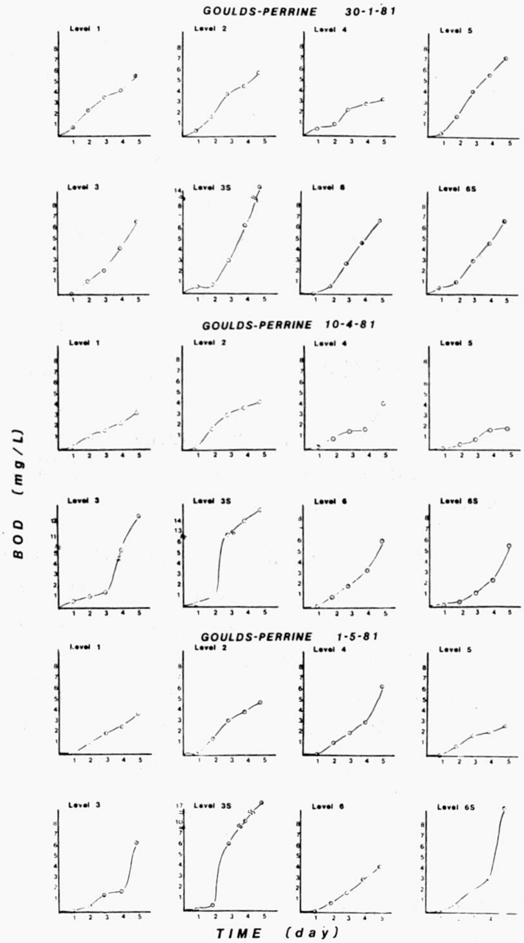

Fig. 5. BOD_5 curves at 6 chlorine concentration levels for the Goulds–Perrine plant

Levels 3S and 3 could be placed in the high-BOD category, levels 6, 6S, 2, and 4 in a medium-BOD category, and levels 1 and 5 in a low-BOD category. Chlorination at level 3 seemed to produce the highest BOD_5 stimulation. Chlorination at level 5 seemed to have inhibited the BOD because at this level it was lower than level 1, the unchlorinated sample.

The BOD curves show that all levels, except level 3, exhibit a "lag" phase of 1 day. The curves showed a rapid rate for level 3 between the third and fifth days, and for level 3S between the second and the fourth day. It was impossible to use the mathematical model for the "ideal" BOD curve to obtain and compare the reaction coefficients k.

5.1.3. Sample (1/5/81). The effluent for (1/5/81) had a TOC of 8.6 mg/dm^3, 3.2 mg/dm^3 of ammonia nitrogen, and 5.3 mg/dm^3 of nitrite and nitrate. As indicated on tab. 2, level 3S exerted the highest BOD (17.6 mg/dm^3), level 5 showed the lowest BOD (2.6 mg/dm^3) and, as in the 2 previous samples, the unchlorinated sample (level 1) was second lowest with 3.8 mg/dm^3 (fig. 5.)

In the 20-day test, levels 3 and 3S exerted the highest BOD (28.2 and 27.4 mg/dm^3), followed by the unchlorinated sample (level 1) with 21.4 mg/dm^3. The lowest BOD's were exerted by levels 5 and 4 (11.3 and 14.7 mg/dm^3, respectively; fig. 6).

All the BOD curves show a "lag" phase of 1 day; level 3 shows a rapid rate between day 4 and 5; level 3S had a dramatic increase from the second to the fifth day; level 6S shows also a very rapid increase in BOD between the third and fifth days. Once more the rate coefficients could not be compared and taking into consideration that it was a secondary effluent with a low carbon content, the BOD curves seem to indicate that the reactions were at the end of the first stage and entering the second one.

5.1.4. General conclusions – Goulds–Perrine plant. In the 3 BOD_5 samples, level 3S exerted the greatest oxygen demand whereas level 1 (unchlorinated sample) had an oxygen demand next to the lowest. Level 3S (level 3 seeded) exhibited a greater demand than 3 (the unseeded sample), by an average of 42%. The increased oxygen demand of level 3S may be attributed to the effect of the seed. However, no significant difference was found between levels 6S and 6. This lack of consistency may be due to the high chlorine dose used for level 6.

The unchlorinated samples (level 1 samples) had BOD's which were 59, 77, and 78% (average 71%) of the BOD of level 3S. This difference suggested that chlorination for 15 minutes at level 3, with the concomitant formation of monochloramines, stimulated the BOD_5.

In all 3 samples, level 3S exerted a higher 5-day BOD than level 6S, further suggesting that lower chlorine dosages exerted greater stimulation on the BOD.

