JOHN SPELLMAN
Governor

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STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
7272 Cleanwater Lane, LU-11 • Olympia, Washington 98504 •

MEMORANDUM
June 1, 1982

To: Fred Fenske

Through: Dick Cunningham

From: Bill Yake

Subject: St. Regis Paper Company Class II (Priority Pollutants) Survey, August 11-12, 1981

INTRODUCTION

On August 11 and 12, 1981, a source/receiving water study was conducted at St. Regis Paper Company mill in Tacoma, Washington. The study was one of a series of source-oriented surveys conducted cooperatively by the Washington State Department of Ecology (WDOE) and Region 10 of the federal Environmental Protection Agency (EPA). The focus of these surveys is to identify and quantify priority pollutants in facility wastewaters as well as in adjacent surface waters and sediments in and near Commencement Bay.

Participants in the source survey were Dan Tangarone and Jim Hileman (EPA, Region 10) and Bill Yake (WDOE, Water Quality Investigations Section). St. Regis was represented by Dick Forsberg. The study of nearby receiving waters and sediments was conducted by Art Johnson and Shirley Prescott (WDOE, Water Quality Investigations Section). The results of the receiving water study are published in a separate report (Johnson and Prescott, 1982).

Setting

The St. Regis facility is located in the Port of Tacoma on the point of land between the Puyallup River and the St. Paul Waterway (see Figure 1). The facility is a softwood kraft paper mill which produces unbleached kraft linerboard, unbleached kraft paper, bleached paper, and bleached market pulp. The plant was built in 1928, purchased by St. Regis in 1930, and has been operated on an essentially continuous basis since 1936. Untreated effluent was discharged to the old bleach plant crib on the Puyallup River until late 1970 when primary clarification was begun and the discharge routed to its present location. Secondary treatment was instituted in 1977.

● = WATER SAMPLES

▲ = SEDIMENT SAMPLES

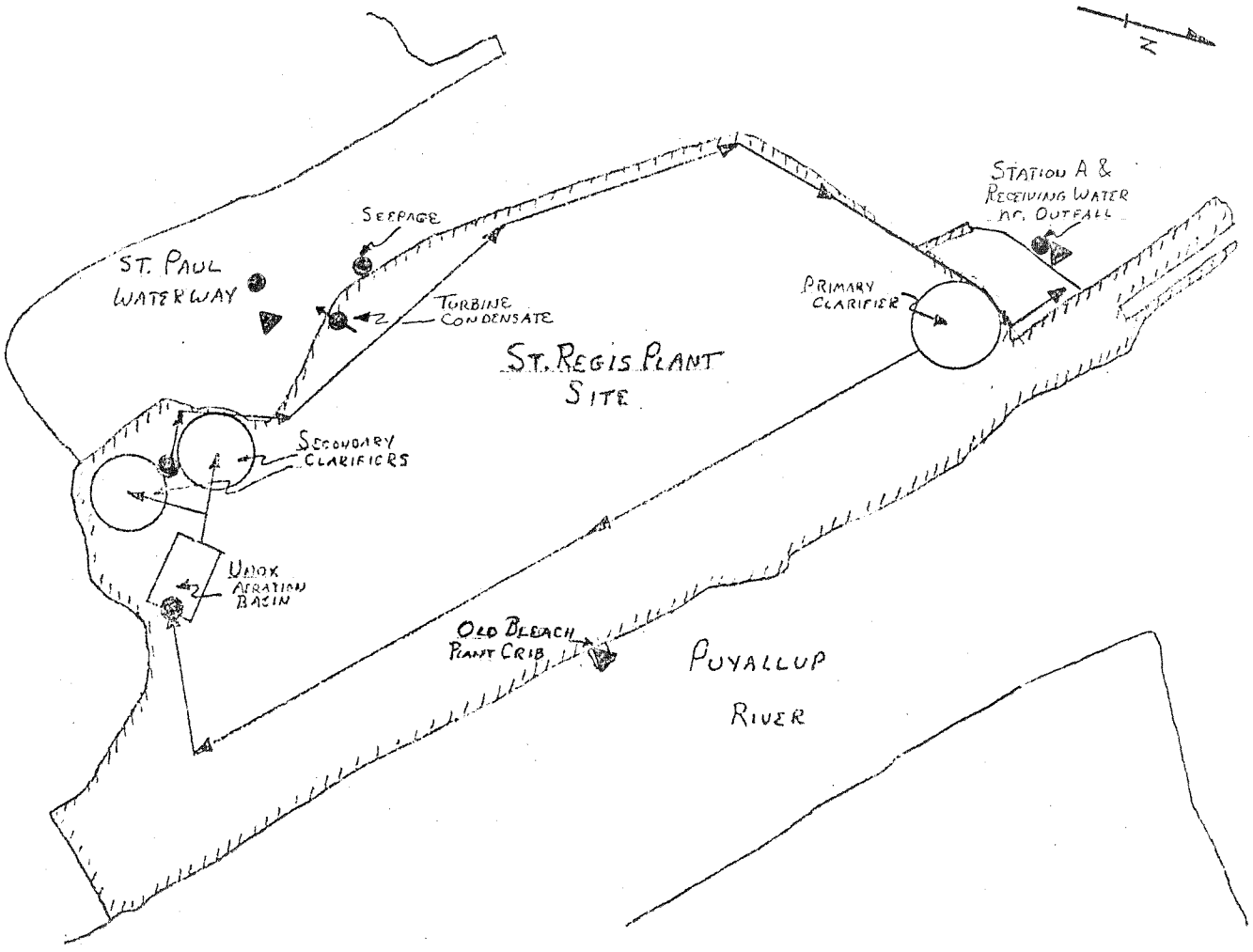

FIGURE 1. - ST. REGIS STUDY AREA

Table 1. Sample times and locations.

