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QUALITY OF GRAYS HARBOR PULP MILL EFFLUENTS
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by
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ABSTRACT

As part of a multi-agency study on low survival of Chehalis River coho salmon, chemical analyses and bioassays of final effluents from the Weyerhaeuser and ITT pulp mills in Grays Harbor were conducted on samples collected during unannounced inspections between March and June, 1989. The primary differences observed in effluent chemistry were order of magnitude higher concentrations of chromium and chloroform in ITT effluent and similarly elevated concentrations of phenols, quaiacols, catechols, resin acids, and fatty acids in Weyerhaeuser effluent. Based on TOX concentrations, the combined load of total halogenated material discharged to the inner harbor was estimated to be 8,800 pounds per day.

Weyerhaeuser effluent failed 3 of 8 rainbow trout bioassays (0-13% survival in 65% effluent) and showed varying degrees of toxicity in 4 of 8 Microtox assays. ITT effluent showed no significant toxicity in these two tests. Both discharges were consistently, extremely toxic in bioassays with Pacific oyster larvae and echinoderm sperm cells. Receiving water dilution may not be adequate to reduce effluent concentrations to no effect levels observed in these two tests. Concentrations of the various chemicals analyzed were too low to account for effluent toxicity indicating new lines of investigation should be followed in future studies. Other potentially responsible constituents are discussed in the report. These data, as well as data collected by EPA and industry, show effluent quality during coho smolt bioassays and live-box studies conducted by other study participants was generally typical of normal discharges.

INTRODUCTION

The Washington Department of Ecology (Ecology) monitored the quality of final effluents from the Weyerhaeuser Cosmopolis and ITT Rayonier pulp mills in Grays Harbor during the spring of 1989. This was part of a two-year multi-agency study to find the cause of low survival of Chehalis River coho salmon (Seiler, 1989). The study was lead by the Washington Department of Fisheries (Fisheries) with other cooperating agencies including the U.S. Fish and Wildlife Service (USFWS), National Marine Fisheries Service (NMFS), Oregon State University, University of Washington, and U.S. Environmental Protection Agency (EPA).

During the first year of the study, Ecology conducted inspections of the Weyerhaeuser (Hallinan, 1989) and ITT (Reif, 1989a) mills, assessed the extent of chemical contamination of Grays Harbor bottom sediments (Johnson and Coots, 1989), and analyzed wastewater samples being tested by other study participants for toxicity to coho smolts (Appendix A). Objectives of Ecology's monitoring program in 1989 were to further analyze the chemical character and toxicity of the Weyerhaeuser and ITT effluents, and evaluate effluent variability, determining in particular if effluents discharged during experiments for the salmon survival study were representative of typical discharges. Preparation of this report afforded the additional opportunity to make some preliminary estimates of contaminant loads to the inner harbor and dilution requirements, based on results of effluent bioassays.

DESCRIPTION OF THE MILLS

Figure 1 shows the location of the mills and their outfalls. Weyerhaeuser discharges effluent to the South Chehalis River Channel twice each day for approximately 2 to 2-1/2 hours during ebb tide (National Pollution Discharge Elimination System (NPDES) permit no. WA-000080-9). ITT has a continuous discharge to the North Chehalis River Channel (NPDES permit no. WA-000307-7). Weyerhaeuser discharges an average of 22 million gallons per day (MGD); the ITT discharge averages 20 MGD.

Both mills use the sulfite process to produce bleached pulp. Weyerhaeuser is a magnesium-based acid sulfite mill that bleaches with chlorine and hypochlorite. ITT is a sodium-based acid sulfite mill using the bleaching sequence chlorine-hypochlorite-chlorine dioxide.

Approximately 15 - 20% of Weyerhaeuser process wastewater is treated by an activated sludge process. The treated effluent and remainder of the process wastewater is passed through a series of four lagoons designated ponds A, B, C, and D. Ponds B, C, and D are aerated. Design retention time of the lagoons is 40 hours. In order to control growth of fecal coliform bacteria (Klebsiella), wastewater pH is reduced to 2.5 - 3.0 by adding sulfuric acid at the outlet of pond C. Waste-activated sludge is also introduced at the pond C outlet.