The BOD_{20} data revealed that levels 3 and 3S had higher BOD than the unchlorinated sample 1 and the other chlorinated samples (levels 6S, 2, 6, 4 and 5).

These data suggest that chlorination at level 3 for 15 minutes, with subsequent quenching, stimulated the biochemical oxygen demand.

Chlorination at levels 4 and 5 seem to inhibit that demand because the BOD_{20} of those samples were 31 and 47% of the unchlorinated sample (level 1). The BOD differences between level 1 and levels 6S, and 6 were considered not significant, being only 6, 7, and 9%, respectively, of level 1.

5.2. VIRGINIA KEY – NEW PLANT

The treatment at Virginia Key – New Plant is an activated sludge process that uses pure oxygen instead of air. Following the established pattern, 1 sample

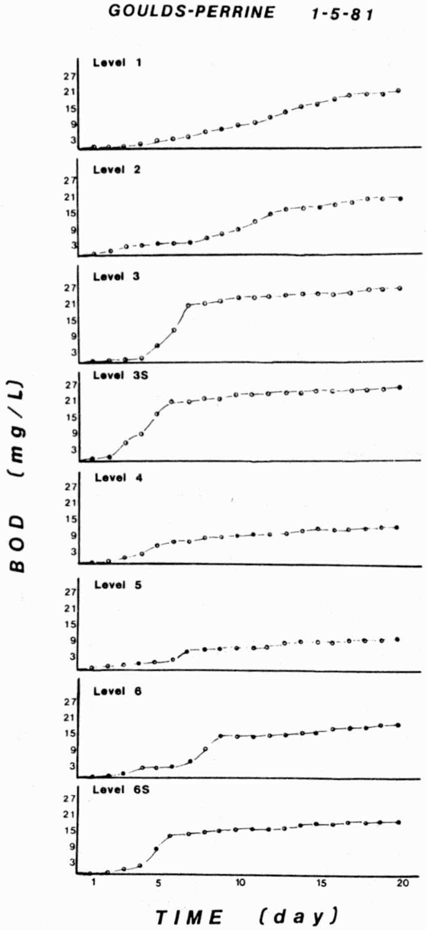

Fig. 6. BOD_{20} curves at 6 chlorine concentration levels for a Goulds–Perrine plant sample

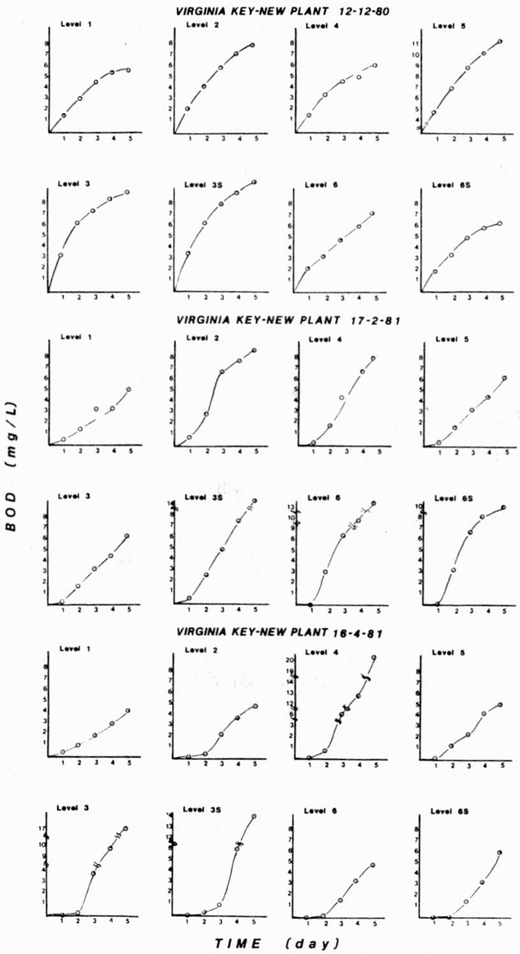

Fig. 7. BOD_5 curves at 6 chlorine concentration levels for the Virginia Key – New Plant

each from level 3 and 6 were seeded after being in contact with chlorine for 15 minutes and then quenched with sodium thiosulfate.

5.2.1. Sample (12/12/80). This sample had a TOC concentration of 9.3 mg/dm^3, 5.0 mg/dm^3 of ammonia nitrogen, and 0.07 mg/dm^3 of nitrite and nitrate nitrogen.

