Publication No. 78-e37
WA-22-0030

STATE OF WASHINGTON
Dixy Lee Ray
Governor

DEPARTMENT OF ECOLOGY
Olympia, Washington 98504 206/753-2800

M E M O R A N D U M

April 21, 1978

To: John Stetson

From: Bill Yake and Mike Morhous

Re: ITT Rayonier, Hoquiam
Class II Inspection

Date: April 21, 1978

Findings and Conclusions:

A Class II inspection of the Grays Harbor division of ITT Rayonier (Hoquiam) was carried out on February 28, 1978 - March 1, 1978. Three wastewater systems were sampled:

1) Process waters from pulp processing at ITT and paper processing at Grays Harbor Paper are clarified and treated in aerated lagoons followed by final clarification. Ammonia is added before primary clarification to resolve the low nutrient nitrogen concentrations in the waste waters. Although sludge is wasted through the effluent diffuser, it was not wasted during the sampling period. The following composite samples were collected: Primary influent, primary effluent, west secondary clarifier effluent and total final effluent. Long-term (20 day) BOD tests were performed and the results are attached. Due particular attention are the high effluent suspended solids concentrations. A large proportion of these solids were volatile. Significant quantities of KES positive (Klebsiella and/or Enterobacter) fecal coliforms were being discharged from this system. A bioassay was performed on the effluent. The results of this bioassay (zero mortalities) were forwarded from Don Kjosness to Roger Stanley in a memorandum dated March 29, 1978.

2) Cooling water is taken from the Grays Harbor estuary. This cooling water was sampled at intake and discharge and results are attached. Increased conductivity, salinity, temperature and PBI values are recorded. Company personnel noted that 'modified spent sulfite liquor' was being discharged to this effluent.

3) River water is treated by alum addition followed by sand filtration. An "old" water treatment system serves the pulping process, while a "new" system serves Grays Harbor Paper. Both backwash effluents discharged in lines also carrying untreated river water overflow. "Old" and "new" backwash effluent lines were sampled during backwash. Mass loadings cannot be calculated because the only available sampling locations carried substantial raw river water overflows. Aluminum content was measured in the "old" backwash and its concentration was substantial.

Laboratory procedures appeared generally acceptable. However, discrepancies observed during review of lab procedures, as well as subsequent lab results, are discussed in the laboratory procedures review portion of this memo.

BY:MM:ee

cc: Dick Cunningham
Central Files

Review of Laboratory Procedures and Techniques

Laboratory procedures were reviewed with Jim Kolp, Environmental Engineer and several laboratory technicians.

The lab uses Reeves Angel 934AH filter papers and both Gooch and Millapore filtering apparatuses. The Gooch analyses are run in duplicate and Millapore analyses are run in triplicate. Procedures appeared to be acceptable. The lab uses a membrane electrode for measuring dissolved oxygen and oxygen depletions. The D.O. meter is standardized with the Winkler Azide method using sodium thiosulfate as the titrant.

A discrepancy was observed with regard to the dilution water used in the BOD_5 analyses. The dilution water used by the lab is simply deioninzed water without the four required reagents; phosphate buffer, magnesium sulfate, calcium chloride or ferric chloride. It was recommended that the lab initiate approved procedures in conducting BOD_5 analyses by proper preparation of the dilution water. It was additionally suggested that dilution water blanks be set up for initial and 5 day D.O. readings. This procedure is used as a control of the dilution water. The 5 day D.O. depletion should be no more than 0.2 ppm. Subsequent to this inspection Jim Kolp indicated their lab was in the process of incorporating DOE's new BOD_5 procedures printed August 1977.

Laboratory procedures involving coliform analyses were reviewed with Jim McLaughlin, Environmental Technician. Laboratory procedures and equipment appeared to be in order. However, there appeared a substantial discrepancy with the comparison of total coliform results. ITT's results were considerably higher than DOE results. It is possible that there is a source of contamination. Jim McLaughlin is checking lab procedures to locate and eliminate the problem.

Substantial discrepancy in ammonia-nitrogen results were noted, however, ITT Rayonier indicated they were having a problem with their specific ion probe, which has subsequently been replaced with a new probe.