8- and 24-hr. Composite Samples

Sample	Installation Date (Time)	Location
UNOX Influent	8/11/81 (1120)	At influent structure at east end of UNOX aeration tank
Secondary Effluent	8/11/81 (0930)	Outfall box between secondary clarifiers

Grab Samples

Sample	Collection Date (Time)	Laboratory Analyses
UNOX Influent	8/11/81 (1150)	Phenols, oil and grease
	8/12/81 (1230)	Oil and grease
Secondary Effluent	8/11/81 (0930)	Phenols, oil and grease, fecal coliforms
	8/12/81 (1010)	Oil and grease
Turbine Condensate	8/12/81 (1030)	COD, PBI, pH, Cond., TS, TNVS, SS, NVSS, NH_3, NO_2, NO_3, O-PO_4, T-PO_4, metals, grease and oils

Field Analyses

Location	Date (Time)	Analyses
UNOX Influent	8/11/81 (1145)	Temp., pH, Cond.
	8/12/81 (1230)	Temp.
Secondary Effluent	8/11/81 (0930)	pH, Cond.
	8/11/81 (1010)	pH, cond., temp.
	8/11/81 (1045)	D.O.
	8/12/81 (0954)	Temp., D.O.
	8/12/81 (1000)	D.O.
Turbine Condensate	8/12/81 (1030)	Temp., D.O.

The plant site is shown in Figure 1. All water used at the plant is purchased from the City of Tacoma. Water use is approximately 30 to 35 MGD. Water use is metered and calculated daily. These values are used to provide a measure of effluent discharged. Although this method may slightly overestimate discharge volume because of evaporative losses through the plant, it is used because an in-line effluent venturi meter is believed to be inaccurate (Forsberg, personal communication).

Wastewater is treated by primary clarification, pure oxygen activated sludge, and secondary clarification. Bleaching wastewaters are routed directly to the activated sludge unit. Neutralization and nutrient addition is provided prior to secondary treatment. Treated wastewaters are discharged to inner Commencement Bay on the seaward side of the plant site (see Figure 1).

In addition to the main discharge, a small discharge of cooling water to the St. Paul Waterway was sampled (estimated flow during this inspection was 10,000 gpd). During low tide, seepage of water was noted from a shoreline depression bordering the St. Paul Waterway. Flow from this depression was not quantified, but was of the same order of magnitude as the small cooling water discharge.

Sampling Design

Wastewater samples were collected at three locations. Sample locations and types are summarized in Table 1 and locations are noted in Figure 1. Laboratories responsible for each of the analyses are summarized in Table 2.

Table 2. Laboratories providing analyses.

Constituents	Responsible Agency	Laboratory
Oils and grease, phenolics, nutrients, COD, solids, PBI, fecal coliform, salinity, metals, color, turbidity	WDOE	WDOE, Tumwater
Daphnid and oyster larvae bioassays	EPA	EPA, Manchester
Sediment (amphipod) bioassays	EPA	EPA, Newport, OR
Organic priority pollutants	EPA	California Analytical Laboratories, Inc., Sacramento, CA

A full range of conventional, priority pollutant, and bioassay analyses was performed on composite samples of the main mill wastewater stream before and after secondary treatment. Composite samples of primary effluent and secondary effluent were collected by St. Regis personnel and split with WDOE for conventional analyses. Selected conventional pollutant analyses were performed on grab samples of small-volume discharges from the turbine condensate discharge and seepage to the St. Paul Waterway. Grab samples were analyzed for phenols and oils, while temperature, pH, conductivity, and dissolved oxygen were determined in the field.

Laboratory and field blanks were obtained for each of the two automatic ISCO composite samplers used to collect priority pollutant samples. Results were reviewed for indications of contamination and, when appropriate, final results modified to account for possible contamination.

Sediment samples were obtained at three locations (Figure 1): near the main outfall; from the St. Paul Waterway; and from a crib in the Puyallup River at the old (discontinued) bleach plant discharge. More detailed information regarding the methods involved in obtaining the sediment samples will be found in the receiving water report (Johnson and Prescott, 1982).

Organic pollutant analytical results reported by California Analytical Laboratories were reviewed by Joseph Blazevich (EPA, Manchester). The data reported here are those with which the EPA reviewer concurred.

Bioassays were conducted on aliquots of all water and sediment samples. Main mill effluent flow was obtained from both St. Regis and City of Tacoma meters which measure city water supplied to the mill. As noted earlier, this method may slightly overestimate discharge volume because of evaporative losses through the mill, however it is used because an in-line venturi meter is believed to be inaccurate.

Flow from the turbine condensate discharge line was estimated using a magnetic flow meter.

RESULTS AND DISCUSSION

The following section discusses results and observations in three general categories: (1) compliance with effluent limitations; (2) specific priority and other pollutants; and (3) bioassay results.

Compliance with Effluent Limitations

The status of St. Regis' NPDES discharge permit is complicated. Discharge permit No. T-3598, setting conditions for St. Regis' discharge of

wastewater, expired December 31, 1977. A new permit was subsequently drafted by WDOE and its conditions accepted by St. Regis. However, EPA, which holds veto power over major state permits, has been holding this new permit in review status and has neither approved nor disapproved the permit. Neither the "old" nor the "pending" permit accounts for federal standards for "Best Conventional Treatment (BCT) or "Best Available Treatment" (BAT) because these standards have not yet been published. Under the present circumstances, it appears that the "old" permit limits provide the only legal basis for determining discharge compliance. Table 3 compares results obtained during this survey with permit limits contained in both the "old" and "pending" permits.

Table 3. Compliance with permit limits; BOD and suspended solids.