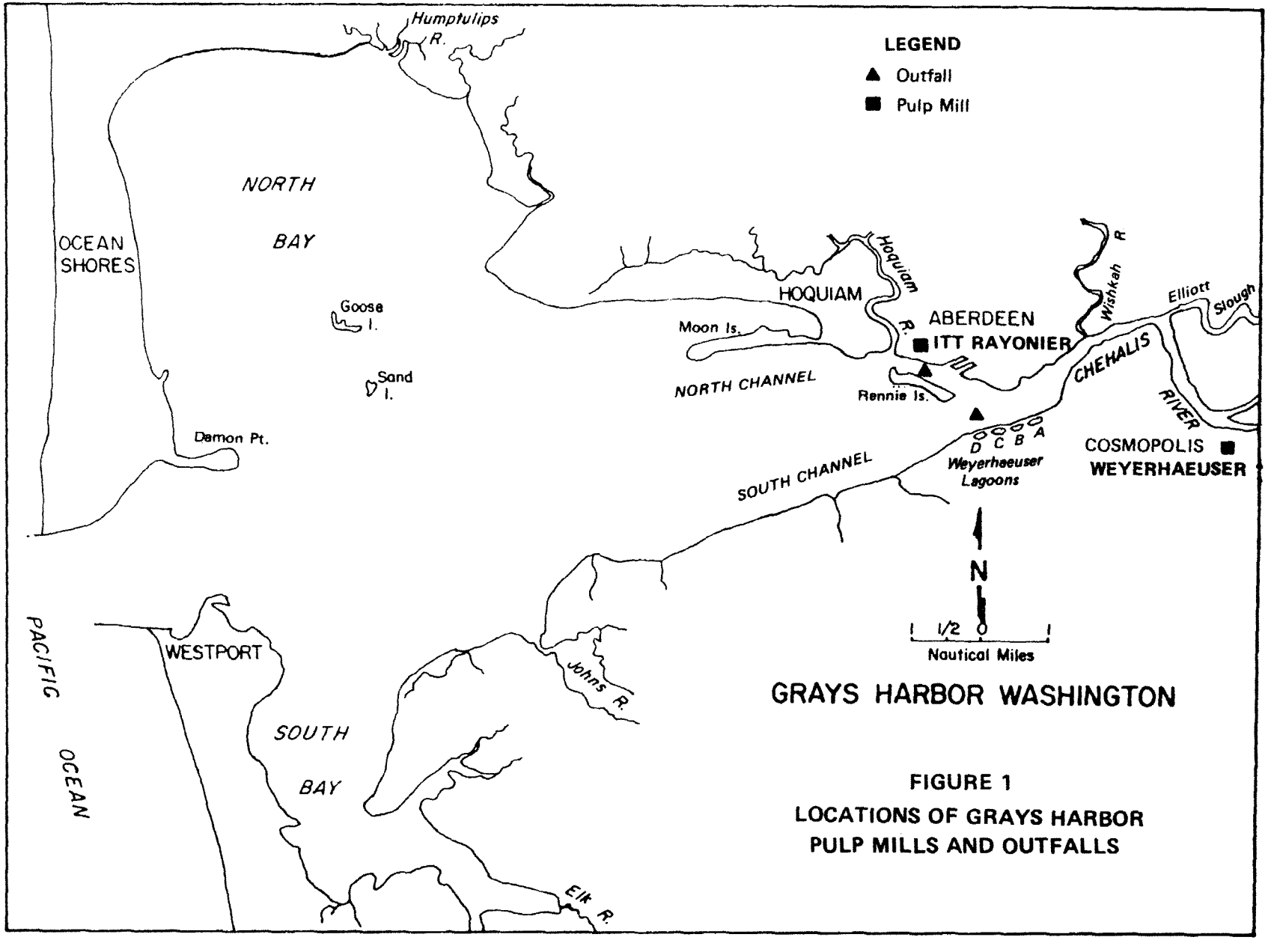

FIGURE 1
LOCATIONS OF GRAYS HARBOR
PULP MILLS AND OUTFALLS

ITT uses an activated sludge process to treat their mill wastewater, the sludge is then settled in three secondary clarifiers. Retention time is approximately 8 hours. ITT's effluent does not require treatment for Klebsiella.

By Ecology order, Weyerhaeuser must achieve fecal coliform control without violating their NPDES permit limit for pH (5 - 9) by March 1, 1991. To meet this requirement, the mill is going to oxygen delignification. This is expected to reduce total suspended solids (TSS) and biochemical oxygen demand (BOD) concentrations to levels allowing direct discharge from pond A, by-passing ponds B, C, and D where re-growth of Klebsiella occurs. Discharge will be continuous rather than intermittent; the existing outfall will be used. An additional change being implemented at both Weyerhaeuser and ITT is maximum chlorine dioxide substitution for chlorine as part of their dioxin control strategy.

STUDY DESIGN

Pulp mill effluent quality was an important or potentially important factor in two experiments conducted during the 1989 salmon survival study. The first was a large-scale bioassay of the Weyerhaeuser and ITT effluents to test their effects on smoltification and survival of coho smolts. This was accomplished by collecting daily tanker truck loads of effluent to feed a system of 3,000 - 6,000 gallon effluent reservoirs and diluters specially constructed to supply effluent at concentrations of 5, 10, and 30 percent. Smolts were exposed for up to 14 days, then held for nine months at the USFWS Marrowstone Island field station during which time the effect of the smolt's exposure to effluent was evaluated through blood cortisol (stress), immune competency, seawater challenge (mortality, gill ATPase, plasma sodium), growth, survival, and autopsy. The coho bioassay began April 21 and ended May 5.

The second experiment potentially influenced by mill effluents was a live box study. Net pens holding approximately 400 coho smolts were deployed by Fisheries at five sites in inner Grays Harbor, including one approximately one nautical mile below each of the pulp mill outfalls, and a control site in North Bay. These fish were also exposed for up to 14 days. They were then transferred to the NMFS facility at Manchester, and held for nine-months. The measurements performed on these fish were similar to those described for the bioassay. Two live box studies were conducted: April 22 - May 7 and May 12 - 28.

Ecology monitored pulp mill effluent quality between March 7 and June 20. This bracketed the bioassay and live box experiments, and covered the period coho smolts move through Grays Harbor to sea. Effluent was collected on eight separate occasions at Weyerhaeuser and four at ITT. Greater sampling effort was devoted to Weyerhaeuser because of its history of failing the rainbow trout bioassay condition of its NPDES permit, and because Weyerhaeuser produces multiple grades of pulp in contrast to the single grade produced by ITT. Two effluent collections were made at Weyerhaeuser and one at ITT during the salmon survival experiments of April 21 - May 28. The mills were not told in advance when samples would be collected.

Selection of chemicals to be analyzed during this study was based on results of Ecology's effluent analyses during the first year of the salmon study and on a review of the literature on toxicity of pulp mill effluents. Target chemicals included metals (cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc), a subset of EPA priority pollutant compounds (volatiles and selected phenols), guaiacols, catechols, resin acids, and fatty acids. Conventional variables analyzed in the effluents were temperature, pH, specific conductance, color, TSS, total recoverable phenolics, and total organic halides (TOX). Flow data were obtained from the mills. Table 1 lists the individual chemicals analyzed.

Hundreds of potentially toxic chemicals have been reported to occur in pulp mill effluent (Holmbom and Lehtinen, 1980; Keith, 1976; Kringstad, et al., 1981; Lindstrom and Osterberg, 1986; McKague, 1981; McLeay and Associates, 1986; Nestmann et al., 1980; Voss, 1983). Recognizing that it was not possible to analyze all possible constituents, the monitoring program relied heavily on bioassays to detect changes in effluent quality as recommended by Walden (1976). The following tests were employed:

- Rainbow trout (Oncorhyncus mykiss, formerly Salmo gairdneri) - Percent survival
- Oyster larvae (Japanese oyster, Crassostrea gigas) - Percent developmental abnormality
- Echinoderm sperm cell (sea urchin, Strongylocentrotus spp., and sand dollar, Dendraster excentricus) - Fertilization success
- Microtox^{R} (Photobacterium phosphoreum, a marine bacterium) - Percent decrease in luminescence

These tests represented a broad range of species and endpoints varying from lethal to sublethal effects. The NPDES permits of both mills require 80% survival of rainbow trout during 96-hour exposure to 65% effluent. The oyster and echinoderm bioassays were selected in view of their ecological relevance to the Grays Harbor estuary and sensitivity to pulp mill effluents. Both bioassays are part of the biomonitoring requirements in new NPDES permits to be issued in draft form during the summer of 1990. The Microtox assay offered the advantages of being a rapid, inexpensive test requiring small sample volumes and being (reportedly) comparable to rainbow trout in sensitivity to pulp mill effluents (Blaise et al., 1987). Coho or other migratory salmonids were not used because routine bioassay methods have not been developed for these species.

