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Correlating BOD and COD in Paper Mill Effluent Streams

Lloyd M. Tuskan
Western Michigan University

CORRELATING BOD AND COD IN PAPER MILL EFFLUENT STREAMS

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Lloyd M. Tuskan
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Faculty Advisor: Van Maltby
Industrial Consultant: Tom Porritt
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ABSTRACT

Biochemical oxygen demand (BOD_5) is a five day test. Chemical oxygen demand (COD) is a two hour test. Both measure the oxygen demand exhibited by organics in a wastewater sample.

It was proposed that if a significant correlation exists between BOD_5 and COD, the faster and simpler COD test could be substituted for the more commonly used BOD_5 test. Three effluent streams were chosen to test: a pulp mill stream, a paper mill stream, and a combined effluent stream. The correlation that existed between BOD_5 and COD in the combined effluent and paper mill streams were 0.90 and 0.92 respectivelty. A correlation of 1.00 would be a perfect linear correlation. The correlation of BOD_5 to COD associated with the pulp mill stream was 0.72.

These results can help a mill predict BOD_5 in a short time allowing for the saving of money, man hours, and time. It will also provide the mill with soluble organic concentrations in their effluent streams on a regular basis.

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I. INTRODUCTION

Over the years, researchers and industrial plant operators have been trying to abandon the BOD_5 analysis since it has a high deviation, and the test is time consuming. However, since all design parameters for biological treatment systems, and evaluation parameters are based on BOD_5 values for determining organic effluent loads. Regulatory agencies continue to use the BOD_5 test as their parameter for measuring organic effluent loads (1).

There are other methods for predicting organic effluent concentrations. They are chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD). For quite a while now, many engineers have been collecting data on correlating these tests with BOD_5.

It has been proposed that by correlating, BOD_5 and COD, a pulp or paper mill could predict mill effluent loads in shorter periods of time. This is because BOD_5 requires five days before test results are determined, while COD results can be obtained in less then three hours. If the tests show a significant correlation between BOD_5 and COD, a mill can figure out its BOD_5 load in less then three hours.

II. BACKGROUND

A. Literature Review

Van Soest (2) did research work on BOD_5/COD ratios. He stated that data accuracy is a key to correlating the two tests. He found in his study that potentially 40 percent of the samples collected were inaccurate. This was based on different operators collecting samples with different methods of grabbing samples.

At all times the COD value of a sample must be higher then the BOD_5 value. It is possible to have an ultimate BOD reach the COD value. The COD value is always higher than the BOD_5 because of the presence of inorganic materials like cooking chemicals, filler clays, alum, ect. These inorganic materials have no BOD_5, but may exhibit a COD value. Organic materials such as lignin also exhibit no BOD_5, but do exhibit a COD value. So, COD is always higher then BOD_5 (2).

In Siberia, Timofeeva (3) has reported on a study done on BOD_5/COD ratios. The study was performed on a kraft pulp mill, and the BOD_5/COD ratios were between 0.6 and 0.7. This was used to predict BOD_5 from COD data. This result was used to reduce the amount of laboratory work required to monitor the wastewater effluent stream. Another study performed in Germany on effluent from a sulfite mill had a 0.3 BOD_5/COD ratio (4).

B. BOD

Biochemical oxygen demand (BOD) is the amount of oxygen consumed in metabolizing biodegradable organics. BOD determination is a laboratory procedure, which tests for the oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the oxygen required to degrade the organic material (1).

Dissolved oxygen is of great fundamental importance in maintaining aquatic life. If the dissolved oxygen gets too low in lakes and streams aquatic life will die because there is not enough oxygen available in the water. If lakes and streams become polluted by industry or other human activities, BOD increases causing a deficiency in dissolved oxygen. This deficiency can kill fish, insects, and other forms of life. BOD levels rise when waters are polluted because the bacteria (bugs) require oxygen and other nutrients such as nitrogen and phosphorous to degrade the organic material. Thus, BOD measurement in lakes and rivers is one of the most important tests when monitoring bodies of water.

The following equation show how the reaction occurs when degrading wastes biochemically (1).

$$C_aH_bO_c + O_2 + \text{nutrients} \xrightarrow{\text{bugs}} CO_2 + H_2O + \text{sludge} + \text{energy}$$

In this reaction the organic waste is oxidized to its lowest energy state (carbon dioxide) through the metabolic action of microorganisms. Products produced other than carbon dioxide are energy, water, and new cells (1).

Measurement of BOD is based on a five day storage reading. The samples are kept in a dark place at 20 degrees Celsius. Temperature and light can effect BOD measurements. The samples should not be exposed to light, in fear that algae might grow. Algae produces oxygen and could give a false BOD reading. Temperature also affects the degradation of organic material. If temperature increases, degradation occurs faster, thus the BOD value will increase (5).