	Secondary Effluent		"Old" Permit		"Pending" Permit	
	St. Regis Sample	WDOE Sample	Monthly Average	Daily Maximum	Monthly Average	Daily Maximum
BOD (lbs/day)	7,800	7,000	6,800	13,400	7,300	14,000
Susp. Solids (lbs/day)	25,000	27,000	14,000	27,000	20,000	38,000

As noted in Table 3, during the survey St. Regis was exceeding "old" permit limits for monthly average BOD and suspended solids loadings. Compliance with regard to the "old" daily maximum suspended solids loading limit was marginal, while BOD loading was within the daily maximum limit. In comparison to "pending" permit limits, monthly average suspended solids loadings were being exceeded and compliance with the monthly average BOD loadings was marginal.

All instantaneous measures of effluent pH indicated compliance with permit limits requiring the effluent to remain in the 6 to 9 range.

Permit requirements for temperature simply re-state water quality standards for permissible increases in receiving water temperature due to source impact. Receiving water temperatures were measured during the receiving water study and are reported by Johnson and Prescott (1982). Determining compliance with the water quality standards is complicated in this case because it is difficult to determine what the ambient (natural background) temperature would have been without the St. Regis

discharge. Johnson and Prescott (1982) noted that in most areas the St. Regis plume was centered horizontally at approximately the 1 meter depth with more saline marine waters below and diluted Puyallup River waters above. Based on the water quality standards, an increase of about 1.1°C would be permissible at the dilution zone boundary. Table 4 shows temperatures and PBI values measured by Johnson and Prescott at Station A located just outside the outfall boom. Also noted are percent effluent values at each depth (based on PBI concentration) and theoretical temperatures at each depth based on mixtures of seawater (temperature = 12.4°C) and effluent (temperature = 38.5°C).

Table 4. Temperature and other data for station A (Johnson and Prescott, 1982).

Depth (meters)	PBI (mg/L)	Percent Effluent	Actual Temperature (°C)	Theoretical Temperature (°C)
0	150	12.5%	15.4	15.7
1	120	10.0%	14.8	15.0
2	9	0.8%	12.7	12.6
4	0	0%	12.4	12.4

As can be seen, actual and theoretical temperatures agree well. If the elevated temperatures at station A are due to the influence of St. Regis effluent then the surface temperature at station A represents an increase of 3.3°C above ambient conditions and thus the discharge appears to have been exceeding permit conditions. It should be noted that the station A surface temperature is outside the dilution zone which terminates one foot below the water surface.

As one moves to more distant stations, other influences seem to predominate and a clear link between elevated temperatures and the St. Regis discharge is difficult to establish. Theoretically, under the conditions experienced during the receiving water study a 5 percent concentration of effluent in the receiving water could result in a maximum temperature increase of 1.1°C. Using PBI data as a conservative tracer, the volume of receiving water which contained greater than 5 percent effluent under the conditions of the survey was a thin (1M) layer of water within an approximate 300-meter radius of the discharge. The lack of a clear relationship between elevated temperatures and plume location beyond Station A indicates that other influences (Puyallup River, solar heating and subsequent stratification, etc.) were predominant at the time of the survey.

Comparison of Laboratory Results

Laboratory procedures were not reviewed during this inspection because of time restrictions. However, both the WDOE and St. Regis effluent composite samples were split with the St. Regis laboratory for comparison of BOD and suspended solids results. These comparisons are given in Table 5.

Table 5. Comparison of split effluent sample results.

	St. Regis Composite Sample		WDOE Composite Sample	
	St. Regis Laboratory	WDOE Laboratory	St. Regis Laboratory	WDOE Laboratory
BOD (mg/L)	29	29	28	26
Susp. Solids (mg/L)	90	94	77	100

Agreement between laboratories was generally excellent, with a moderate discrepancy on the suspended solids analysis of the WDOE composite sample.

Specific Priority and Other Pollutants

The results of pollutant analyses are summarized in the following tables: conventional water quality analyses - Tables 6a and 6b; priority pollutant analyses - Table 7a and 7b; effluent priority pollutant loadings - Table 14 (found on page 25); and, tentatively identified organic compounds - Table 8.

Organics

Two 24-hr. composite samples of St. Regis mill wastewaters were analyzed for the 113 organic priority pollutants. One sample was collected immediately before wastewaters entered the pure oxygen (UNOX) activated sludge system; the other sample was collected after secondary treatment and clarification, prior to discharge. The results of these analyses, as well as a prior effluent analysis by St. Regis and analyses of sediments collected near the effluent outfall are summarized in Table 7a. Results of analyses of sediments collected from the crib at the old bleach plant discharge are summarized in Table 7b. Mass spectra of non-priority organics

Table 6a. Conventional analytical results - main mill waste stream.

	Primary Effluent St. Regis Sample	UNOX Influent WDOE Sample	Secondary Effluent St. Regis Sample	Secondary Effluent WDOE Sample	Permit Limits "Old Permit" Monthly Average	"Old Permit" Daily Maximum	Pending Permit Monthly Average	Pending Permit Daily Maximum
Flow (MGD)		32.2	32.2	32.2				
BOD_5 (mg/L)	200	190	29	26				
(lbs/day)		51,000	7,800	7,000	6,800	13,400	7,300	14,000
Total Suspended Solids (mg/L)	160	170	94	100				
(lbs/day)		45,700	25,000	27,000	14,000	27,000	20,000	38,000
COD (mg/L)	850	900	520	500				
Color (P.U.)	940	980	1,400	1,300				
PBI (mg/L)	2,500	2,900	1,200	1,200				
Turbidity (NTU)	120	140	89	91				
pH (S.U.)	7.6	9.3	6.9	6.5		6-9[1]		5-9[1]
				6.6+				
		8.7**		6.45**				
				6.35**				
Specific Conductivity (μmhos/cm)	1,420	1,390	1,360	1,360				
		1,550+		1,560+				
		1,400**		1,390**				
				1,350**				
Salinity (o/oo)	0.9		0.8					
Total Solids (mg/L)	1,300	1,300	1,200	1,100				
Total Non-volatile Solids (mg/L)	910	890	920	890				
Total Suspended Solids (mg/L)	160	170	94	100				
Total Non-volatile Suspended Solids (mg/L)	35	49	10	13				
NH_3-N (mg/L)		10		4.6				
NO_2-N (mg/L)		0.10		0.10				
NO_3-N (mg/L)		0.20		<.05				
Ortho-P (mg/L)		2.2		3.5				
Total Phosphate (mg/L)		6.7		4.3				
Dissolved Oxygen (mg/L)				0.2**				
				3.9**				
				1.05**				
Temperature (°C)		38.2**		39.2**		2		--[2]
		38.2**		37.8**				
Recoverable Phenolics (mg/L as Phenol)		0.39		0.39				
		1.7*		0.049*				
Grease & Oil (mg/L)		2*		1*				
		1*		<1*				
Fecal Coliform (col/100 ml)				36*				