It should also be noted that ITT Rayonier analyzed settleable solids on the 24 hour composite samples. Considerable settleable solids were reported in the west secondary clarifier effluent and final effluent composites. By comparison, DOE collected a settleable solids grab on the final effluent each of the two days of this inspection and settleable solids were not detectable on other grab samples. Apparently the 24 hour compositing period provides sufficient time for the solids to flocculate and settle out.

24 Hour Composite Sampler Installations

Sampler	Date and Time Installed	Location
1. Primary influent aliquot - 250 ml/30 min.	2/28/78 - 0950	In well, center of primary clarifier
2. Primary effluent aliquot - 250 ml/30 min.	2/28/78 - 1005	Outfall, perimeter of primary clarifier.
3. West secondary clarifier effluent aliquot - 250 ml/30 min.	2/28/78 - 1019	Outfall, perimeter of West secondary clarifier
4. Total secondary effluent (ITT Composite Sampler)	2/28/78 - 0600	Permanent location on total effluent line.

Grab Samples

	Date and Time	Analysis	Sample Location
1.	2/28/78-0945,1030,1410	BOD/COD/Solids/Nutr./pH/Cond	HCE eff. (3 samples of 1000 ml Composited)
2.	2/28/78-1015	Total, Fecal & KES Coliforms	W.Sec.Clar. Eff. as above
3.	2/28/78-1138	SS/Solids/Cond/pH/Aluminum	Old plant backwash, sample port under dock
4.	2/28/78-1415:3/1/78-1050	SS	Total secondary eff. as above.
5.	2/28/78-1105	Total & Fecal Coliforms	Primary influent as above.
6.	2/28/78-1055	Total & Fecal Coliforms	Primary effluent as above.
7.	2/28/78-1115	Total, Fecal & KES Coliforms	Total secondary effluent as above.
8.	3/1/78-1130	SS/Solids/Cond./pH	New plant backwash, wooden junction box.

Flow Measuring Device

1. Type - In line, could not be calibrated
2. Dimensions

a. Meets standard criteria ☐ Yes ☐ No Explain:

b. Accuracy check

	Actual Instan. Flow	Recorder Reading	Recorder Accuracy (% of inst. flow)
1.			
2.			
3.			

☐ is within accepted 15% error limitations

☐ is in need of calibration

Field Data

Parameter	Date and Time	Sample Location	Result
Temp.	2/28/78-1105	Primary influent	24.5°C
Temp.	2/28/78-1055	Primary effluent	24.°C
Temp.	2/28/78-1015	W. Sec. Clar. Eff.	26°C
Cond, pH	2/28/78-1015	W. Sec. Clar. Eff.	See attached results
Temp.	2/28/78-1340	Influent cooling water	12°C
Temp.	2/28/78-1355	Effluent cooling water	30.5°C
Temp.	3/1/78-0930	HCE Effluent	36°C
Cond., pH	3/1/78-0930	HCE Effluent	See attached results
Temp.	3/1/78-0950	Primary influent	23.2°C

(over)

Parameter	Date & Time	Sample Location	Result
Cond., pH	3/1/78-0950	Primary influent	See attached results
Temp.	3/1/78-1015	Primary effluent	22°C
Temp.	3/1/78-1025	W. Sec. Clar. Eff.	25°C
pH, Cond.	3/1/78-1025	W. Sec. Clar. Eff.	See attached results
Temp.	3/1/78-1050	Total Sec. Eff.	24°C
pH, Cond.	3/1/78-1050	Total Sec. Eff.	See attached results
Temp.	3/1/78-1150	Inf. cooling water	5°C
Cond.	3/1/78-1150	Inf. cooling water	265 µmhos
Temp.	3/1/78-1200	Eff. cooling water	15°C
Cond.	3/1/78-1200	Eff. cooling water	1180 µmhos/cm

The following table is a comparison of laboratory results from 24 hour composite(s) together with NPDES permit effluent limitations. Additional results pertinent to inspection have also been included.