The BOD_5 values were relatively low, ranging from a high of 11.5 to a low of 5.7 mg/dm^3 (tab. 3, fig. 7). The range was also fairly narrow, the largest difference being 50% of the highest value. The plots of the BOD's show no lag phase for any of the levels so that the oxygen demand was exerted immediately and continuously from the first day. Hence, it can be concluded that the bacterial populations did not need any acclimatization to the new environment, and that chlorination did not impair their growth or form compounds detrimental to the bacteria. Level 1 (the unchlorinated sample) exerted the lowest BOD, being 50% of the highest one, level 5. As mentioned before, and as shown on tab. 3, the BOD differences between levels were small. If an arbitrary difference of 25% is adopted as a division line, the values could be grouped in 3 brackets: a high one, which includes levels 3, 3S, and 5, a middle one, which includes levels 3 and 6, and a low value bracket containing levels 1, 4, and 6S (tab. 3, fig. 7).

Table 3

BOD values at different levels of chlorination for 3 effluent samples from Virginia Key – New Plant

		1	2	3	4	5	6	7	8
12/12/80	BOD_5 (mg/dm^3)	11.5	10.2	9.4	8.2	7.3	6.4	6.3	5.7
TOC = 9.3 mg/dm^3	Level	5	3S	3	2	6	6S	4	1
NH_3–N = 5.0 mg/dm^3									
K–N = n/a	Chlorine added (mg/dm^3)	100	70	70	2	110	110	85	0
NO_2+NO_3 = 0.07									
17/2/81	BOD_5 (mg/dm^3)	14.6	13.5	10.2	8.9	8.1	6.5	6.4	5.2
TOC = 7.4 mg/dm^3	Level	3S	6	6S	2	4	3	5	1
NH_3–N = 8.0 mg/dm^3									
K–N = 16.5 mg/dm^3	Chlorine added (mg/dm^3)	105	125	125	2.9	110	105	120	0
NO_2+NO_3 = n/a									
	BOD_{20} (mg/dm^3)	66.5	65.1	59.2	58.8	50.4	44.3	41.0	20.3
	Level	3S	6	3	6S	4	1	2	5
16/4/81	BOD_5 (mg/dm^3)	19.8	17.0	13.7	6.1	5.3	4.9	4.9	4.2
TOC = 14.9 mg/dm^3	Level	4	3	3S	6S	5	6	2	1
NH_3–N = 12.0									
K–N = n/a	Chlorine added (mg/dm^3)	140	125	125	170	160	170	3.3	0
NO_2+NO_3 = 0.07									

n/a – not analyzed.

Since the effluent was a secondary one from a "pure-oxygen" plant, it is very likely that the oxidation process was advanced and that nitrification had started, explaining the shape of the BOD curves.

Because the BOD curves do not show any lags and resemble the first order decreasing kinetics, the k values are positive. This was the only sample where the k values were consistently positive.

5.2.2. Sample (17/2/81). This effluent sample had a TOC concentration of 7.4 mg/dm^3, slightly lower (1.9 mg/dm^3) than the one obtained in (12/12/80); its ammonia nitrogen, however, was 8.0 mg/dm^3 or 3.0 mg/dm^3 higher than the previous effluent (12/12/80).

The BOD values ranged from a maximum of 14.6 to a low of 5.2 mg/dm^3, or 64% of the highest value (tab. 3, fig. 7). As indicated on tab. 3, the BOD values tapered gradually and if an arbitrary difference of 25% was adopted as a division line, the BOD values could be grouped in 3 brackets: a high-bracket, containing levels 3S and 6, a middle-bracket, which includes levels 2, 4, and 6S, and a low-bracket containing levels 1, 3, and 5.

The plots of the BOD's showed a definite 1-day lag phase for levels 6 and 6S, a half-day lag for levels 3 and 4, and a slight lag, or positive slope, for the others (1, 2, 3S, and 5). The shapes of the BOD curves indicated that the reactions lagged the ones in the sample of (12/12/80), but no explanation can be formulated.

On the other hand, in the sample of (12/12/80), it appears that chlorination of this effluent stimulated the BOD, the greatest stimulation being at level 3S and 6.

For this sample, BOD_{20} tests were carried out (fig. 8). As indicated in tab. 3, level 3S exerted the highest demand (66.5 mg/dm^3) followed very closely by 6, as in the BOD_5. Level 5 was the lowest BOD value, and levels 1 and 2 were next to the lowest with 44.3 and 41.0 mg/dm^3, respectively (tab. 3, fig. 8).