C. COD

The chemical oxygen demand (COD) test is used as a measure of the oxygen equivalent to the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxident (5). The COD test measures organic content of natural waters, municipal wastewaters, and industrial wastes. The COD test can be used by industrial companies when they want to check their waste stream quickly.

The COD test can not be used to differentiate between biologically oxidizable and inert organic matter. Also, the test provides no information concerning the rate at which organic matter is being oxidized. The test can also be affected by inorganic constituents such as chloride. Such constituents must be removed before COD can be determined.

The COD test is used to measure the oxygen equivalent of the organic matter using a strong oxidizing agent, potassium dichromate. The chemical reaction is represented as follows:

$$C_aH_bO_c + CrO_7^{-2} + H^+ \xrightarrow[\text{catalyst}]{\text{heat}} Cr^{+3} + CO_2 + H_2O$$

To determine the amount of organic matter present, the amount of potassium dichromate used to oxidize the organic matter is measured. The reaction takes place in heat with the addition of a catalyst, silver sulfate. The end products are Chromium plus three ion, carbon dioxide, and water (1).

III. Experimental

A. Sampling

The correlation between BOD_5 and COD was done on pulp and paper mill effluent from S. D. Warren, Muskegon, Michigan. The tests were performed on three waste streams: a pulp mill, paper mill, and combined effluent stream. The combined effluent stream consisted of wastes from the entire mill.

The effluent was collected over an eight hour work day. Five samples were grabbed from each stream during this time period. Process variables were also monitored in case any upsets occurred. The samples were stored in a cooler packed with ice, and were transported to Western Michigan University for testing.

The samples were then stored in a refrigerator at the National Council of the Paper Industry for Air and Stream Improvement (NCASI) laboratory. The samples were initially filtered to remove all insoluble matter. The samples then were separated into two containers: one for BOD_5 testing and the other one for COD testing. The COD test samples were mixed with sulfuric acid to drop the pH to below two. In appendix 6, there is a chart showing storage and holding conditions for tests.

B. Preparation

Before the tests could be run, nutrients had to be made for the BOD_5 tests. The nutrients were made a week in advance. These nutrients were made following the procedures described in Standard Methods (6). The nutrients consisted of a phosphate buffer, magnesium sulfate solution, calcium chloride solution, and ferric chloride solution.

There are several ways to perform the COD test. The closed reflux micro digestion procedure in standard Methods was chosen (6). This method calls for prepared vials which contain potassium dichromate, silver sulfate, sulfuric acid, and mercuric sulfate. As explained earlier, the potassium dichromate is the oxidizing agent and the silver sulfate is the catalyst. The sulfuric acid is used for keeping the pH low, while the mercuric sulfate is there to complex halides, so they would not interfere with the test.

A known molarity of ferrous ammonium sulfate (FAS) must also be prepared. FAS is used to titrate the remaining potassium dichromate in the sample vials. This information is used to calculate COD.

C. Procedures

1. <u>BOD</u>

Following are the steps that were used to determine the amount of BOD_5 in mg of oxygen per liter.

* Aeration of 55 liters of distilled water for approximately a half hour. Purpose is to add as much oxygen to the water as possible.
* The addition of nutrients to the aerated distilled water.
    - 1 ml/L phosphate buffer
    - 1 ml/L magnesium sulfate solution
    - 1 ml/L calcium chloride solution
    - 1 ml/L ferric chloride solution
* Calibrate the dissolved oxygen meter using Winkler titration in Standard Methods (6).
* Fill two BOD bottles with dilution water. Check the initial dissolved oxygen, stopper and cap. These are the unseeded blanks. They are used to check the quality of the dilution water. Depletion should not be greater than 0.2 mg/L .
* Add seed (microorganisms) to the aerated dilution water.
* Fill two BOD bottles with seeded blanks. Check the initial dissolved oxygen of the bottles, stopper, and cap. These blanks will be used when calculating the BOD of the

samples.

* Add effluent to each BOD bottle. The amount of sample addition varies with the strength of the waste. In appendices 1, 2, and 3, there is raw data showing how much sample was added. Also in appendix 5, there is a diagram showing the BOD bottle preparation procedure. The bottles are filled with the seeded dilution, checked for initial dissolved oxygen, stoppered, and capped.
* The bottles are now placed in storage for five days at a temperature of 20 degrees Celsius in a dark place.
* The final dissolved oxygen is taken on the bottles.
* BOD_5 is calculated.