	DOE				ITT Analysis				
	Prim. Inf.	Prim. Eff.	W. Sec. Clar.	Final Eff.	Prim. Inf.	Prim. Eff.	W. Sec. Clar.	Final Eff.	NPDES ***
BOD_5 mg/l	900	850	149	65	932	898	334	98	
lbs/day	164,800	155,700	- -	11,900	170,700	164,400	- -	17,900	30,300[2]
BOD_{20} mg/l								228	
TSS mg/l	120	65	700	390	134	48	510	400	
lbs/day	22,000	11,900	- -	71,400	24,500	8790	- -	73,300	
Total Plant Flow MGD								21.96	35[1]
Turbidity (NTU's)	55	53	16	25	48	53	0.59	0.65	
Total Sus. Vol. Solids (mg/l)	80	34	600	230					
lbs/1000 gal wastewater	.688	.284	5.01	1.92					.30[3]
Color (color units)	1700	1500	5880	5830					
pH	4.4	3.9	7.4	7.8					6-9[4]
	10.4*	8.6*	6.6*	6.4*					
	3.7**	3.0**	6.4*	7.5**					
			7.5**		3.7	3.3	6.8	7.0	
COD	2,920	2,720	2,720	2,280	2719	2500	2292	1974	
Spec. Cond. (umhos/cm)	2,490	2,391	2,500	2,300					
	4,200*	2,800*	3,050*	2,950*					
	2,950**	2,800**	2,750**	2,600**	2500**	2600**	2800	2500	
Total Alkalinity ($mgCaCO_3$/l)				158					
Color	1,701	1,501	5,825	5,883					
Total Coliforms (#/100 ml)	<1,000	<1,000	46,000	40,000	8,500	- -	- -	10^6	
			31,000[5]	25,000[5]	- -	- -	- -	1500	
Fecal Coliforms (#/100 ml)	< 100	90 est.	1,700 est	600 est					
			4,000[5]	4,600[5]					
KES (% positive)			100%	100%					
NH_3-N (mg/l)	61.0	57.0	5.0	5.6	8.0	8.0	< 0.1	< 0.1	
NO_2-N (mg/l)	<0.02	< 0.02	<0.02	< 0.02					
NO_3-N (mg/l)	<0.02	< 0.02	<0.02	< 0.02					
O-PO_4-P (mg/l)	0.4	0.5	N.D.	0.1	0.45	.41	0.10	0.17	
T-PO_4-P (mg/l)	0.8	0.2	4.7	2.4					
Total Solids (mg/l)	3040	2880	3020	3320					
Total Non. Vol. Solids (mg/l)	1270	1160	1820	2080					
Total Sus. Non. Vol. Solids	40	31	100	160					
Settleable Solids (mg/l)				N.D.*	10	2.5	90	37	
% Total Solids					.21	.22	0.21	0.21	
PBI (mg/l)								14,400	

* Field Analysis - grab "<" is "less than" and ">" is "greater than"
** Field analysis - composite
*** As of December 31, 1977
1) Daily average, includes discharge from Grays Harbor Paper Co.
2) Daily average, when Chehalis River flow at Hoquiam is less than 2000 cfs.
3) "Suspended combustible solids".
4) When Chehalis River flow at Hoquiam is less than 4000 cfs.
5) March 1, 1978

The following table is a comparison of laboratory results from 24 hour composite(s) together with NPDES permit effluent limitations. Additional results pertinent to this inspection have also been included.

	DOE			ITT Analysis			NPDES **
	HCE[3] grab Composite	Cooling Water Inf.	Cooling Water Eff.	HCE grab Composite	Cooling Water Inf.	Cooling Water Eff.	[illegible] average)
BOD_5 mg/l	6200			6400			
lbs/day	54,810			56,600			
TSS mg/l	8			9			
lbs/day	70			80			
Total Plant Flow MGD				1.06			14[1]
COD	18,000			16,457			
pH	10.1 9.35*	7.7	7.0	9.1			
PBI		0	500			1335	
Spec. Cond. (µmhos)	12,200 14,250*	161 265*	9000 1180*	11,100*			
Color	34,611						
Total Coliforms (#/100 ml)	<10			50			
Fecal Coliforms (#/100 ml)	<10						
NH_3-N (mg/l)	2.0[2]						
NO_2-N (mg/l)	0.8[2]						
NO_3-N (mg/l)	< 0.02			1.53			
D-PO_4-P (mg/l)	0.4						
T-PO_4-P (mg/l)	N.D.						
Total Solids (mg/l)	23,700						
Total Non. Vol. Solids (mg/l)	10,700						
Total Sus. Non Vol. Solids (mg/l)	4						
Salinity		0.1 $^0/_{00}$	4.6 $^0/_{00}$			4.95 $^0/_{00}$	
% Total Solids				2.13			