The plots of the BOD_{20} tests showed a low rate of oxygen demand in levels 1, 2, and 5 (with lowest BOD values) and the relatively high rate in levels 3, 3S, 4, 6, and 6S between the fifth and eleventh or twelfth days. Like the 5-day, the BOD_{20} test suggests that chlorination at certain concentrations stimulated the BOD. However, chlorination at levels 2 and 5 inhibited the 20-day BOD.

5.2.3. Sample (16/4/81). Chemical analyses of the effluent indicated that its TOC was 14.9 mg/dm^3, twice the concentration of the effluent of (12/12/80), its ammonia nitrogen was 12.0 mg/dm^3, and the nitrite and nitrate nitrogen was 0.07 mg/dm^3.

The BOD_5 values ranged from a maximum of 19.8 mg/dm^3 for level 4 to a minimum of 4.2 mg/dm^3 for level 1 (tab. 3, fig. 7). The BOD values for this sample could be placed in 3 brackets: high (3 and 4), medium (3S and 6S), and a low one which included levels 1, 2, 5, and 6 (tab. 3). The difference between the average for the 2 highest values and the average for the 4 lowest ones was 74% of the high average.

The plots of the BOD's show a lag phase of 1 day for levels 2, 4, and 5; levels

2, 3, 3S, 6 and 6S show a 2-day lag phase. The curves showed a fairly high rate of demand for levels 3, 3S and 4 between day 2 and 5. The shape of the curves suggested that the mathematical analysis and comparison of the rate coefficients k was impossible. As in the other samples, the shape of the curves suggested that the reactions were at the end of the first stage or at the beginning of the second stage.

5.2.4. General conclusions for the Virginia Key – New Plant. In all 3 BOD_5 tests, the unchlorinated sample (level 1) has the lowest demand. Level 3S exerted the highest BOD in 1 sample, the second in another, and the third in the last sample. Level 3S exerted a greater BOD than its unseeded counterpart 3 in 2 samples (9 and 125% higher) but was 19% lower in the sample of (16/4/81). Level 6, however, exerted a

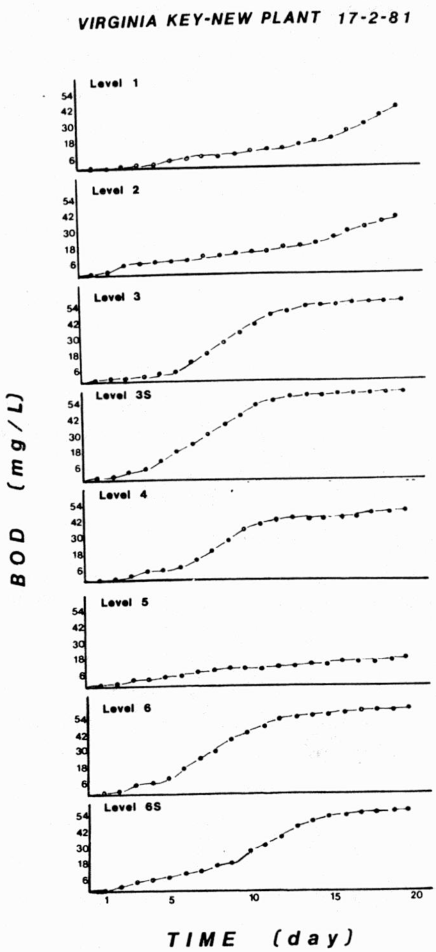

Fig. 8. BOD_{20} curves at 6 chlorine concentration levels for the Virginia Key – New Plant