BOD_5 Calculation:

$$\text{mg/L BOD} = \frac{\text{DO sample} - [[\text{DO seeded blank}][(300\text{ ml} - \text{ml sample})/300]]}{\text{ml sample}/300\text{ ml}}$$

DO = Dissolved Oxygen (mg/L)

2. <u>COD</u>

The procedures for COD are listed below. COD is calculated in mg of oxygen per liter. The procedures follow standard methods closed reflux (6).

* Two blanks are prepared by adding 2 ml of distilled water to the digestion vials. These are used to tell how much potassium dichromate is present.
* The effluent samples are added to the digestion vials. Appendix 4 shows how much sample was added to each vial. If the samples had contained high strength waste where all the potassium dichromate could be consumed, then the samples would be diluted.
* The samples are placed in a heating chamber for two hours at 150 degrees Celsius.
* The samples are titrated with FAS to determine potassium dichromate consumption.
* COD is calculated.

COD Calculation:

$$\text{mg/L COD} = \frac{(A - B) * M * 8000 * \text{dilution factor}}{\text{ml of sample}}$$

A = ml of FAS used for blank
B = ml of FAS used for sample
C = molarity of FAS

IV. DISCUSSION

Correlating BOD_5 and COD is possible in pulp and paper effluent streams. However, the same correlation can not be used in each waste stream because each stream is made up of different organic components. For this correlation to exist, sampling and handling techniques have to performed consistently without deviation, and process variables have to be monitored for process spills.

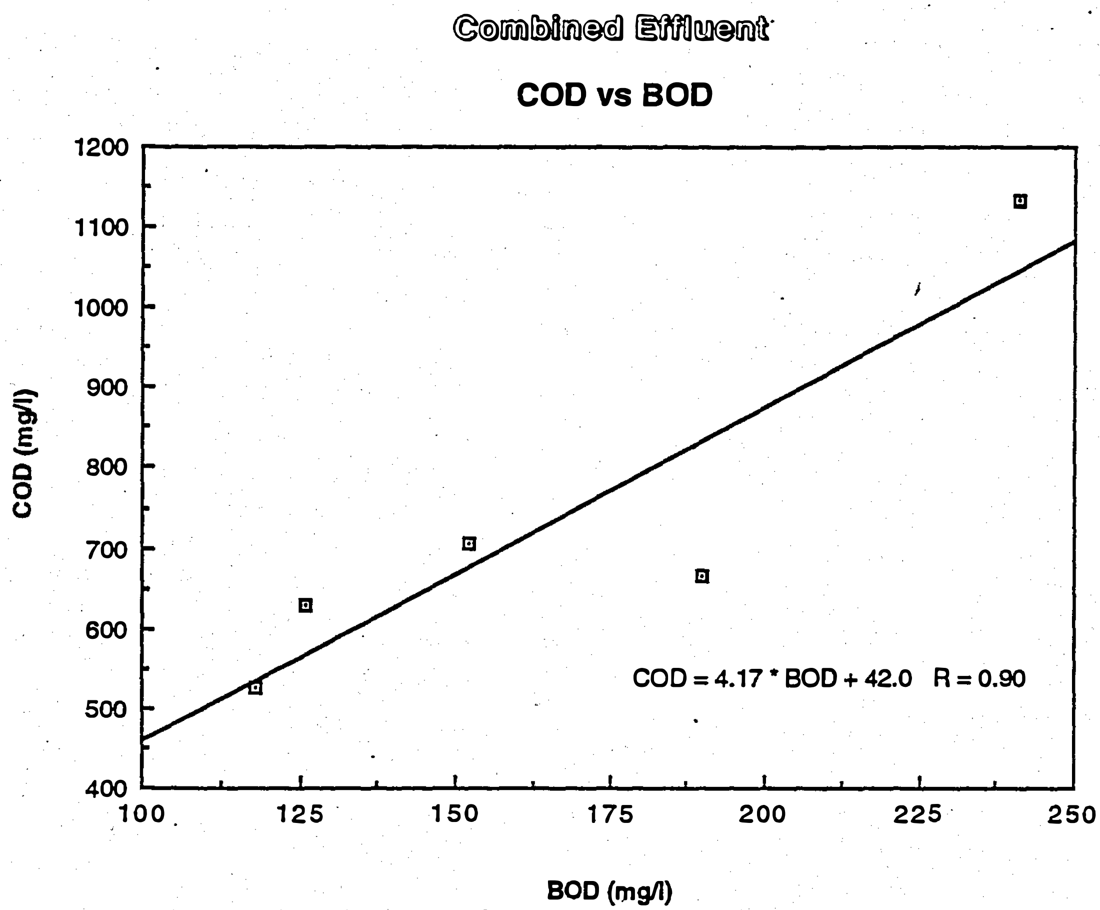
The following three graphs show the linear relationship of the results. The equation on each graph is the line depicting the relationship of COD to BOD_5 in a best fit line. The R value stands for the coefficient of correlation which is a measure of the strength of the linear relationship between two random variables x and y (7).