* Field Analysis "<" is "less than" and ">" is "greater than"

** As of December 31, 1977.

1) Daily average

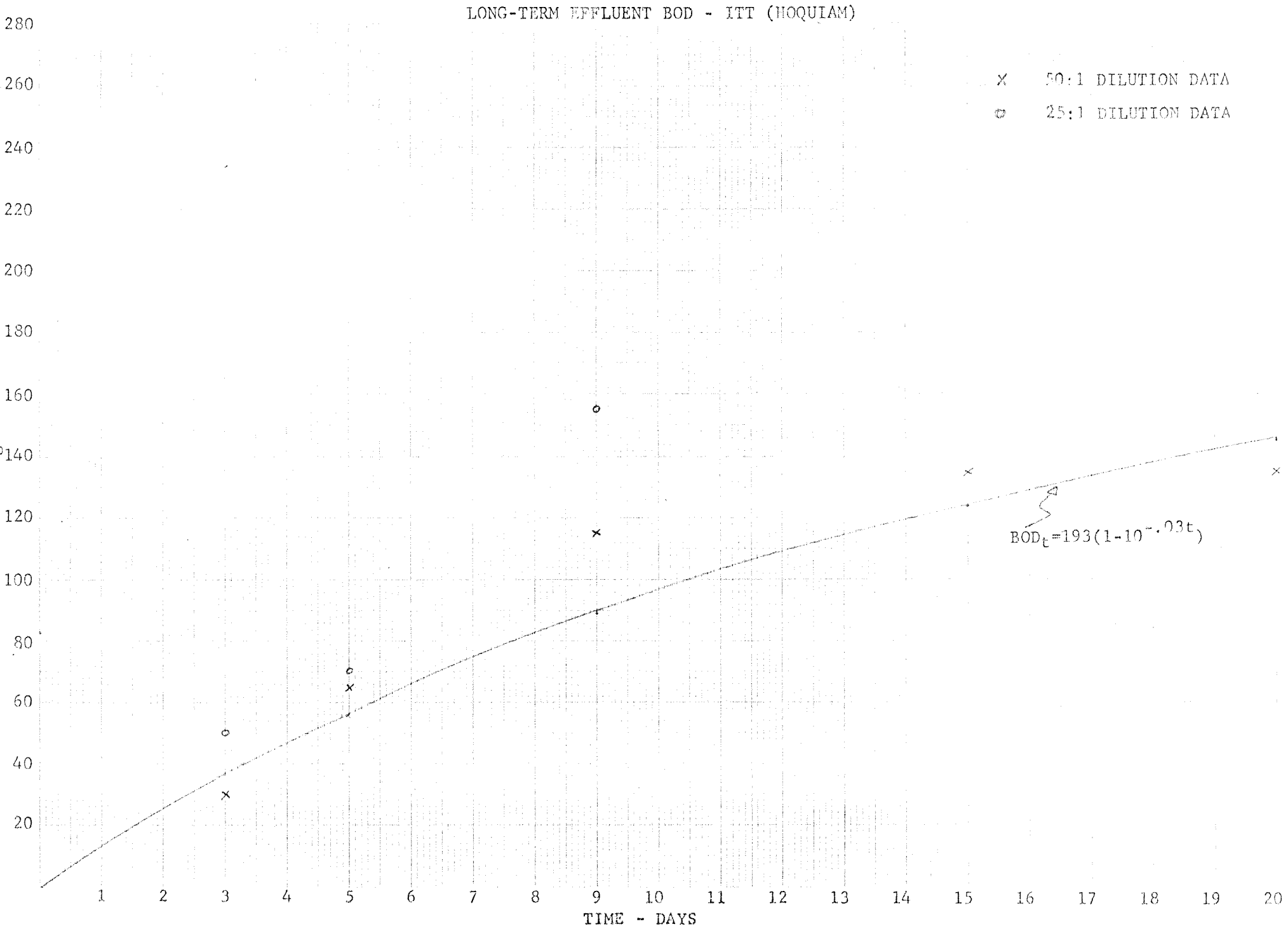
2) Validity questionable, due to excess color.