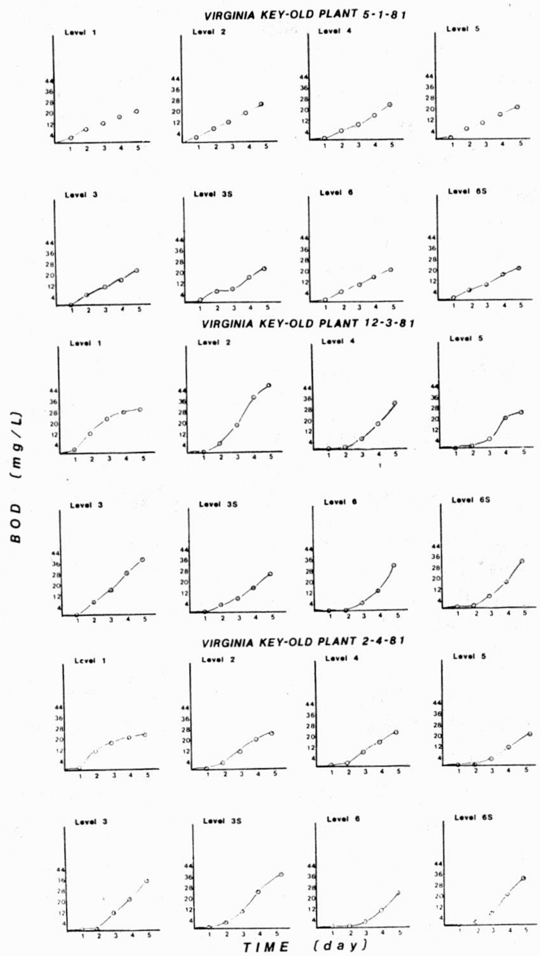

Fig. 9. BOD_5 curves at 6 chlorine concentration levels for the Virginia Key – Old Plant

higher BOD than its seeded counterpart 6S in 2 samples (14 and 32% higher), but in the last sample, 6S exhibited 24% higher BOD than level 6 (unseeded).

A comparison of the averages for each high BOD group against the unchlorinated sample showed that the samples chlorinated at level 1 exerted only 45, 63, and 77% of the high values, or an average of 62% lower.

Since level 3S exhibited the greatest BOD in the 3 effluents from the Goulds–Perrine treatment plant, it is interesting to compare these levels in the Virginia Key – New Plant with the unchlorinated levels 1. Level 1 samples were 44, 36, and 69% (average 50%) of level 3 samples. This reinforces the idea that chlorination for 15 minutes at level 3, followed by quenching with sodium thiosulfate, stimulates the BOD_5. The result of comparing the high-BOD's groups with level 1 also suggests that chlorination incrases BOD. The BOD_{20} data demonstrated that chlorination at levels 3 and 6, both seeded and unseeded, stimulated the biochemical oxygen demand. However, chlorination at levels 2 and 5 seemed to inhibit BOD because these samples had BOD that were 50 and 54% of the BOD of level 1 samples.

Table 4

BOD values at different levels of chlorination for 3 effluent samples from Virginia Key – Old Plant

		1	2	3	4	5	6	7	8
5/1/81	BOD_5 (mg/dm^3)	26.7	25.1	24.6	24.0	23.8	23.6	23.2	23.2
TOC = 19.3 mg/dm^3	Level	2	4	3	3S	1	5	6	6S
NH_3–N = 7.2 mg/dm^3									
K–N = 22.0 mg/dm^3	Chlorine added	3	110	100	100	0	125	130	130
NO_2+NO_3 = n/a	(mg/dm^3)								
	BOD_{20} (mg/dm^3)	131.2	125.3	121.7	121.1	109.5	106.6	54.4	53.1
	Level	6S	5	4	6	3S	3	1	2
12/3/81	BOD_5 (mg/dm^3)	48.3	41.7	34.5	34.5	33.6	31.5	27.0	25.8
TOC = 36.2 mg/dm^3	Level	2	3	4	6S	6	1	3S	5
NH_3–N = 8.0 mg/dm^3									
K–N = n/a	Chlorine added	85	105	110	120	120	0	105	115
NO_2+NO_3 = n/a	(mg/dm^3)								
2/4/81	BOD_5 (mg/dm^3)	40.0	37.4	34.5	26.4	25.2	24.8	24.6	23.2
TOC = 8.6 mg/dm^3	Level	3S	3	6S	2	1	4	6	5
NH_3–N = 3.2 mg/dm^3									
K–N = n/a	Chlorine added	105	105	135	2.2	0	110	135	115
NO_2+NO_3 = 5.3 mg/dm^3	(mg/dm^3)								

n/a – not analyzed.

5.3. VIRGINIA KEY – OLD PLANT

The treatment at Virginia Key – Old Plant consists of standard activated sludge. The plant used air at the time this research was conducted.

5.3.1. Sample (5/1/81). The effluent used in this sample contained 19.3 mg/dm^3 of total organic carbon (TOC), 7.2 mg/dm^3 of ammonia nitrogen, 22.0 mg/dm^3 of Kjeldahl nitrogen and 0.04 mg/dm^3 of nitrite and nitrate nitrogen. The BOD_5 values in this sample were fairly similar, ranging from 26.7 mg/dm^3 for the highest (level 2) to 23.2 mg/dm^3 for the lowest (levels 6 and 6S) (tab. 4, fig. 9).