In Figure 1, the combined effluent stream, the R value is 0.90, which shows a strong linear relationship between BOD_5 and COD. This graph shows good variability of the BOD_5 range. This range is from 115 mg/L to 250 mg/L.

In Figure 2, the pulp mill effluent, a 0.72 correlation is derived from the line. This BOD_5 and COD correlation is low due to the low variability of BOD_5 waste. It ranges only from 71 mg/L to 77 mg/L.

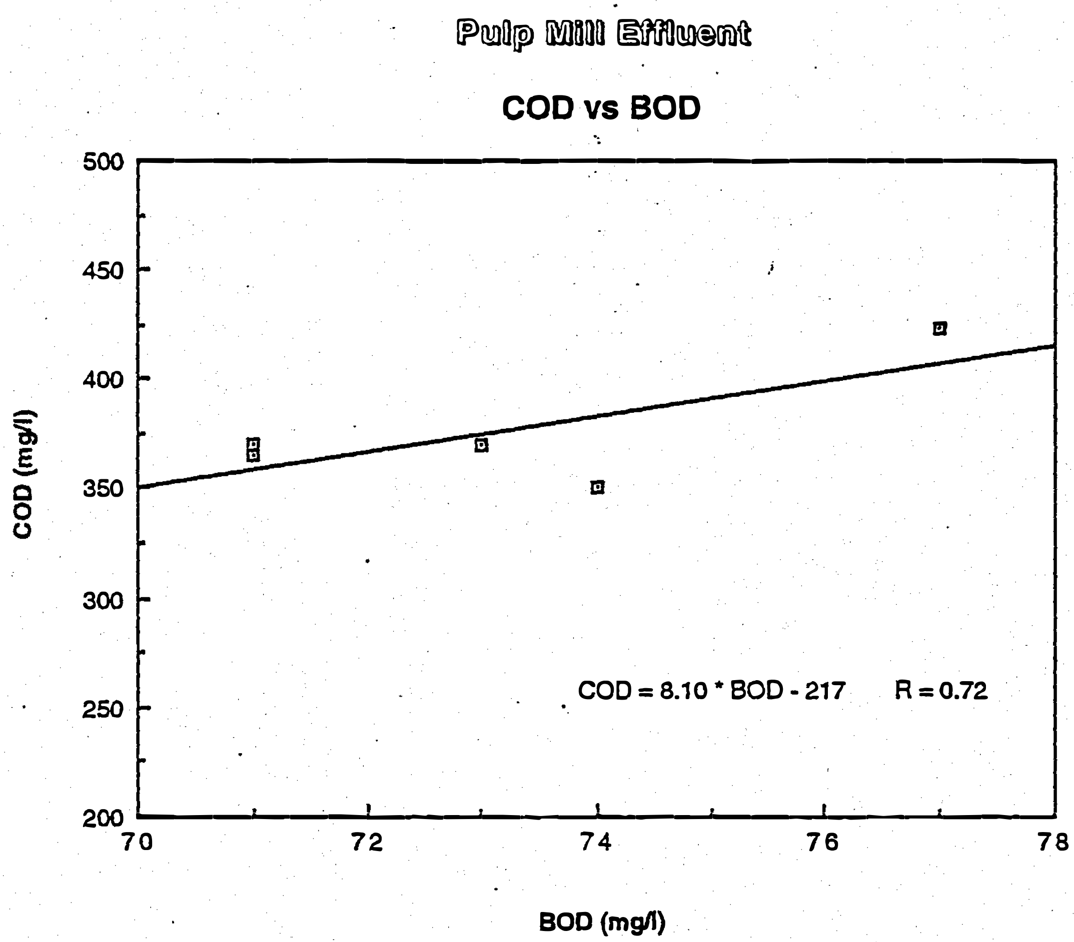
The paper mill stream showed the best correlation between BOD_5 and COD with 0.92 value of R. This stream, shown in Figure 3, has wide range of BOD_5: 175-650 mg/L. This correlation showed the most variability.