*Grab sample, lab analysis.
**Grab sample, field analysis.
+Composite sample, field analysis.
[1]Range of acceptable instantaneous pH values.
[2]"No temperature increase shall be permitted which results in a water temperature of 66°F, nor shall an increase arising from the permittee's discharge be permitted in excess of "t", calculated by t = 52/(T-32) and "T" represents the resulting water temperature."

Table 6b. Conventional analytic results - other sources.

	Turbine Condensate	Seepage to St. Paul Waterway
Flow (MGD)	.012	
COD (mg/L)	62	(830)[1]
Color (P.U.)		46
PBI (mg/L)	45	18
Temperature (°C)	49	
pH (S.U.)	8.1	7.2
Spec. Cond. (μmhos/cm)	293	31,700
Salinity (o/oo)		20.3
Total Solids (mg/L)	220	
T. Non-vol. Solids (mg/L)	160	
T. Susp. Solids (mg/L)	14	
T. Non-vol. Susp. Solids (mg/L)	4	
NH_3-N (mg/L)	0.06	
NO_2-N (mg/L)	0.01	
NO_3-N (mg/L)	0.80	
O-PO_4-P (mg/L)	0.06	
T-PO_4-P (mg/L)	0.10	
Dissolved Oxygen (mg/L)	2.7**	0.0**
Grease and Oils (mg/L)	2*	
Total Metals (μg/L)		
As	<1	170
Cd	<10	
Cr	10	
Cu	20	
Hg	<0.2	0.32
Ni	<50	
Pb	<100	
Zn	110	

*Grab sample, lab analysis.
**Grab sample, field analysis.
[1]High in chloride, may have caused interference.

Table 7a. Priority pollutant analytical results - main mill waste stream and sediment near diffuser.

	UNOX Influent WDOE Date (µg/L)	Final Effluent St. Regis Consolidated Permit (µg/L)	Final Effluent WDOE (µg/L)	Sediment Near Diffuser WDOE (µg/Kg d.w.)
Total Metals				
As	8	5	16	21,000
Cd	<10	10	<10	2,200
Cr	40	50	20	25,000
Cu	410	210	100	160,000
Hg	0.24	1	<0.2	80
Ni	50	50	<50	25,000
Pb	<100	140	<100	70,000
Zn	110	90	53	100,000
Acid Extractables				
Phenol	68	5	--	91,000
2,4,6-trichlorophenol	3.7	1	--	T
Pentachlorophenol	--	--	--	840
Volatiles				
Chloroform	1,900	1,096	1,800	T
Dichlorobromomethane	6.0	--	7.0	--
1,1,1-trichloroethane	--	1	--	--
Toluene	13	9	3.0	T
Base Neutrals				
Naphthalene	--	--	4.4	7,200
Anthracene/phenanthrene	--	--	--	640

-- = None detected.
T = Trace; above level of detection, but below limit of quantification.

Table 7b. Priority pollutant analysis - sediment from old bleach plant crib.

	Sediment at Old Bleach Plant Eff. (µg/Kg d.w.)
Total Metals	
As	23,000
Cd	1,200
Cr	25,000
Cu	180,000
Hg	350
Ni	41,000
Pb	100,000
Zn	120,000
Acid Extractables	
Phenol	1,200
Volatiles	
Toluene	29
Base Neutrals	
Napthalene	2,100
Acenapthene	290
Anthracene/penanthrene	1,100
Fluorene	310
Fluoranthene	1,350
Pyrene	1,090
Benzo(a)anthracene/chrysene	290
Di-n-octyl phthalate	1,350

Table 8. Organic compounds, other than priority pollutants, tentatively identified during survey.