METHODS

Sampling Methods

Weyerhaeuser samples were collected from the catwalk immediately upstream of the outfall gate on Pond D (Figure 2). Sampling was conducted over a period of two hours during one of the twice-daily discharge cycles. ITT samples were collected over a four-hour period from the effluent pipe in the wet well at the outfall. A longer sampling time was employed at ITT because of its continuous discharge.

Table 1. Effluent analyses.

Conventionals

pH
specific conductance
color
total suspended solids
total recoverable phenolics
total organic halides

Metals

cadmium
chromium
copper
lead
mercury
nickel
silver
zinc

Volatiles

chloromethane
bromomethane
vinyl chloride
chloroethane
methylene chloride
acetone
carbon disulfide
1,1-dichloroethene
1,1-dichloroethane
trans-1,2-dichloroethene
cis-1,2-dichloroethene
chloroform
1,2-dichloroethane
2-butanone
1,1,1-trichloroethane
carbon tetrachloride
vinyl acetate
bromodichloromethane
1,2-dichloropropane
trans-1,3-dichloropropene
trichloroethene
dibromochloromethane
1,1,2-trichloroethane
benzene
cis-1,3-dichloropropene
2-chloroethylvinylether

Volatiles (Continued)

bromoform
4-methly-2-pentanone
2-hexanone
tetrachloroethene
1,1,2,2-tetrachloroethane
toluene
chlorobenzene
ethylbenzene
styrene
total xylenes

Phenols/Guaiacols/Catechols

4-chloro-3-methylphenol
pentachlorophenol
2,4,6-trichlorophenol
2-nitrophenol
guaiacol
2-methylphenol
2-chlorophenol
2,4,5-trichlorophenol
4-allylguaiacol
4-propenylguaiacol
acetophenone
4-nitrophenol
2,4-dimethylphenol
4-methylphenol
phenol
2,4-dichlorophenol
tetrachloroguaiacol
4,5,6-trichloroguaiacol
6-chlorovanillin
5,6-dichlorovanillin
tetrachlorocatechol
4-chlorocatechol
4,5-dichloroguaiacol
trichlorosyringol
4,5-dichlorocatechol
a-terpineol
4-chloroguaiacol
3,4,5-trichlorocatechol

Resin Acids/Fatty Acids

hexadecanoic acid
octadecanoic acid

Table 1. (Continued)

Resin Acids/Fatty Acids (Continued)

linoleic acid
levopimaric acid
oleic acid
pimaric acid
palmitoleic acid
sandaracopimaric acid
neoabietic acid
retene
abietic acid
9,10-dichlorostearic acid
dichlorodehydroabietic acid
14-chlorodehydroabietic acid
12-chlorodehydroabietic acid
dehydroabietic acid
eicosatrienoic acid
palustric acid
isopimaric acid

Bioassays

rainbow trout
microtox[R]
oyster larvae
echinoderm sperm cell

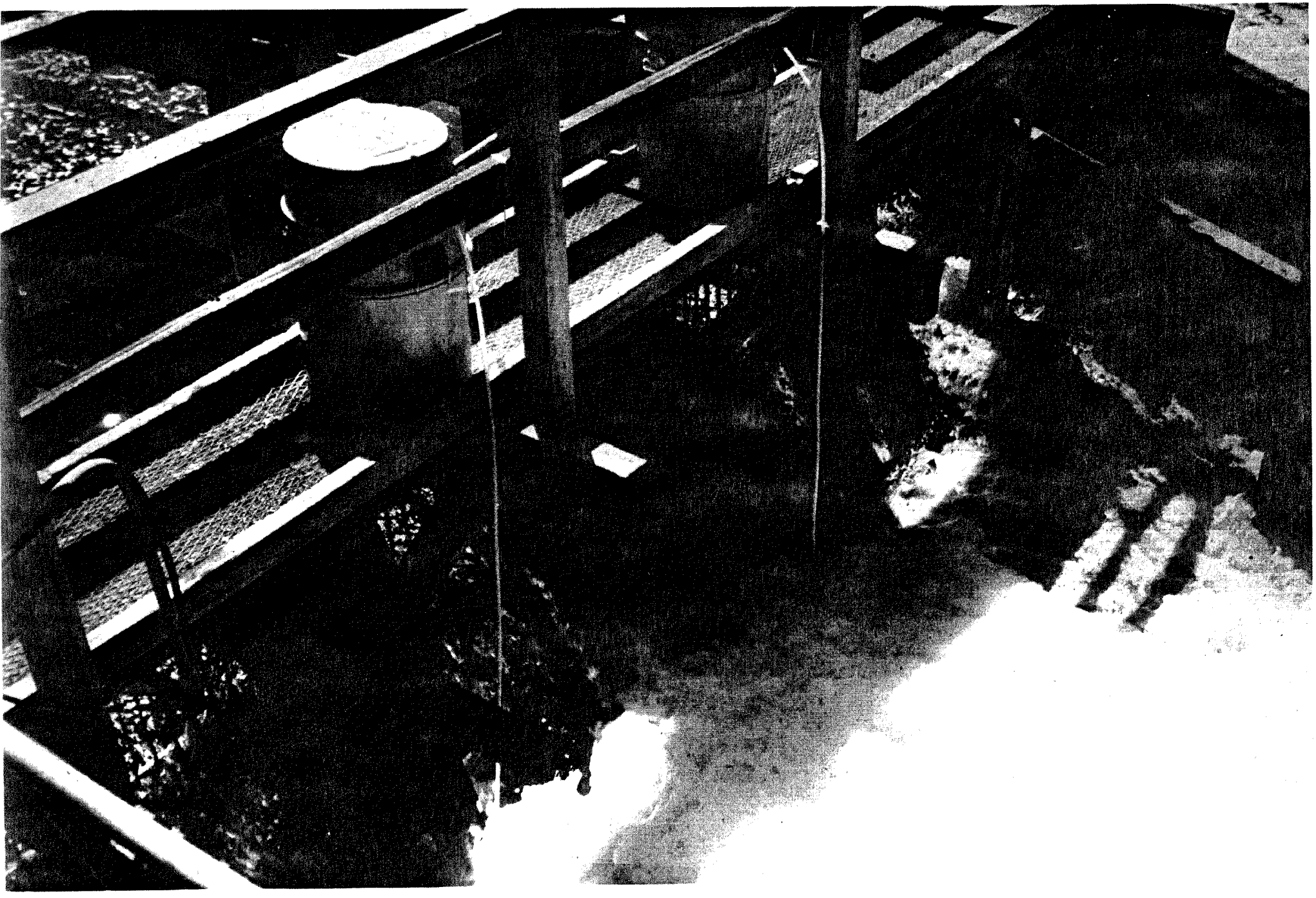

Figure 2. Collecting duplicate effluent samples at Weyerhaeuser

Temperature and pH were measured in the field on four grabs per sampling event. TOX and volatiles samples were single grabs collected midway through each sampling period. Remaining chemical analyses were conducted on samples collected with an ISCO automatic compositor fitted with a stainless steel intake strainer (3/8 inch openings), teflon sampling tube, and glass sample carboy. Weyerhaeuser samples were collected by lowering the sampling tube into the waste stream. ITT samples were collected by plumbing the sampling tube (without strainer) directly into the discharge pipe. Sampling equipment was cleaned prior to use by washing with Liqui-Nox^R detergent, followed by sequential rinses with tap water, 10% nitric acid, de-ionized water, pesticide-grade methylene chloride, and pesticide-grade acetone.