Figure 1



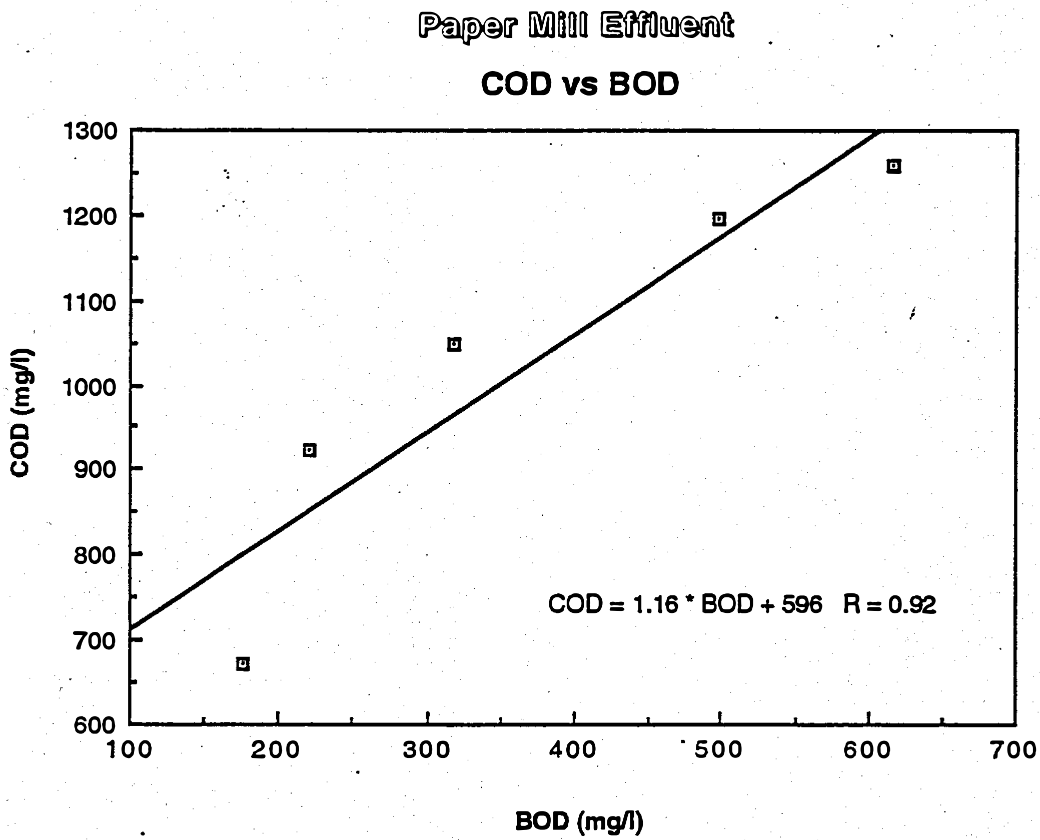
Combined Effluent
COD vs BOD
1200
1100
1000
900
800
700
600
500
400
COD (mg/l)
100
125
150
175
200
225
250
BOD (mg/l)
COD = 4.17 * BOD + 42.0   R = 0.90

Figure 2



Pulp Mill Effluent
COD vs BOD
500
450
400
350
300
250
200
COD (mg/l)
70
72
74
76
78
BOD (mg/l)
COD = 8.10 * BOD - 217
R = 0.72

Figure 3



Paper Mill Effluent
COD vs BOD
1300
1200
1100
1000
900
800
700
600
COD (mg/l)
COD = 1.16 * BOD + 596   R = 0.92
100
200
300
400
500
600
700
BOD (mg/l)

V. CONCLUSIONS

Pulp and paper effluent streams can be used to correlate BOD_5 and COD if process variables are monitored. Some process variables that might alter a correlation between BOD_5 and COD could be starch spills, temperature swings, or pH changes.

A correlation factor between BOD_5 and COD can only be used in an individual waste stream. The correlation of BOD_5 and COD from a paper mill stream can not be used to correlate BOD_5 to COD in a pulp mill stream. The two streams are different because they contain different types of chemicals, organics, and inorganics.

VI. RECOMMENDATIONS

* A long term study correlating BOD_5 and COD in one waste stream.

* A study done on correlating BOD_5 and COD on the individual components that are contained within the waste stream.

VII. REFERENCES

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4. Forsch W. A., "Investigations into effects of different biological process for treatment of pulp mill effluents" 19 (1): 22-28 (1986).