	UNOX Influent	Final Effluent	Receiving Water nr. Outfall	Sediment near Outfall	Old Bleach Plant Crib Sediment	Receiving Water St. Paul Waterway	St. Paul Waterway Sediment
Propanoic acid	TI	--	--	--	--	--	--
Hexanoic acid	--	--	--	TI	--	--	--
Benzoic acid	--	--	--	TI	--	--	--
Benzene acetic acid	--	--	--	TI	--	--	--
Benzene propanoic acid	--	--	--	TI	--	--	--
Tetradecanoic acid	--	--	--	--	--	--	TI
Pentadecanoic acid	--	--	--	--	--	--	TI
Hexadecanoic acid	--	--	TI	TI	TI	TI	TI
Octadecanoic acid	--	--	--	--	TI	--	TI
Methylhexadecanoate	--	--	TI	--	TI	--	--
Methyloctadecanoate	--	--	TI	--	--	--	--
Methylcyclopentaneundecanoate	--	--	--	--	--	--	TI
Octane	--	--	--	TI	--	--	--
2,6-dimethyl octane	--	--	--	TI	--	--	--
4-methyl phenol	--	--	--	TI	TI	--	TI
α,α,4-trimethyl-(S)-3-cyclohexene-1-methanol	TI	--	--	TI	--	--	TI
1-methyl-3-(1-methylethyl)benzene	--	--	--	TI	--	--	TI
Napthalene,1,2,3,5,6,7,8,8A-octahydro-1,8A-dimethyl-7-(1-methylethenyl-,[1S-(1α,7α,8Aα)]	--	--	--	--	TI	--	--
Napthalene,1,2,3,5,6,8A-hexahydro-4,7-dimethyl-1-(1-methylethyl)-(1S-cis)	--	--	--	--	TI	--	--
1,3,6,10-cyclotetradecatetraene,3,7,11-trimethyl 14-(1-methylethyl)-[S-(E,Z,E,E)]-	--	--	--	--	TI	--	--
1S,-3S,6R-(-)-4 carene	--	--	--	TI	--	--	--
1-(4-hydroxy-3-methoxy-phenyl) ethanone	TI	--	--	--	--	--	--
1-(1-cyclohexene-1-yl) ethanone	TI	--	--	TI	TI	--	TI
4-hydroxyl-4-methyl-2-pentanone	--	--	--	TI	--	--	--
2,3,4-trimethyl-2-cyclopenten-1-one	--	TI	--	--	--	--	--
3-hexen-2-one	--	--	--	TI	--	--	--
3-methyl-2-cyclohexen-1-one	--	--	--	--	TI	--	--
1,3,3-trimethyl-bicyclo[2.2.1]heptan-2-one	--	TI	--	--	--	--	--
3-hydroxy-4-methoxy-benzaldehyde	TI	TI	TI	--	--	--	--
4-hydroxy-3-methoxy-benzaldehyde	--	--	--	--	--	--	TI
Sulfur	--	--	--	--	TI	--	--
Thiobismethane	TI	TI	--	--	--	--	--
Dimethyldisulfide	TI	TI	--	TI	--	--	--
Dimethyltrisulfide	--	--	--	--	TI	--	--

found in samples were matched by computer with spectra in the EPA-NIH data bank. Results were reviewed by Joseph Blazevich (EPA-Manchester) and matches which passed this review are reported as "tentatively identified" compounds in Table 9.

Many of the compounds found and previously reported in bleached pulp mill effluents result from the physical and chemical degradation of wood fiber to form pulp and the subsequent chlorination of these compounds when the pulp is bleached. As McKague (1981) notes, "Lignin is partially degraded to a variety of monomeric phenols during the production of pulp and paper. Most of the phenols produced are substituted guaiacols or catechols whose formation may be rationalized by cleavage of bonds linking the basic propylguaiacol building blocks in lignin and by subsequent reactions such as chlorination during bleaching of the pulp." The resulting wastewater stream contains a wide array of chemicals. Nestmann, *et al.* (1980) state, "About 300 compounds have been reported in the literature as constituents of pulp-mill effluent." A partial summary of the classes of compounds which have been identified is given in Table 9.

The specific compounds present in any pulp mill effluent vary as a function of pulp source (hardwood, softwood), type of pulping process (sulfite, kraft, thermomechanical), presence or absence of bleaching, and degree and type of treatment (primary, aerated lagoons, air- or oxygen-activated sludge, etc.). Nonetheless, it appears that the adverse biological effects of compounds found in pulp mill waste streams may be roughly grouped in three categories:

I. Compounds which are acutely toxic to fish and other aquatic and marine organisms: These compounds include resin acids, chlorinated resin acids, unsaturated fatty acids, other acidic compounds (epoxystearic acid, dichlorostearic acid), and chlorinated phenolics (Easty, *et al.*, 1978). Compounds toxic to aquatic organisms, and found specifically in kraft mill effluents, include: inorganic sulfides, methyl mercaptan, sulfate soaps, resin, and fatty acid fractions of sulfate soaps (Walden, 1976). The acute toxicity of pulp mill effluents is generally substantially decreased by secondary treatment of wastewaters.

II. Sublethal effects; specifically inducement of abnormal shell development in oyster larvae. The oyster larvae bioassay test has been widely used in studying the effects of pulp mills (especially sulfite mills) on

Table 9. Summary of compounds identified in pulp mill effluents.

Compound Class	Literature Source
Chlorinated aliphatic hydrocarbons	1,2,3,4
Aromatic hydrocarbons	1,2
Chlorinated aromatic hydrocarbons	1
Phenolics	1,2,4,5,6
Chlorophenols	1,2,5,6
Catechols	1
Chlorocatechols	1,5
Vanillin	5,6
Chlorovanillin	5
Aldehydes	1
Chloroaldehydes	1,3,5
Quinones	1
Chloroquinones	1
Resin and carboxylic acids	1,2,4,5
Chlorinated resin & carboxylic acids	1,2,4
Ketones	1,6
Chlorinated ketones	3
Unsaturated fatty acids	4
Chlorinated unsaturated fatty acids	4
Esters of fatty acids	1

1. Nestmann, *et al.* (1980)
2. Wallin and Condren (1981)
3. Kringstad, *et al.* (1981)
4. Easty, *et al.* (1978)
5. Kachi, *et al.* (1980)
6. McKague (1981)

marine receiving waters. Based on the limited literature reviewed, no information clearly linking specific effluent components to abnormal shell development was located. Oyster larvae development is, however, quite sensitive to pulp mill effluents. Secondary treatment generally reduces the effects of the wastewaters with respect to this bioassay.

III. Mutagenic effects: Recently, researchers have begun using the Ames test to isolate mutagens in pulp mill effluents. Initial indications are that most of the mutagens are noted in the neutral fraction of the effluent. Kringstad, *et al.*, (1981) notes that "80% of the mutagenic activity present... was found in the neutral fraction... The fraction containing phenolic and acidic material did not show significant mutagenic activity, even after being concentrated 10 times..." Specific compounds which have shown strong mutagenic effects are listed in Table 10:

Table 10. Mutagenic compounds isolated from pulp mill effluents.