The BOD_{20} values are shown in fig. 10. Level 6S exerted the highest BOD_{20} – 131.2 mg/dm^3, followed by levels 5, 6, and 4 with similar values – 125.3, 121.7, and 121.1 mg/dm^3, respectively. Level 1 (the unchlorinated sample) and level 2 showed the lowest BOD_{20} values – 54.4 and 53.1 mg/sm^3, respectively (tab. 4). The highest 5-day BOD value, level 2, exerted the lowest 20-day value. Conversely,

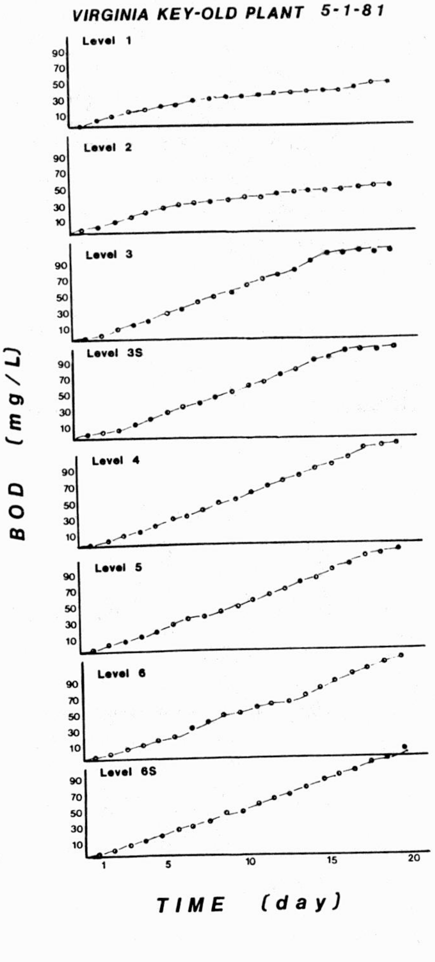

Fig. 10. BOD_{20} curves at 6 chlorine concentration levels for the Virginia Key – Old Plant

level 6S which had the lowest BOD_5 exerted the highest 20-day BOD. The BOD_5 values suggest that chlorination at level 2 seems to enhance the biochemical oxygen demand. The 20-day values also suggest that chlorination at levels 3, 4, 5, and 6 stimulated the biochemical oxygen demand (fig. 10).

5.3.2. Sample (12/3/81). This sample contained 36.2 mg/dm^3 of TOC and 8.0 mg/dm^3 of ammonia nitrogen. Nitrates and Kjeldahl nitrogen determinations were unavailable. As before, samples 3S and 6S were seeded with raw wastewater. BOD determinations were made after diluting the wastewater sample 1 : 3 with dilution water.

The BOD_5 values can be grouped into 3 ranges: high, medium, and low. Levels 2 and 3 can be placed in the high BOD group, with 48.3 and 41.7 mg/dm^3, respectively (tab. 4, fig. 9). The medium BOD group includes levels 4, 6S, 6, and 1, 34.5, 33.6, and 31.5 mg/dm^3, respectively. The low BOD group consisted of levels 3S and 5 with 27.0 mg/dm^3 and 25.8 mg/dm^3, respectively. The sample from level 3 that was seeded, 3S, had a much lower BOD than its counterpart level sample from level 3.

The BOD plots show that levels, 1, 2, 3, and 3S had a 1-day "lag" phase and levels 4, 5, 6, and 6S had "lag" phases of 2 days.

As in the sample obtained on (5/1/81), the shape of the BOD curves indicated that is was not possible to compare the rate coefficients (k values). This was corroborated by computing the k values, which proved to be negative. The 5-day BOD results suggest that chlorination at levels 3 and 6 stimulated BOD.

5.3.3. Sample (2/4/81). The third sample at the Virginia Key – Old Plant contained 38.4 mg/dm^3 of TOC, 8.0 mg/dm^3 of ammonia nitrogen, 18.5 mg/dm^3 of Kjeldahl nitrogen, and 0.02 mg/dm^3 of nitrite and nitrate nitrogen. Samples 3S and 6S were seeded with raw wastewater after chlorination and quenching. BOD determinations were made after diluting the wastewater in 1 : 2 dilution water.

Levels 3 and 3S showed the greatest BOD_5, followed closely by level 6S (40.0, 37.4, and 34.5 mg/dm^3, respectively) (tab. 4, fig. 9). Levels 1, 2, 4, 5, and 6 can be clustered in what may be called the "low-BOD" group, ranging from 23.2 to 26.4 mg/dm^3.

A plot of the BOD curves indicated the presence of a "lag" phase in every curve. This "lag" phase lasted 2 days for levels 3, 4, 5, 6, and 6S and 1 day for levels 1, 2, and 3S.