3) Hot caustic effluent

	DOE		NPDES (Monthly Average)
	Old Filter Plant Backwash	New Filter Plant Backwash	
pH	7.5	7.4	
Spec. Cond. µmhos	63	73	
Total Solids mg/l	98	137	
Total Non. Vol. Solids mg/l	75	105	
Total Sus. Solids mg/l	58	100	
Total Sus. Non. Vol. Solids	50	82	
Aluminum mg/l	6.4		
Settleable Solids mg/l	3.5	9.0	

* Field Analysis

"<" is "less than" and ">" is "greater than"


LONG-TERM EFFLUENT BOD - ITT (HOQUIAM)
50:1 DILUTION DATA
25:1 DILUTION DATA
$BOD_t = 193(1-10^{-.03t})$
280
260
240
220
200
180
160
140
120
100
80
60
40
20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
TIME - DAYS

Long-Term Effluent BOD Results

BOD was determined for 25:1 and 50:1 dilutions after 3, 5, 9, 15 and 20 days. Results were somewhat erratic. 25:1 dilution results were consistently higher than 50:1 dilution results and dissolved oxygen in the 25:1 dilutions was completely exhausted on the 15 and 20 days tests. Because of this the rate constant (K) was calculated for the 50:1 dilution results only. This was done by performing a linear regression on the variable time (T) in days and $[T/BOD_t]^{1/3}$; where BOD_t is the biochemical oxygen demand existed after T days. These data are presented in Table 1.

Table 1. Long-Term BOD Data

Time (T)	25:1 BOD_t (mg/l)	50:1 BOD_t (mg/l)	50:1 $[T/BOD_t]^{1/3}$
3	50	30	.464
5	70	65	.425
8	155	115	.428
15	188	135	.481
20	180	135	.529

Linear regression yield a linear equation of the form:

$$\text{Eq. 1 } [T/BOD_t]^{1/3} = A + TB$$

The rate constant was then determined according to Equation 2:

$$\text{Eq. 2 } k = 2.61^{\,B/A}$$

For the data used: $A = .0048$

$B = .4151$

$K = 0.030$

Thus, BOD exertion in this effluent procedes more slowly than typical domestic wastes for which k is typically approximately 0.1 and 60-65% of ultimate BOD is exerted after 5 days. By contrast a k = 0.03 indicates only approximately 30% BOD satisfaction after five days.

To determine the BOD satisfaction curve of the classical form:

Eq. 3 $BOD_t = BOD_u (1-10^{-kt})$ where BOD_u = Ultimate BOD it is necessary to determine BOD_u.

This was done by applying actual 50:1 BOD_t data to Equation 3 rearranged to the form of Equation 4:

Eq. 4 $$BOD_u = \frac{BOD_t}{1-10^{-0.03_t}}$$

The results of these calculations are presented in Table 2.

Table 2. Ultimate BOD calculations

T	BOD_t	BOD_u
3	30	160
5	65	223
9	115	248
15	135	209
20	135	180
	Mean	193

The mean value (193 mg/l) was chosen to represent the ultimate BOD.

Thus the idealized equation for BOD satisfaction in these wastes is given in Equation 5:

Eq. 5 $BOD_t = 193 (1-10^{-0.03_t})$

These results indicate that BOD_5 may be an insuffcient indication of waste strength, particularly if organic materials are retained in Grays Harbor for periods of time in excess of 5 days. Retention of oxygen demanding organics in either soluable or particulate form (after coagulation-flocculation induced by contact with sea water) would exert oxygen depletion effects in excess of those predicted by BOD_5 data.

In addition the presence of very high COD and TSS concentrations in the effluent suggest the possiblility of materials which may exert oxygen demands in terms of months or years, rather than days.