Compound	Reference
1,3-dichloroacetone	1
2-chloropropenal	1
tetrachloropropene	2
pentachloropropene	2

1. Kringstad, *et al.*, (1981)
2. Nestmann, *et al.*, (1980)

Several other compounds found in pulp mill wastewaters have also been shown to have mutagenic effects including some of the halomethanes, chlorinated ethanes and ethenes, chlorinated acetones and aldehydes; neoabietic acid, benzl chloride, and some halogenated p-cymenes (Kringstad, *et al.*, 1981; Nestmann, *et al.*, 1980).

There are, then, a wide variety of organic chemicals in pulping wastewaters. The overlap between the chemicals listed above and the 113 organic "priority pollutants" is

marginal and is limited primarily to the chlorinated aliphatics, phenol, and chlorinated phenols. In addition, many of the compounds listed above were isolated from and identified in pulping wastewaters using different sampling, extraction, and analytical techniques than those employed during this study. It is, therefore, possible that non-priority compounds with adverse biological effects may have been present in the wastewater samples, but were not extracted and/or identified.

The priority pollutants found in wastewater samples before and after secondary treatment are noted in Table 7a. Table 11 compares priority pollutant concentrations in the final effluent to EPA criteria for these pollutants in receiving waters to protect marine and aquatic life, as well as human health. Ratios of effluent concentration to receiving water criteria are calculated. If these ratios are greater than 1, they are flagged and provide a rough estimate of the dilution ratio required to bring effluent concentrations down to criteria concentrations.

Chloroform: Chloroform was the priority pollutant found in the highest concentration (1,800 to 1,900 μg/L) in St. Regis wastewaters. It was also reported in St. Regis' consolidated permit (1,096 μg/L) and appears to be a common substance in bleached pulp wastewaters (Wallin and Condren, 1981; Kringstad, *et al.*, 1981; Nestmann, *et al.*, 1981; Easty, *et al.*, 1978). The effluent loading of 480 lbs/day is the highest loading rate for an organic priority pollutant noted in sources monitored to date. Chloroform was also noted in receiving water and sediment samples obtained near the outfall (Johnson and Prescott, 1982).

Chloroform is commonly formed when freshwaters containing organic matter are chlorinated. As noted in Table 11, the effluent chloroform concentration exceeds two of the EPA receiving water criteria. In addition, the receiving water report (Johnson and Prescott, 1982) notes that increased mortality to oyster larvae have been noted at concentrations as low as 50 μg/L. The large chloroform loading from St. Regis is probably one of the most significant findings of this study and is discussed in some detail by Johnson and Prescott (1982).

Dichlorobromomethane: Another halomethane, dichlorobromomethane, was noted at much lower concentrations (6 to 7 μg/L) in both influent and effluent samples. It has also been previously noted in pulp mill effluents (Wallin and Condren, 1981; Kringstad, *et al.*, 1981). Concentrations noted were well below EPA receiving water criteria.

Table 11. Comparison of main effluent priority pollutant results to USEPA receiving water criteria (all concentrations expressed in μg/L).

Pollutant	Effluent Load (lbs/day)	Effluent Conc. (μg/L)	Water Quality Criteria: Freshwater Criteria Acute	Freshwater Criteria Chronic	Freshwater Sample/Criteria Ratio Acute	Freshwater Sample/Criteria Ratio Chronic	Saltwater Criteria Acute	Saltwater Criteria Chronic	Saltwater Sample/Criteria Ratio Acute	Saltwater Sample/Criteria Ratio Chronic	Human Health, Food Intake (Fish)* Criteria	Human Health, Food Intake (Fish)* Sample/Criteria Ratio
Arsenic	4.3	16	440[1]	40[1]	.04	0.40	508[1]	Unk.	0.03	Unk.	.0175*	/910/
Chromium	5.4	20	2,200[2,3]	44[3]	.01	0.45	10,300	Unk.	0.002	Unk.	3.4×10^{6}	6×10^{-5}
Copper	26.9	100	12[2]	5.6	/8.3/	/18/	23	4.0	/4.3/	/25/	None	None
Zinc	14.2	53	180	47	0.3	/1.1/	170	58	0.3	0.9	None	None
Chloroform	483	1,800	28,900	1,240	0.06	/1.5/	Unk.	Unk.	Unk.	Unk.	15.7*	/110/
Dichlorobromomethane	1.9	7.0	11,000	Unk.	0.001	Unk.	12,000	6,400	0.001	0.001	15.7*	0.45
Toluene	0.81	3.0	17,500	Unk.	2×10^{-4}	Unk.	6,300	5,000	5×10^{-4}	0.001	424,000[t]	7×10^{-6}
Napthalene	1.2	4.4	2,300	620	.002	.007	2,350	Unk.	.002	Unk.	Unk.	Unk.

[1] Criteria for trivalent inorganic arsenic.
[2] Based on a total hardness of 50 mg/L as $CaCO_3$.
[3] Criteria for trivalent chromium.
Unk. = Unknown.
* = These criteria assume human consumption of fish from waters with pollutant concentrations as noted. Concentrations given are those which EPA calculated would result in one additional cancer per 10^6 exposures.
t = Based on toxicity.

Toluene: Toluene (methylbenzene) was identified in both influent and effluent samples (13 and 3 μg/L, respectively) as well as in St. Regis' consolidated permit effluent analysis (9 μg/L). The source of this toluene is not known, but it is structurally similar to many of the benzene ring-based compounds found in pulping wastewaters. Toluene's presence in pulp mill effluents appears to be common (Nestmann, *et al.*, 1980; Wallen and Condren, 1981). The concentrations seen were far below EPA receiving water criteria.

Napthalene: Napthalene was detected in the effluent sample at 4.4 μg/L. Although napthalene has been associated with the pulp and paper industry (Wallen and Condren, 1981), it is not generally reported as a characteristic compound in pulp mill effluents and is generally associated with solvents, lubricants, and motor fuels. The source of this compound in St. Regis' effluent is unknown.