Approximately 15 liters of effluent were composited from each mill for chemical analysis. At Weyerhaeuser, the compositor was set to collect 600 - 700 mL of effluent every 5 minutes; sampling frequency at ITT was 900 - 1,000 mL every 15 minutes. Because the compositors could not hold the large volumes required for bioassays (approximately 90 liters), all bioassay samples were composites of four grabs spaced over the sampling period.

Field blanks were prepared during four of the eight effluent collections. These consisted of blank water (distilled, de-ionized water passed through activated carbon filters) pumped through a compositor set up at the effluent sampling site, and transferred to appropriate sample containers. TOX and volatiles field blanks were poured directly into sample containers. All samples were kept on ice during collection and while being transported to the Ecology/EPA Manchester Laboratory the following day. The pH of resin and fatty acids samples was adjusted to 10 in the field by adding concentrated sodium hydroxide; samples for analysis of phenols (phenols, quaiacols, and catechols) were adjusted to pH 2 with concentrated sulfuric acid. Sample containers and handling are further described in Appendix B.

Effluent Analysis

Methods of chemical analysis and bioassays are referenced in Table 2. The method for phenols, guaiacols, and catechols (NCASI[1] Method CP-86.01, "Chlorinated Phenolics in Water by In-situ Acetylation/GC/MS Determination") was modified slightly to scale it up to larger sample volumes during acetylation and extraction, and by adding ascorbic acid prior to acetylation to improve recovery of catechols. Also, 2,6-dibromophenol was used in place of trichlorophenol (a target compound) as the internal standard. Resin and fatty acids analysis used methyl-o-methylpodocarpate as the internal standard in place of n-propyldehydroabietate (dehydroabietic acid also a target compound) as described in the method (NCASI Method RA/FA-86.01, "Resin and Fatty Acids by Extraction/Ethylation/GC/FID and GC/MS Determination").

[1]National Council of the Paper Industry for Air and Stream Improvement, Inc.

Table 2. Analytical methods.

Analysis	Method	Reference	Laboratory
Temperature	ASTM Precision Thermometer	-	Field Measurement
pH	Orion pH Meter	-	"
Specific Conductance	Conductivity Meter (Method 120.1)	EPA (1983)	Ecology/EPA Laboratory, Manchester, WA
Color	Colorimetric, Nessler Tubes (Method 110.1)	"	"
Total Suspended Solids	Gravimetric, Dry at 103° C (Method 160.2)	"	"
Total Recoverable Phenolics	Colorimetric, Technicon (AAII) (Method 420.2)	"	"
Total Organic Halides	Carbon Absorption, Microcoulimetric - Titration (Method 450.1)	"	"
" " "	Carbon Absorption, Microcoulimetric - Fitration (Method 9020)*	EPA (1986)*	Sound Analytical Services, Inc., Tacoma, WA*
Cadmium, Chromium, Lead, Silver	AA (Method nos. EP1-213.R, 218.R, 239.R, 272.R)	EPA (1983)	Ecology/EPA Laboratory, Manchester, WA
Copper, Nickel, Zinc	ICP (Method EP1-200.7)	EPA (1983)	"
Mercury	Cold Vapor AA (Method EP1-245.R)	EPA (1983)	"
Volatiles	Purge and Trap/GC/MS (Method 624)	EPA (1984)	Analytical Resources Inc., Seattle, WA
Phenols, Guaiacols, Catechols	GC/MS (Method CP-86.01)	NCASI (1986a)	Ecology/EPA Laboratory, Manchester, WA
Resin Acids, Fatty Acids	GC/FID; GC/MS (Method RA/FA-86.01)	NCASI (1986b)	"
Rainbow Trout Bioassay	96-hour Static	Ecology (1980)	"
Microtox Bioassay	15-minute Static	Beckman (1982)	"
Oyster Larvae Bioassay	48-hour Static	ASTM (1986)	EVS Consultants, Seattle, WA
Echinoderm Sperm Cell Bioassay	60-minute Static	Dinnel et al. (1987)	"

* 3 May, 12 June, and 20 June samples only

The bioassay procedures can be briefly described as follows: In the rainbow trout bioassay, ten fish (average weight 0.7 gm) were placed in each of three glass tanks containing effluent diluted to 65% with Manchester city water. The tests were run for 96 hours along with a control (dilution water) and reference toxicant (cadmium chloride). Weyerhaeuser samples had been adjusted to pH 7.1 - 7.4 in the laboratory by adding sodium hydroxide to each tank. Cumulative mortalities were recorded at 24, 48, 72, and 96 hours. Dissolved oxygen (D.O), pH, temperature, hardness, and alkalinity were monitored through the test.

After osmotic adjustment with sodium chloride to 20 g/L, Microtox samples were diluted to bacterial suspensions with final effluent concentrations of 0%, 5.7%, 11.4%, 22.7%, and 45.5%. Weyerhaeuser samples were adjusted to pH 6.8 - 7.8 with sodium hydroxide. Duplicate measurements of light output were made at 5, 15, and 30 minutes. Phenol was used as a reference toxicant. The data were corrected to allow for light absorbance by the dark-colored effluents. Because light output stabilized at 15 minutes, the data reported here are based on the 15 minute readings.

Pacific oysters, thermally conditioned to stimulate gonad maturation, were induced to spawn by heating to 29 °C in dilution water (1 μm-filtered, UV-sterilized seawater). Eggs from three females and 10-20 mL of sperm suspension from one male were combined in a 1 L glass beaker. Fertilized eggs were washed through a 250 μm mesh Nitex screen and suspended in 2 L of dilution water.