Once more, the BOD curves did not lend themselves to be compared by means of the reaction coefficient k. The curves, and the low values for the nitrate nitrogen suggest that the BOD reactions were at the end of the first stage and/or entering the second one. The BOD values suggest that chlorination at levels 3 and 6, stimulated the biochemical oxygen demand.

5.3.4. General conclusions for Virginia Key – Old Plant. All 3 effluent samples had some color and odor. The relatively high concentrations of TOC and the subsequent high BOD values indicate that of the 3 treatment plants investigated, the effluents from Virginia Key – Old Plant were the "strongest".

A comparison of the 3 samples indicates that levels 2 and 3 could be placed in a high BOD_5 group whereas levels 1, 4, 5, and 6 represent a group with low BOD. This suggests that with a contact time of 15 minutes followed by quenching, certain concentrations of chlorine did, in some cases, increase the BOD_5 of a secondary effluent. At the same time, it seems that high doses of chlorine could reduce the BOD of the same effluents. It should be noted, however, that in sample (12/3/81) level 3S, with a BOD of 27 mg/dm^3, was next to the lowest BOD (level 5) whereas level 3 (the unseeded counterpart) exerted a BOD of 41.7 mg/dm^3 or 54$^0/_0$ higher.

The differences between levels 2 and 3 and the unchlorinated level 1 are neither dramatic nor consistent. In the sample obtained on (5/1/81), the BOD of levels 2 and 3 were only 12 and 3$^0/_0$ higher than the BOD of level 1. In the sample of (12/3/81), levels 2 and 3 were 53 and 32$^0/_0$ higher than level 1. In the sample of (2/4/81), levels 2 and 3 exerted a BOD, 5 and 48$^0/_0$ higher than the BOD of level 1.

In the BOD_{20}, on the other hand, level 2 showed a BOD slightly lower than level 1 whereas the BOD of level 3 was 96$^0/_0$ higher than level 1.

The BOD_{20} tests indicate that levels 5 and 6S exerted the highest demand, which was the opposite from the 5-day BOD of the same sample. Conversely level 2, which exerted the highest 5-day demand, had the lowest BOD_{20}.

5.4. INTERPLANT COMPARISONS

Figure 11 is a summary of the BOD_5 results as a function of the frequency of ranking of the BOD_5 exerted by wastewater samples chlorinated at different levels (fig. 11).

The unchlorinated sample (level 1) exerted the lowest BOD_5 in 3 samples from the same plant; was next to the lowest in the 3 samples from another plant; ranked sixth in descending order in 1 sample and fifth in 2 samples from the third plant.

In the 3 BOD_{20} determinations, level 1 ranked third, sixth and eighth, in descending order, in a scale of 8 rankings.

Samples chlorinated at level 2 exerted a medium-to-low BOD_5 except in 1 plant where it exerted the highest BOD on 2 occasions.

In the BOD_{20}, level 2 was among the low-exerting in 2 runs and last in the third.

Chlorination at level 3 (the level corresponding to the peak in the "breakpoint" curve) exerted the second highest BOD_5 in 4 of the 9 runs; was third highest in 3 other runs, and fifth and sixth in 2 other runs, respectively.

In the BOD_{20}, level 3 exerted the highest BOD in 1 run, and was third and sixth in the other 2.