5. Metcalf and Eddy, Water Resources and Environmental Engineering, 2nd edition, Mcgraw-Hill, United States, 1979.

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VIII. APPENDICES

APPENDIX 1

PAPER MILL SAMPLES BOD RAW DATA

ML OF SAMPLE	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	BOD5
5	7.8	4.4	3.4	174.5
5	7.9	4.4	3.5	180.5
10	8	0		
10	8	0		
15	8	0		
15	8	0		
20	8	0		
20	8	0		
30	7.9	0		
30	7.9	0		
5	8	3.8	4.2	222.5
5	8	3.9	4.1	216.5
10	8	0		
10	8	0		
15	8	0		
15	8	0		
20	7.9	0		
20	7.9	0		
30	7.9	0		
30	7.9	0		
5	8	2.1	5.9	324.5
5	8	2.3	5.7	312.5
10	8	0		
10	8	0		
15	7.9	0		
15	8	0		
20	7.9	0		
20	7.9	0		
30	7.9	0		
30	7.9	0		
1	8.4	4.4	4	497.35
1	8.4	3.6	4.8	737.35
1	8.4	4.3	4.1	527.35
1	8.5	4.6	3.9	467.35

APPENDIX 2

PULP MILL SAMPLES RAW DATA BOD5

ML OF SAMPLE	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	BOD
1	7.8	7.2	0.6	30.5
1	7.8	7.2	0.6	30.5
2	7.9	7	0.9	60.5
2	7.9	7	0.9	60.5
5	7.9	6.2	1.7	72.5
5	8	6.2	1.8	78.5
7	8	5.8	2.2	73.35714
7	8	5.8	2.2	73.35714
1	8	7.2	0.8	90.5
1	8	7.2	0.8	90.5
2	8	7	1	75.5
2	8	7	1	75.5
5	8	6.2	1.8	78.5
5	8	6.2	1.8	78.5
7	8	5.7	2.3	77.64285
7	8	5.8	2.2	73.35714
1	8	7.2	0.8	90.5
1	8	7.2	0.8	90.5
2	8	7	1	75.5
2	8	7	1	75.5
5	7.9	6.3	1.6	66.5
5	8	6.4	1.6	66.5
7	8	5.9	2.1	69.07142
7	8	5.9	2.1	69.07142
1	8	7.1	0.9	120.5
1	8	7.1	0.9	120.5
2	8	7	1	75.5
2	7.9	7	0.9	60.5
5	8	6.3	1.7	72.5
5	8	6.3	1.7	72.5
7	8	5.8	2.2	73.35714
7	8	5.8	2.2	73.35714
1	8	7.1	0.9	120.5
1	7.9	7.1	0.8	90.5
2	7.9	6.9	1	75.5
2	7.9	6.9	1	75.5
5	8	6.2	1.8	78.5
5	7.9	6.2	1.7	72.5
7	7.9	5.8	2.1	69.07142
7	7.9	5.9	2	64.78571

APPENDIX 3

COMBINED EFFLUENT RAW DATA BOD5

ML OF SAMPLE	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	BOD5
1	7.9	6.6	1.3	240.5
1	7.9	6.6	1.3	240.5
2	7.9	6.2	1.7	180.5
2	7.9	6.2	1.7	180.5
5	7.9	4.9	3	150.5
5	7.9	4.9	3	150.5
7	7.9	3.8	4.1	154.7857
7	7.9	3.8	4.1	154.7857
1	7.9	7	0.9	120.5
1	7.9	7	0.9	120.5
2	7.9	6.5	1.4	135.5
2	7.9	6.6	1.3	120.5
5	7.9	5.4	2.5	120.5
5	7.9	5.3	2.6	126.5
7	7.9	4.4	3.5	129.0714
7	7.9	4.4	3.5	129.0714
1	7.9	7.1	0.8	90.5
1	7.9	7.1	0.8	90.5
2	7.9	6.6	1.3	120.5
2	7.9	6.6	1.3	120.5
5	7.9	5.4	2.5	120.5
5	7.9	5.4	2.5	120.5
7	7.9	4.7	3.2	116.2142
7	7.9	4.7	3.2	116.2142
0.5	7.9	7	0.9	240.5
0.5	7.9	7	0.9	240.5
1	7.9	6.5	1.4	270.5
1	7.9	6.5	1.4	270.5
2	7.9	5.8	2.1	240.5
2	7.9	5.8	2.1	240.5
5	7.9	3.4	4.5	240.5
5	7.9	3.4	4.5	240.5
1	7.8	6.7	1.1	180.5
1	7.9	6.7	1.2	210.5
2	7.9	6	1.9	210.5
2	7.9	6.2	1.7	180.5
5	7.8	4.5	3.3	168.5
5	7.9	4	3.9	204.5
7	7.8	2.8	5	193.3571
7	7.9	2.9	5	193.3571

Appendix 4

PAPER MILL SAMPLES RAW DATA COD

ML OF SAMPLE	DILUTION	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	COD
1	2	6.45	4	2.45	672
1	2	8.9	6.45	2.45	672
2	2	11.1	8.9	2.2	882
2	2	13.2	11.1	2.1	966
3	2	15.2	13.2	2	1050
3	2	17.2	15.2	2	1050
4	2	19.45	17.2	2.25	840
4	2	21.7	19.45	2.25	840
5	3	2.3	0	2.3	1197
5	3	4.6	2.3	2.3	1197
BLANK		7.75	4.6	3.15	
BLANK		11.1	7.75	3.35	