One priority pollutant, acenapthene, which was not noted in wastewaters during this survey has been reported in pulp mill wastewaters at a relatively high concentration: 1,000 μg/L (Nestmann, *et al.*, 1980). Although it was not isolated in the wastewater samples, it was identified in sediment samples from both the old bleach crib and St. Paul Waterway.

In addition to priority organic pollutants, other compounds found in the samples were "tentatively identified" as explained earlier by computer matching of mass spectra with records in the EPA-NIH data bank. Concentrations of these compounds were not determined. These compounds are noted in Table 8. Compounds "tentatively identified" in wastewater samples are addressed below.

3-hydroxy-4-methoxy benzaldehyde: This compound was identified in both wastewater samples. It is a positional isomer of vanillin (more commonly reported in pulping wastewaters as 4-hydroxy-3-methoxy benzaldehyde). The mass spectra of these two isomers are very similar. Vanillin is a common constituent of kraft pulp mill wastewaters and is noted to be one of the major phenols in unbleached white water (McKague, 1981). This author reported concentrations of 230 to 490 μg/L in untreated kraft mill effluent. Keith (1976) reported concentrations of 70 to 410 μg/L in treated kraft mill effluent.

1-(4-hydroxy-3-methoxy phenyl) ethanone (also known as [AKA] Apocynin, acetovanillone, 4-hydroxy-3-methoxy-acetophenone): This compound was found in the UNOX influent sample. It is reported by McKague (1981) as being one of the major phenols in unbleached white water. This author reported concentrations of 90 to 320 μg/L in untreated kraft mill effluent. Nestmann, *et al.*, (1980) report a concentration of 1,000 μg/L in pulp and paper mill effluents. Keith (1976) reports concentrations of 120 to 370 μg/L in treated kraft mill effluents.

α,α,4-trimethyl-(S)-3-cyclohexene-1-methanol (AKA: α-terpineol, p-menth-1-en-8-ol: This compound was found in the UNOX influent sample and was identified by Keith (1976) in wastewaters from two unbleached kraft mills. Treatment appeared to lower concentrations in effluents to 2 μg/L or less. This compound can be found in various plant oils including "long-leaf pine oil" (Windholz, *et al.*, 1976). This compound was also noted in sediment samples taken near the outfall and in the St. Paul Waterway. The only reference to its biological properties was found in the Merck Index (Windholz, *et al.*, 1976) which notes that it is an antiseptic.

1,3,3-trimethyl-bicyclo[2.2.1]heptan-2-one (AKA: d-fenchone: This compound was identified in the effluent sample. Keith (1976) mentions that other investigators have noted an increase in fenchone concentrations after treatment of pulp mill wastewaters. Keith reports a concentration of 15 μg/L in secondary treated effluent from a kraft mill. This compound was not noted in any of the receiving water or sediment samples, and no reference was found to its biological effects.

Other "tentatively identified" compounds noted in the St. Regis wastewater samples were 1-(1-cyclohexene-1-yl) ethanone, thiobismethane (AKA dimethyl sulfide), and dimethyldisulfide. Little additional relevant information regarding these compounds was found during literature review.

Metals

Four metals were quantified in the St. Regis effluent: arsenic; chromium; copper; and zinc. In addition, chromium, copper, and zinc were detected in the turbine condensate discharge and arsenic and mercury were detected in the seepage to the St. Paul Waterway. Sediment metals were also determined and are discussed in more

detail in the receiving water report (Johnson and Prescott, 1982). These data are included in Tables 6b, 7a, 7b, and 11. Main effluent metals loadings are noted in Table 14.

Copper was detected in elevated concentrations in both the UNOX influent (410 μg/L) and final effluent (100 μg/L). St. Regis' consolidated permit application reported an effluent concentration of 210 μg/L. Elevated copper concentrations in kraft mill effluents have been noted previously. Singleton, *et al.*, (1982), for instance, reported a concentration of 260 μg/L of copper (all of which was present in the dissolved form) from the Weyerhaeuser Kraft Mill in Everett. The source of this copper is presently unknown, but should not be difficult to ascertain by sampling the effluents from discrete processes.

Johnson and Prescott (1982) reviewed Commencement Bay sediment metals data. The St. Regis outfall and bleach plant crib sediment samples are anomalous, in that they contain copper at higher concentrations relative to other metals (Zn, Pb, etc.) when compared to other Commencement Bay sediments. As noted earlier, the bleach plant crib served as the St. Regis outfall location until 1970. Thus, elevated copper concentrations in both the crib sediment and the sediment collected near the present outfall may be due to copper in St. Regis' effluent.

The only other notably elevated metal concentration was the 170 μg/L of arsenic found in the seep (tide pool) on St. Regis' St. Paul Waterway shore at low tide. The sources of this arsenic is unknown. The flow from this seep was low and thus the loading from this source is low.

Conventional Parameters

The results of conventional analyses of St. Regis survey samples are contained in Tables 6a and 6b. BOD, suspended solids, temperature, and pH are discussed in the permit compliance section.

The results of the conventional analyses are typical of treated kraft mill effluent. Effluent dissolved oxygen was relatively low (0.2 to 3.9 mg/L) but initial dilution in the receiving water was adequate to prevent a significant decrease in receiving water dissolved oxygen concentrations.

Color and Pearl-Benson Index (PBI) values for the influent and effluent samples were typical of kraft wastewaters. As is usual, secondary treatment substantially increased the color of the

wastewater. The PBI test was initially developed to provide a measure of the strength of spent sulfite liquor. The test is positive for organic compounds with phenolic radicals which are not fully substituted and has been subsequently applied to wastewaters from various wood and pulp operations. Because PBI is non-specific in its response to a range of phenolic-type compounds, results are difficult to interpret. PBI was decreased by about 50 percent by secondary treatment. PBI values and oyster larvae bioassay results have often been correlated. Correlations vary depending on the source of the sample water and it appears that no clear cause/effect relationship has been established between PBI and larval abnormalities. Oyster larvae test results, discussed later, showed a decrease in adverse response in wastewater after secondary treatment.