Oyster bioassays were conducted in triplicate at test concentrations ranging from 0.1 to 18% effluent using 250 mL glass beakers containing 100 mL of test solution. The pH of Weyerhaeuser samples was adjusted to 7.0 with sodium hydroxide. Within one hour of fertilization, each beaker was inoculated at 30 embryos per mL, and incubated for 48 hours at 20 °C. A 5 mL subsample, preserved in buffered formalin, was examined for abnormal larvae, defined as those that failed to transform to fully shelled, straight-hinge, "D-shaped" larvae. Positive controls (cadmium chloride), regular controls (zero percent effluent), and salinity controls were run concurrently. Salinity, D.O., temperature, and pH were measured at termination of the test.

Because of the seasonal availability of echinoderms in spawning condition, three species (purple sea urchin, green sea urchin, and sand dollar) were used in the sperm cell fertilization bioassay. Dilution water was 1 μm-filtered, UV-sterilized seawater. Tests were conducted in triplicate at concentrations ranging from 0.1 to 50% effluent, and included a reference toxicant (sodium dodecylsulfate), regular controls, and salinity controls. Weyerhaeuser pH was adjusted as described above.

Spawning was induced by injecting potassium chloride into the coelomic cavity. Sperm cells were exposed in 15 mL glass test tubes at 15 °C for 60 minutes. Eggs were added and fertilization allowed to proceed for 20 minutes. Contents of the test tubes was preserved in buffered formalin. The toxicity of the effluents was based on fertilization success of the eggs; an unfertilized egg being defined as one without a normal fertilization membrane.

Accuracy and Precision of Chemical Data

The quality of the chemical data was evaluated by examining results of matrix spikes, surrogate compound spikes, method blanks, field blanks, and duplicate field samples. Spike recoveries in effluent samples are summarized in Appendix C.

Table 3 summarizes the field blank results. Low concentrations of TOX, chromium, mercury, zinc, and fourteen organic compounds were detected in one or more blanks. Of these, significant contamination relative to concentrations measured in field samples was observed for mercury, acetone, methylene chloride, phenol, 2-methylphenol, 4-chloro-3-methylphenol, pentachlorophenol, and acetophenone. As a result, these are not reported as being detected in mill effluents. Blank contamination for the remaining metals and organic compounds was judged not to be significant (i.e., generally less than field samples by a factor of 10 or more).

In order to assess total variability of the chemical data (i.e., analytical plus field variability), one set of field samples was collected in duplicate during every other sampling event. Table 4 summarizes these results. Because of the large and variable number of organic compounds detected in the effluents, only results for consistently quantified compounds representative of the several chemical classes analyzed are shown; complete results for duplicates are tabulated in Appendix D.

Agreement between duplicates was generally good, indicating sampling and analytical methods were not significant contributors to data variability. As shown in Table 4, measurements of specific conductance, color, TSS, total recoverable phenolics, TOX, cadmium, copper, zinc, chloroform, toluene, 2,3,6-trichlorophenol, tetrachloroguaiacol, 3,4,5-trichlorocatechol, tetrachlorocatechol, 6-chlorovanillin, and 9,10-dichlorostearic acid compared closely, with the relative range of duplicates averaging 15% or better. Results were somewhat less precise for lead, chromium, 4-methylphenol, quaiacol, and dehydroabietic acid, averaging between 23% and 37%. Duplicates showed poor agreement for nickel, 12-chlorodehydroabietic acid, and oleic acid, which differed by more than 50% on average.

Quality Assurance for Bioassays

Control mortality during rainbow trout bioassays was less than 10%. Estimated LC50s for the reference toxicant, cadmium chloride, were within the range of 1 - 9 μg/L that has been observed in rainbow trout bioassays at the Manchester laboratory over the past three years. Control abnormality during oyster larvae bioassays was also less than 10%. Fertilization success in controls during echinoderm sperm cell bioassays exceeded 80%. (Sensitivity of the sperm assay is maximized when control fertilization success is less than 100%, indicating there is not an overabundance of sperm). Responses to reference toxicants during the oyster and echinoderm test were also within expected historical ranges. There were negligible effects in the salinity controls indicating that increased oyster larvae abnormality and reduced fertilization success observed in the effluents were not caused by lower salinity. Water quality during the above tests remained within acceptable ranges.

Table 3. Chemicals detected in transfer blanks (μg/L).

Date	3/07		4/05		5/31		6/20	
Conventional Variables								
TOX	40	U	9		2		6	
Metals								
chromium	10	U	0.2	U	0.3		0.5	
mercury	0.06	U	0.18		0.06	U	0.06	U
zinc	6.1		2.2		2	U	7.7	B
Volatiles								
toluene	0.6	U	0.3	B	0.8	U	0.6	U
acetone	430		61	B	2.2		0.6	U
methylene chloride	1.1	B	1.3	B	1.8	B	2.2	B
Phenols								
phenol	2	B	4	B	0.9	B	2	B
2-methylphenol	0.2	B	0.5	B	0.1	B	0.2	B
4-methylphenol	1	U	0.2	B	0.1		0.1	
4-chloro-3-methylphenol	1	U	0.1	B	0.6	U	1	U
pentachlorophenol	1	U	0.1	B	0.6	U	1	U
acetophenone	0.3	B	0.4	B	0.8	B	2	B
Resin Acids								
dehydroabietic	1	U	1	U	0.2	B	0.8	
Fatty Acids								
hexadecanoic	NA		0.7	B	4	B	2	B
octadecanoic	NA		2	B	6	B	4	B
oleic	1	U	1	U	3		1	U
linoleic	1	U	2	B	1	U	1	U

U = not detected at dection limit shown
B = also detected in method blanks
NA = not analyzed

Table 4. Precision of field duplicates (relative percent difference; mean ± SD, n = 4).

Conventional Variables	
specific conductance	3 ± 4%
color	4 ± 6%
TSS	9 ± 6%
total recoverable phenolics	0%
TOX	11 ± 11%
Metals	
cadmium	6 ± 10%
chromium	29 ± 26%
copper	14 ± 18%
lead	27 ± 22%
nickel	55 ± 36%
zinc	14 ± 11%
Volatiles	
chloroform	5 ± 9%
toluene	3 ± 3%
Phenols	
4-methylphenol	23 ± 18%
2,4,6-trichlorophenol	3 ± 6%
Guaiacols	
guaiacol	27 ± 33%
tetrachloroguaiacol	3 ± 7%
Catechols	
3,4,5-trichlorocatechol	9 ± 17%
tetrachlorocatechol	15 ± 17%
Other Chlorophenols	
6-chlorovanillin	3 ± 6%
Resin Acids	
dehydroabietic	37 ± 34%
12-chlorodehydroabietic	82 ± 64%
Fatty Acids	
oleic	54 ± 11%
9,10-dichlorostearic	0%

Table 5. General effluent characteristics.