PULP MILL SAMPLES RAW DATA COD

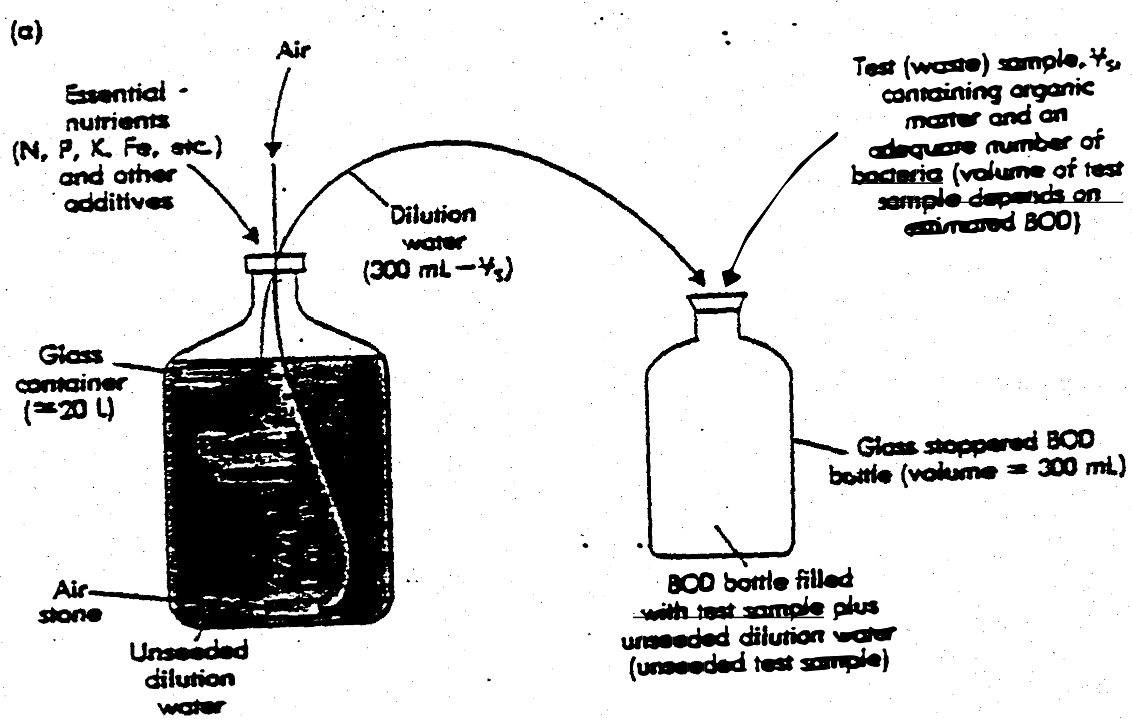
ML OF SAMPLE	DILUTION	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	COD
1	1	19.95	17.35	2.6	344.4
1	1	22.52	19.95	2.57	357
2	1	2.42	0	2.42	420
2	1	4.82	2.42	2.4	428.4
3	1	7.4	4.82	2.58	352.8
3	1	9.9	7.4	2.5	386.4
4	1	12.48	9.9	2.58	352.8
4	1	14.98	12.48	2.5	386.4
5	1	17.52	14.98	2.54	369.6
5	1	20.08	17.52	2.56	361.2
BLANK		13.93	10.5	3.43	
BLANK		17.35	13.93	3.42	