Bioassay Results

Bioassays were performed on both water and sediment samples. The oyster larvae and daphnid bioassays were used to assess water and wastewater samples, while the amphipod bioassay was used to assess sediments. The results of these tests are summarized in this section.

Oyster Larvae and Daphnid Bioassay Results

Oyster larvae and daphnid bioassays were conducted by the EPA laboratory in Manchester, Washington. The results of these tests were reported in detail in a January 22, 1982 memorandum (Cummins, 1982) to James Hileman (Region 10, EPA). The results of these tests have been abstracted here. The reader is directed to the original memorandum for the full details of the tests.

The daphnid acute bioassay was performed by exposing daphnids for 48 hours to 100 percent concentrations of UNOX influent and secondary effluent. Survival was 5 percent and 80 percent, respectively, with control exhibiting 100 percent survival. As noted by Cummins (1982), "It was not possible to make direct comparisions between daphnid responses and the oyster larval responses because of the differences in the sample concentrations tested. However, the results of the daphnid assay confirmed the relative acute toxicity described by the oyster larvae test; i.e., the UNOX influent was more acutely toxic than the secondary treatment effluent."

Briefly, the oyster larvae bioassay involves seeding oyster embryos to a test solution. In this case, wastewater samples were diluted from original strength to .02 percent to 20 percent strength with uncontaminated sea water. After 48 hours, normal and abnormal larvae are counted and percent mortality and abnormality are calculated. Control tests are run and mortality and abnormality results can then be corrected to yield net values.

Larvae used in the oyster larvae test suffered relatively high control mortalities and abnormalities; exceeding the 10 percent abnormality criterion set by ASTM for these tests. The most likely cause of this problem was poor quality gametes. Despite this, Cummins states, "net (emphasis added) larval abnormality and mortality values were calculated as shown to provide some comparative information on the relative toxicities of the samples that is considered useful."

Table 12 summarizes the results of these tests. Increased abnormalities were noted in the 20 percent and 2 percent dilution of UNOX influent and secondary effluent. Both mortality and abnormality seemed to be more marked in the UNOX influent sample, indicating that secondary treatment reduced the toxicity of wastewater to oyster larvae. The response noted was typical of kraft wastewaters. The specific components of this type of wastewater which are responsible for the abnormality response are not well defined. Common interferences with this test (low dissolved oxygen, low salinity, extreme pH values) were probably not responsible for observed abnormalities as these parameters stayed within acceptable ranges.

Amphipod Bioassay Results

Amphipod bioassays were conducted by the EPA Marine Science Center in Newport, Oregon. The results of these tests are included in an interim report (Swartz, *et al.*, 1981). This test is presently in the research and development stage and in the case of the St. Regis sediment samples, was performed without replication. For these reasons, the results should be interpreted with caution.

Bioassays were performed by adding 20 individual amphipods (*Rhepoxynius abronius*) to a test beaker containing a 2-cm layer of sediment and 800 ml of seawater. After 10 days, the contents of the beaker was seived and surviving amphipods counted. Yaquina Bay control sediments had a mean survival of 18.2 individuals. The results of the St. Regis samples are summarized in Table 13.

Table 13. Amphipod bioassay results.

Sample	Number of Amphipods Surviving (out of 20)
Sediment near St. Regis Outfall	0
Old Bleach Crib Sediment	0
St. Paul Waterway Sediment	3

Table 12. Oyster larvae bioassay test results.

Percent Sample	UNOX Influent	Final Effluent	Commencement Bay near St. Regis Outfall	St. Paul Waterway	Dash Point (Background)
	Mean Net Mortality				
100%			0*	22.8	0*
20%	17.8	2.5			
2%	5.9	0.5			
0.2%	0*	0*			
0.02%	0*	0*			
	Weighted Mean Net Abnormality				
100%			100	98.3	2.7
20%	100	100			
2%	91.4	18.8			
0.2%	0*	1.8			
0.02%	3.8	0*			

*Control mortality or abnormality greater than observed in test.

Amphipod survival was very low in these sediments. Further interpretation is provided in the WDOE St. Regis receiving water report (Johnson and Prescott, 1982).

CONCLUSIONS AND RECOMMENDATIONS

During this survey, St. Regis was discharging priority pollutant loadings as noted in Table 14.

Table 14. St. Regis effluent - priority pollutant loadings.

Constituent	Loading (lbs/day)
Chloroform	483
Copper	26.9
Zinc	14.2
Chromium	5.4
Arsenic	4.3
Dichlorobromomethane	1.9
Naphthalene	1.2
Toluene	0.81

The impact of these and "conventional" pollutant loadings on the receiving waters, as well as the status of sediments in the study area, are addressed in the receiving water report (Johnson and Prescott, 1982).

One of the most significant findings was the high chloroform concentrations in the final mill effluent. The chloroform loading from this source (483 lbs/day) is the highest loading for an organic priority pollutant so far attributed to a Commencement Bay source. The potential biological impacts of this chloroform loading are discussed in some detail in the receiving water report (Johnson and Prescott, 1982).

The sampling and analytical method employed did not lend itself to detection of a number of additional chlorinated and unchlorinated organic compounds which have been reported in the literature dealing with wastewaters from pulp mills. Additional sampling, including perhaps concentration of samples on XAD resin, and more specific analytical approaches may result in the identification of additional potentially toxic and/or mutagenic compounds.

Memo to Fred Fenske
St. Regis Paper Company Class II (Priority Pollutants Survey, August 11-12, 1981

The permit status of St. Regis is complicated by the lack of EPA action on the proposed permit and because of EPA delay in issuing BAT/BCT regulations. Based on the "old" permit conditions, St. Regis was exceeding monthly average BOD and suspended solids limits, while compliance with daily maximum suspended solids limits was marginal during the survey. pH limits were being met.

BY:cp

Attachment

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