Variable	Weyerhaeuser (n=8) Average (Range)	ITT (n=4) Average (Range)
flow (MGD)	22.2 (18.4 - 27.0)	20.4 (20.0 - 20.9)
temperature (°C)	20.5 (17.4 - 23.4)	21.6 (18.4 - 24.9)
pH (S.U.)	2.6 (2.2 - 3.0)	7.0 (6.8 - 7.5)
specific conductance (μmhos/cm)	3,300 (2,200 - 4,300)	1,600 (1,350 - 1,850)
color (units)	1,840 (1,070 - 2,460)	1,840 (1,130 - 2,420)
TSS (mg/L)	152 (74 - 380)	68 (37 - 150)
total recoverable phenolics (μg/L)	13.9 (10.0 - 18.8)	6.2 (4.1 - 8.0)
TOX (mg/L)	27.2 (22.5 - 39.0)	22.2 (16.0 - 26.0)

RESULTS AND DISCUSSION

Chemical Analysis[2]

General Effluent Quality -- Table 5 summarizes results showing general characteristics of the effluents. Weyerhaeuser and ITT discharges were comparable in average flow (22.2 vs. 20.4 MGD), temperature (22.2 vs. 21.6 °C), color (1,840 NTU for both discharges), and, to a lesser degree, TOX (27.2 vs. 22.2 mg/L). Specific conductance (3,300 vs. 1,600 μmhos/cm), TSS (152 vs. 68 mg/L), and total recoverable phenolics (13.9 vs. 6.2 μg/L) concentrations in Weyerhaeuser effluent averaged approximately twice those in ITT effluent. The average pH of the effluents was 2.6 at Weyerhaeuser and 7.0 at ITT.

Potentially Toxic Constituents -- The results of analyses for metals and organic compounds are summarized in Table 6. Cadmium, chromium, copper, lead, nickel, and zinc were routinely detectable in both discharges. Silver was not detected in either discharge at a detection limit of 0.5 μg/L.

Chromium was consistently elevated in ITT's wastewater (average concentration of 67 vs 8.7 μg/L). ITT has traced the source of chromium in their effluent to contaminated sodium chloride used in generating chlorine dioxide. A more highly refined salt is now being used. Chromium concentrations in the final effluent are currently at about 10 μg/L (Kjosness, 1990, personal communication).

Other than chromium, metals concentrations compared closely between the two mills. Weyerhaeuser effluent contained an average of 0.3 μg/L cadmium, 10 μg/L copper, 2.7 μg/L lead, 19 μg/L nickel, and 44 μg/L zinc. ITT effluent averaged 0.7 μg/L cadmium, 8.8 μg/L copper, 2.2 μg/L lead, 7.6 μg/L nickel, and 30 μg/L zinc.

More organic compounds were detected in Weyerhaeuser's effluent than ITT's. Higher concentrations also tended to occur for Weyerhaeuser, probably reflecting the fact that less of the total flow is subjected to activated sludge treatment. The predominant compounds detected in Weyerhaeuser effluent were chloroform, 2-butanone, 4-methylphenol, 3,4,5-trichlorocatechol, tetrachlorocatechol, dehydroabietic acid, chlorodehydroabietic acid (2 isomers), dichlorodehydroabietic acid, oleic acid, hexadecanoic acid, and octadecanoic acid, each having an average concentration of 10 μg/L or more.

Chloroform concentrations in ITT's discharge were an order of magnitude above those at Weyerhaeuser, ranging from 110 - 170 μg/L compared to 0.7 - 18 μg/L. Lower chloroform levels in Weyerhaeuser effluent may be due to the greater opportunity for volatilization afforded by longer retention time (40 hours vs. 8 hours at ITT) and greater surface area provided by the ponds. Other than chloroform, individual organic compounds detected in ITT effluent never exceeded 5 μg/L and were typically at about 1 μg/L or less. Compounds

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[2]Complete data are in Appendices E and F

Table 6. Potentially toxic constituents detected in effluents (μg/L).

Chemical	Weyerhaeuser Detection Frequency (n=8)	Weyerhaeuser Average Conc. (Range)	ITT Detection Frequency (n=4)	ITT Average Conc. (Range)
Metals				
cadmium	4	0.3 (0.2U - 1.0)	4	0.7 (0.5 - 0.9)
chromium	6	8.7 (5.1 - 23)	4	67 (45 - 87)
copper	8	10 (4 - 16)	4	8.8 (3.9 - 13)
lead	8	2.7 (1.0 - 5.4)	4	2.2 (1.3 - 3.3)
nickel	8	19 (15 - 27)	3	7.6 (1.9 - 20U)
zinc	8	44 (21 - 110)	4	30 (22 - 39)
Volatiles				
chloroform	8	13 (0.7 - 18)	4	135 (110 - 170)
2-butanone	6	20 (1.0U - 39)	0	1.0U (0.1U-6.2U)
toluene	8	4.6 (1.4 - 13)	1	0.6U (0.6U - 0.8U)
bromodichloromethane	1	0.2U (0.2U - 0.4)	3	0.6 (0.2U - 1.1)
1,2-dichloropropane	0	0.6U (0.6U all)	1	0.6U (0.5 - 0.7U)
Phenols				
4-methylphenol	8	28 (10 - 54)	3	0.4 (0.2 - 1U)
2,4-dimethylphenol	5	0.2 (0.1 - 1U)	0	0.5U (0.5U - 1U)
2-chlorophenol	5	0.3 (0.1 - 1U)	0	0.5U (0.5U - 1U)
2,4-dichlorophenol	8	0.2 (0.6 - 5)	3	0.4 (0.2 - 1U)
2,4,6-trichlorophenol	8	7 (2 - 15)	3	0.7 (0.5 - 1)
Guaiacols				
guaiacol	8	2 (0.5 - 5)	3	0.4 (0.1 - 1U)
4-allylguaiacol	4	0.4 (0.2 - 1U)	0	0.5U (0.5U - 1U)
4-chloroguaiacol	5	0.3 (0.1 - 1U)	0	0.5U (0.5U - 1U)
4,5-dichloroguaiacol	8	2 (0.2 - 3)	4	0.8 (0.3 - 2)
4,5,6-trichloroguaiacol	7	1 (0.3 - 3)	4	0.3 (0.1 - 0.6)
tetrachloroguaiacol	8	4 (1 - 7)	4	1 (0.6 - 2)
Catechols				
4-chlorocatechol	7	0.9 (0.4 - 2)	2	0.3 (0.1 - 1U)
4,5-dichlorocatechol	8	6 (1 - 14)	4	0.6 (0.3 - 1)
3,4,5-trichlorocatechol	8	27 (5 - 56)	4	4 (1 - 5)
tetrachlorocatechol	8	10 (2 - 19)	4	2 (1 - 4)
Other Chlorophenols				
trichlorosyringol	7	9 (0.4 - 35)	0	0.5U (0.5U - 1U)
6-chlorovanillin	4	0.9 (0.5U - 2)	4	0.9 (0.4 - 2)
5,6-dichlorovanillin	5	1 (0.5U - 2)	4	0.9 (0.4 - 2)
Resin Acids				
abietic	1	0.6U (0.4U - 3)	0	0.4U (0.4U - 0.5U)
dehydroabietic	8	15 (1 - 36)	2	0.4U (0.3 - 0.5U)
12-chlorodehydroabietic	8	25 (1 - 50)	3	0.6 (0.5U - 1.6)
14-chlorodehydroabietic	8	10 (0.5 - 22)	1	0.2U (0.2 - 0.5U)
dichlorodehydroabietic	8	11 (1 - 27)	0	0.5U (0.4U - 0.5U)
palustric	2	0.6U (0.4U - 3)	0	0.5U (0.4U - 0.5U)
isopimaric	3	0.9 (0.4U - 2)	0	0.5U (0.4U - 0.5U)