COMBINED EFFLUENT SAMPLES RAW DATA COD

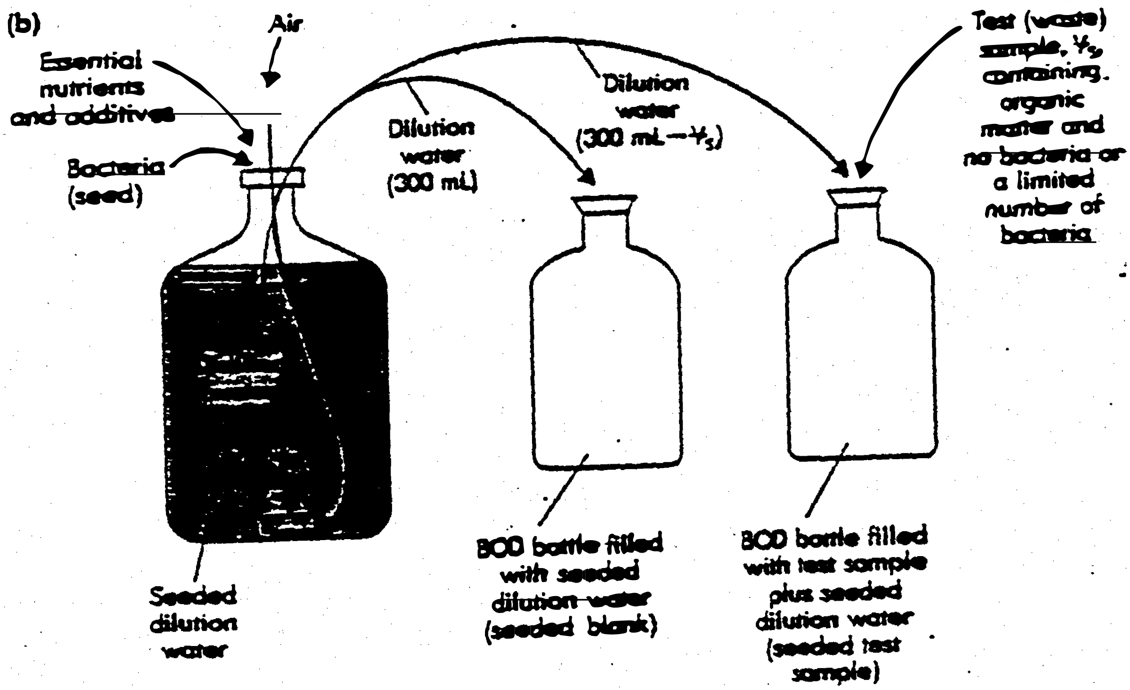
ML OF SAMPLES	DILUTION	INITIAL D.O.	FINAL D.O.	DISSOLVED OXYGEN	COD
1	1	1.6	0.05	1.55	735
1	1	3.3	1.6	1.7	672
2	1	5.2	3.3	1.9	588
2	1	6.9	5.2	1.7	672
3	1	8.9	6.9	2	546
3	1	11	8.9	2.1	504
4	2	12.95	11	1.95	1134
4	2	14.9	12.95	1.95	1134
5	2	17.42	14.9	2.52	655.2
5	2	19.92	17.42	2.5	672
BLANK		23.3	19.92	3.38	
BLANK		3.22	0	3.22	

APPENDIX 5

(a)



(b)



Reference Guide

SAMPLE COLLECTION, PRESERVATION, HOLDING TIME

Parameter	Container	Preservation	Approximate Volume	Holding Time
Alkalinity	P, G	cool, 4°C	500 ml	14 days
Biological Oxygen Demand (BOD)	P, G	cool, 4°C	1000 ml	48 hours
Chemical Oxygen Demand (COD)	P, G	cool, 4°C, H_2SO_4 to pH<2	200 ml	28 days
Chloride	P, G	cool, 4°C	500 ml	28 days
Chromium, Hexavalent	P, G	cool, 4°C	500 ml	24 hours
Cyanide, Total and Amenable	P, G	cool, 4°C, NaOH to pH>12	1000 ml	14 days
Fluoride	P	cool, 4°C	200 ml	28 days
Metals, Total (excluding CrVI, Hg)	P	cool, 4°C, HNO_3 to pH<2	500 ml	6 months
Metals, Dissolved (excluding CrVI, Hg)	P	filter 0.45 μm, HNO_3 to pH<2, cool 4°C	500 ml	6 months
Mercury	P, G	cool, 4°C, HNO_3 to pH<2	500 ml	28 days
N. Ammonia	P, G	cool, 4°C, H_2SO_4 to pH<2	250 ml	28 days
N. Nitrate	P, G	cool, 4°C	250 ml	48 hours
N. Nitrite	P, G	cool, 4°C	500 ml	48 hours
N.T. Kjeldahl	P, G	cool 4°C, H_2SO_4 to pH<2	500 ml	28 days
Oil & Grease	G	cool, 4°C, H_2SO_4 to pH<2	1000 ml	28 days
Oxygen, Dissolved	G	None	300 ml	Analyze immediately
pH	P, G	None	100 ml	Analyze immediately
Phosphorus, T	P, G	cool, 4°C, H_2SO_4 to pH<2	250 ml	28 days
Solids, Suspended	P, G	cool, 4°C	500 ml	7 days
Solids, Dissolved	P, G	cool, 4°C	500 ml	7 days
Solids, T	P, G	cool, 4°C	500 ml	7 days
Sulfate	P, G	cool, 4°C	500 ml	28 days
Volatile Organics	G, Teflon® lined septum	cool, 4°C	2 - 40 ml aliquots	14 days

P - plastic *HNO_3 - nitric acid* *G - glass* *H_2SO_4 - sulfuric acid*