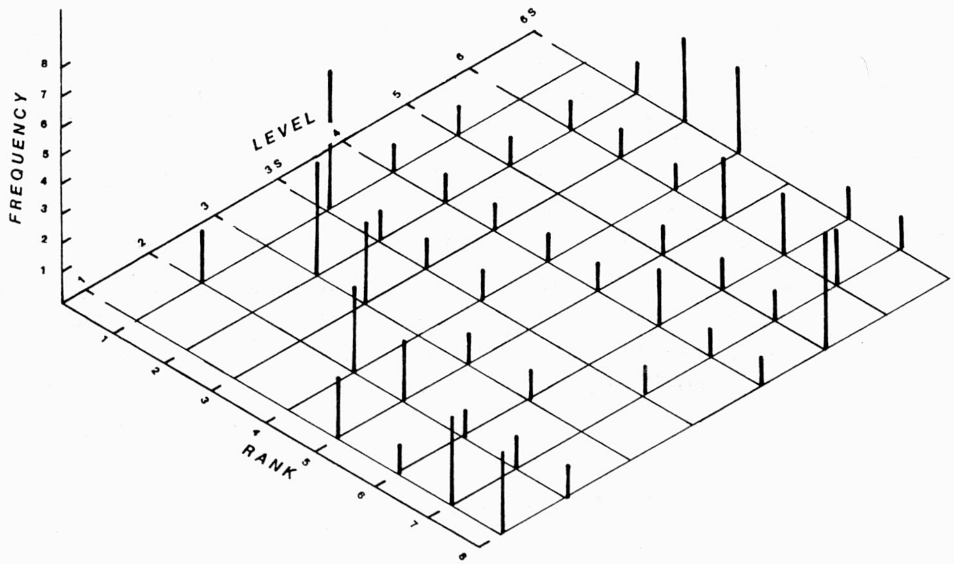

Fig. 11. Frequency of ranking of the BOD exerted by wastewater samples chlorinated at different chlorine concentration levels (1 – highest; 3 – lowest for a given wastewater sample)

Level 3S (level 3 but seeded with unchlorinated sewage, after quenching the chlorine) exerted the highest BOD in the 3 runs from 1 plant and in 2 other runs from 2 plants, it was the second highest BOD in 1 run (being only 1.3 mg/dm^3 lower than the highest), and was third, fourth and seventh in the other 3 runs.

In the BOD_{20}, level 3S exerted the highest BOD in 1 sample, was the second highest, with 0.8 mg/dm^3, and fifth in the other one.

The BOD values of level 4 were evenly distributed among all ranks, suggesting that chlorination at this level did not appreciably affect the BOD.

The frequency distribution of the BOD's for level 5 suggests that chlorination at this level may reduce the BOD somewhat.

There is a slight indication that chlorination at level 6 decreases the BOD. However, level 6S shows higher BOD, perhaps reflecting the impact of the bacterial seeding.

6. CONCLUSIONS

Within the limitations of the precision and accuracy of the BOD test it was concluded that, in general, chlorination up to the breakpoint showed a tendency to increase the BOD.

More specifically:

1. The unchlorinated sample (level 1) tended to exert a low BOD_5 – it was either the lowest or among the lowest BOD's in all nine runs.

2. Chlorination at levels 2 and 3 (both before the breakpoint) showed a slightly higher BOD_5 than level 1, however, the BOD_5 values for samples chlorinated at level 4 (also before the breakpoint) indicate that chlorination at this level did not appreciably affect the BOD.

3. In 5 out of 9 runs, the highest BOD_5 was exerted by level 3S (identical to sample 3 but seeded with raw sewage), however, no significant differences were observed among the BOD_5 or BOD_{20} values for levels 3 and 3S (level 3 seeded).

4. There was a slight indication that chlorination at level 5 (after the breakpoint) reduced the BOD_5 with respect to level 1 (the unchlorinated sample).

5. Chlorination at level 6 (also after the breakpoint) did not significantly affect the BOD_5 when compared with level 1 or level 5 and the BOD_5 and BOD_{20} of level 6S (level 6 seeded) did not differ significantly or consistently from level 6 (unseeded).

6. The absence of significant differences in BOD_5 and BOD_{20} between the seeded and unseeded samples indicates that enough heterotrophic bacteria survive the chlorination process used in these experiments.

7. Chlorination at certain levels of secondary effluents may oxidize some organic compounds present and the oxidation may render the compounds more amenable to bacterial degradation thus increasing the BOD of those effluents.

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WPŁYW CHLOROWANIA NA BIOCHEMICZNE ZAPOTRZEBOWANIE TLENU

Redukcja BZT jest powszechnie stosowaną miarą efektywności procesu oczyszczania ścieków. Tradycyjnie chlor używany jest w oczyszczalniach ścieków w celu dezodoryzacji, redukcji zapotrzebowania tlenu i dezynfekcji. W artykule przedstawiono badania nad wpływem dodatku chloru przy pięciu różnych stężeniach (przed i po punkcie przebicia) na poziom BZT w ściekach poddanych jego działaniu. Stwierdzono, że dawki chloru poniżej punktu przebicia powodowały wzrost BZT.

ВЛИЯНИЕ ХЛОРИРОВАНИЯ НА БИОХИМИЧЕСКУЮ ПОТРЕБНОСТЬ В КИСЛОРОДЕ

Восстановление БПК является общепринятой мерой эффективности процесса очистки сточных вод. Традиционно хлор используется на станциях очистки сточных вод для дезодорирования, восстановления потребности в кислороде и дезинфекции. В статье описаны исследования по влиянию добавки хлора при пяти различных концентрациях (до и после точки пробоя) на уровень БПК в сточных водах, подвергнутых его действию. Отмечено, что дозы хлора ниже точки пробоя вызывали повышение БПК.