U = not detected at detection limit shown

Table 6. (Continued)

Chemical	Weyerhaeuser Detection Frequency (n=8)	Weyerhaeuser Average Conc. (Range)	ITT Detection Frequency (n=4)	ITT Average Conc. (Range)
Fatty Acids				
oleic	7	30 (0.4U - 97)	2	2 (0.4U - 3)
linoleic	3	0.6 (0.4U - 4)	0	0.5U (0.4U - 0.5U)
hexadecanoic	6	32 (5 - 64)	3	4 (2 - 5)
octadecanoic	6	32 (3 - 70)	3	2 (2 - 2)
palmitoleic	4	6 (0.4U - 16)	2	1 (0.5U - 3)
9,10-dichlorostearic	6	6 (2 - 10)	3	2 (1 - 3)
Miscellaneous				
a-terpineol	1	0.5U (0.4U - 1U)	0	0.5U (0.5U - 1U)

U = not detected at detection limit shown

Table 7. Estimated loads of selected, potentially toxic constituents.

Chemical	Weyerhaeuser (average flow 22.2 MGD) Average Conc. (ug/L)	Weyerhaeuser Load (lbs./day)	ITT (average flow 20.4 MGD) Average Conc. (ug/L)	ITT Load (lbs./day)	Combined Load (lbs./day)
Metals					
cadmium	0.3	0.1	0.7	0.1	0.2
chromium	8.7	1.6	67	11	13
copper	10	1.8	8.8	1.5	3.3
lead	2.7	0.5	2.2	0.4	0.9
nickel	19	3.4	7.6	1.3	4.7
zinc	44	8.1	30	5.1	13
Organics					
chloroform	13	2.4	135	23	25
other volatiles	24	4.4	3.3	0.6	5.0
chlorophenols*	119	22	15	2.5	24
resin and fatty acids	152	28	11	1.8	30
TOX (mg/L)	27.2	5,030	22.2	3,770	8,800

* phenols, guaiacols, catechols, other chlorophenols

present in the highest concentrations at ITT were tetrachloroguaiacol, 3,4,5-trichlorocatechol, tetrachlorocatechol, and several fatty acids. Chemical structures for some of these compounds are shown in Figure 3.

Loads to Receiving Waters -- An estimate of the daily loads of potentially toxic constituents discharged by Weyerhaeuser and ITT to Grays Harbor is provided in Table 7. The loads were calculated using average chemical concentrations measured during Ecology's monitoring program and monthly average plant flows reported by industry for the same period. The estimated combined daily loads from the mills ranged from 0.2 pound/day of cadmium to 30 pounds/day of resin and fatty acids. Weyerhaeuser represented the major loads of chlorophenols (22 pounds/day) and resin and fatty acids (28 pounds/day). ITT contributed most of the load for chromium (13 pounds/day) and chloroform (23 pounds/day). Loads for other metals and volatiles were equivalent between the mills. Loading estimates for TOX were 5,030 pounds/day from Weyerhaeuser and 3,770 pounds/day from ITT, showing the individual chlorinated compounds analyzed represent a small fraction of total halogenated material discharged to the harbor.

Bioassays

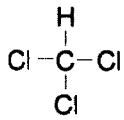
Toxicity to Bioassay Organisms -- Table 8 shows the results of effluent bioassays. Weyerhaeuser effluent elicited a toxic response in each of the four types of bioassays employed. ITT effluent was non-toxic in the rainbow trout and Microtox bioassays (one Microtox assay showed marginal evidence of toxicity), but was toxic in the oyster and echinoderm bioassays.

Weyerhaeuser effluent was either highly toxic or non-toxic to rainbow trout. There was essentially 100% mortality (0 - 13% survival) in the three samples collected March 21, May 31, and June 20; effluents collected on the five other occasions had 100% survival. Low survival was never observed on two consecutive sampling dates. The most acutely toxic effluent was the June 20 sample in which all trout died by the second day of the test (data not shown). The mortalities in the March 21 and May 31 samples occurred on the third and fourth day, with a few fish surviving to the end of the test.

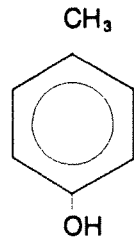
Microtox assays of Weyerhaeuser's effluent gave variable results showing EC50s ranging through, approximately, 24%, 30%, 56%, 87%, and >100% (no effect) effluent. Four of the eight effluent samples showed little or no toxicity by this test.

Weyerhaeuser and ITT discharges were consistently extremely toxic to Pacific oyster larvae and echinoderm sperm cells. For both effluents, the oyster bioassay was the more sensitive of the two tests.

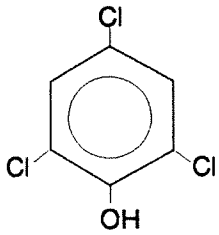
ITT effluent had greater toxicity to oyster larvae - by about a factor of four - than Weyerhaeuser effluent, with average EC50s of 0.2% (range 0.1 - 0.3%) and 0.8% (range 0.4 -1.3%), respectively. Both effluents had a similar level of toxicity in the echinoderm bioassay; EC50s averaged 6.8% effluent at ITT and 5.9% effluent at Weyerhaeuser. Oyster



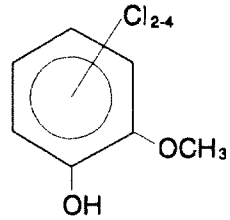
Chloroform



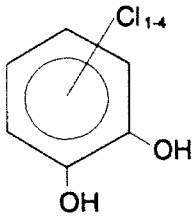
4 - Methylphenol



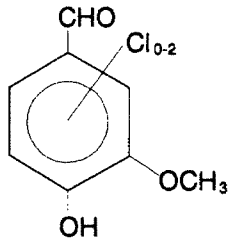
2,4,6 -Trichlorophenol



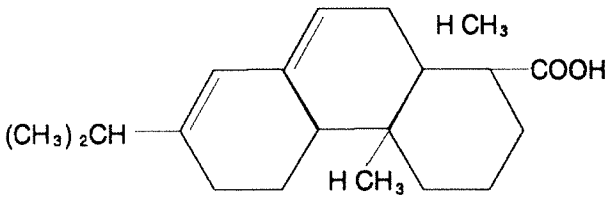
Chloroguaiacols



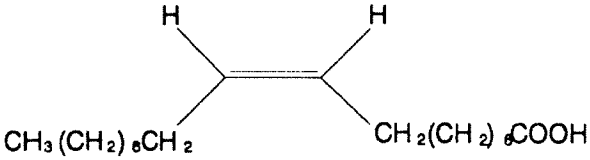
Chlorocatechols



Chlorovanillins



Abietic acid



Oleic acid

Figure 3. Structures of selected compounds detected in Grays Harbor pulp mill effluents.

Table 8. Bioassays of effluents

Date	Rainbow Trout Survival[a]	Microtox EC50[b]	Pacific Oyster Larvae Abnormality EC50[c]	LOEC[d]	NOEC[e]	Echinoderm Fertilization Success EC50	LOEC	NOEC	Species
Weyerhaeuser									
3/07	100	29.7	0.5	0.5	0.1	4.3	3.0	1.0	purple urchin
3/21	13	24.0	0.6	0.1	<0.1	14.6	3.0	1.0	green urchin
4/05	100	86.7	1.0	0.5	0.1	5.0	3.0	1.0	green urchin
4/24	100	>100	1.1	3.2	1.0	9.2	3.0	1.0	green urchin
5/17	100	>100	0.6	0.5	0.1	1.1	1.0	0.1	sand dollar
5/31	3	>100	0.9	1.0	0.5	6.4	1.0	0.1	sand dollar
6/12	100	56.1	1.3	1.0	0.5	2.6	1.0	0.1	sand dollar
6/20	0	56.9	0.4	0.5	0.1	4.0	3.0	1.0	sand dollar
ITT									
3/07	100	>100	0.1	0.1	<0.1	5.1	6.0	3.0	purple urchin
4/15	100	>100	0.2	0.5	0.1	9.4	3.0	1.0	green urchin
4/24	100	>100	0.3	0.5	0.1	8.7	0.1	<0.1	green urchin
5/31	100	85.5	0.3	0.5	0.1	3.9	1.0	0.1	sand dollar

[a] percent survival in 65% effluent

[b] percent effluent concentration causing 50% loss of light emmission

[c] percent effluent concentration at which 50% of test population shows an effect

[d] lowest observed effect concentration

[e] no observed effect concentration

larvae bioassays conducted by Ecology in 1988 showed toxicity was comparable to present results with EC50s of 0.2% for ITT and 0.3% for Weyerhaeuser (Reif, 1989a; Hallinan, 1989).

Ecology's experience with Microtox, oyster larvae, and echinoderm bioassays at other Washington pulp mills is limited, but suggests the Grays Harbor effluents are not uniquely toxic by these tests. The following EC50s have been observed at other mills: Microtox - 58.9%, 67.3%, >100%; oyster larvae abnormality - 0.5%, 1.7%, 3.0%; echinoderm sperm cell 0.6%, 2.4% (Reif, 1989b, 1990). Similar data have been collected by NCASI, but are not presently available (Hall, 1990, personal communication).

Dilution in the Receiving Waters -- The oyster larvae and echinoderm bioassays have been proposed for predicting effluent dilution requirements and as receiving water quality criteria (Woelke, 1972; Dinnel and Stober, 1987). The drafts of the new NPDES permits being issued for the Grays Harbor mills require these bioassays be conducted at dilution ratios existing on the edge of the effluent dilution zone[3]. Dilution studies are being required of both mills.

Based on results of the present study, receiving water dilution required to reduce effluent concentrations to average EC50s measured in the oyster and echinoderm bioassays would be approximately 120:1 and 15:1 for Weyerhaeuser, and 500:1 and 17:1 for ITT, respectively. The minimum effective concentration, however, is an unmeasured value lying somewhere between the NOEC and the lower of the EC50 (a calculated value) and LOEC (actual test dilution). The new NPDES permits require a determination that the NOEC from chronic bioassays is met at the edge of the dilution zone. For the oyster larvae bioassay the average NOEC was 0.3% for Weyerhaeuser effluent and 0.1% for ITT effluent, requiring dilution ratios of approximately 330:1 and 1,000:1, respectively. The average NOEC in the less sensitive echinoderm test was 0.7% for Weyerhaeuser (140:1) and 1.0% for ITT (100:1).

Weyerhaeuser conducted a dilution study under conditions of continuous discharge during June, 1988 (Weyerhaeuser Technical Center, 1988). Final effluent, tagged with rhodamine dye, was discharged for 32 hours. The study was done during moderate river flow (2,450 cfs) and tidal exchange (5.2 - 6.8 feet). The extent of effluent dilution found during this study is shown in Figures 4 - 6. Most of the upper South Chehalis River Channel for a distance of approximately three miles below the Weyerhaeuser outfall failed to achieve dilution to either the oyster or echinoderm NOEC. Based on the oyster larvae NOEC alone, several miles of the upper harbor subsurface waters (5 -10 feet) during flood tide are added to the area which failed to attain adequate dilution. Surface waters upstream of the outfall were generally at dilutions of 500:1 or greater during flood.

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[3]Ecology defines the dilution zone as having a width equal to the diffuser length plus 50 feet plus half the water depth, an upstream and downstream boundary of 150 feet plus the water depth, and a vertical extent from one foot below the water surface to one foot above the bottom.

6/23/88
Effluent Dispersion Study
Day 2 Continuous Discharge
Average Surface to 10'

Figure 4 (from Weyerhaeuser Tech. Center, 1988)

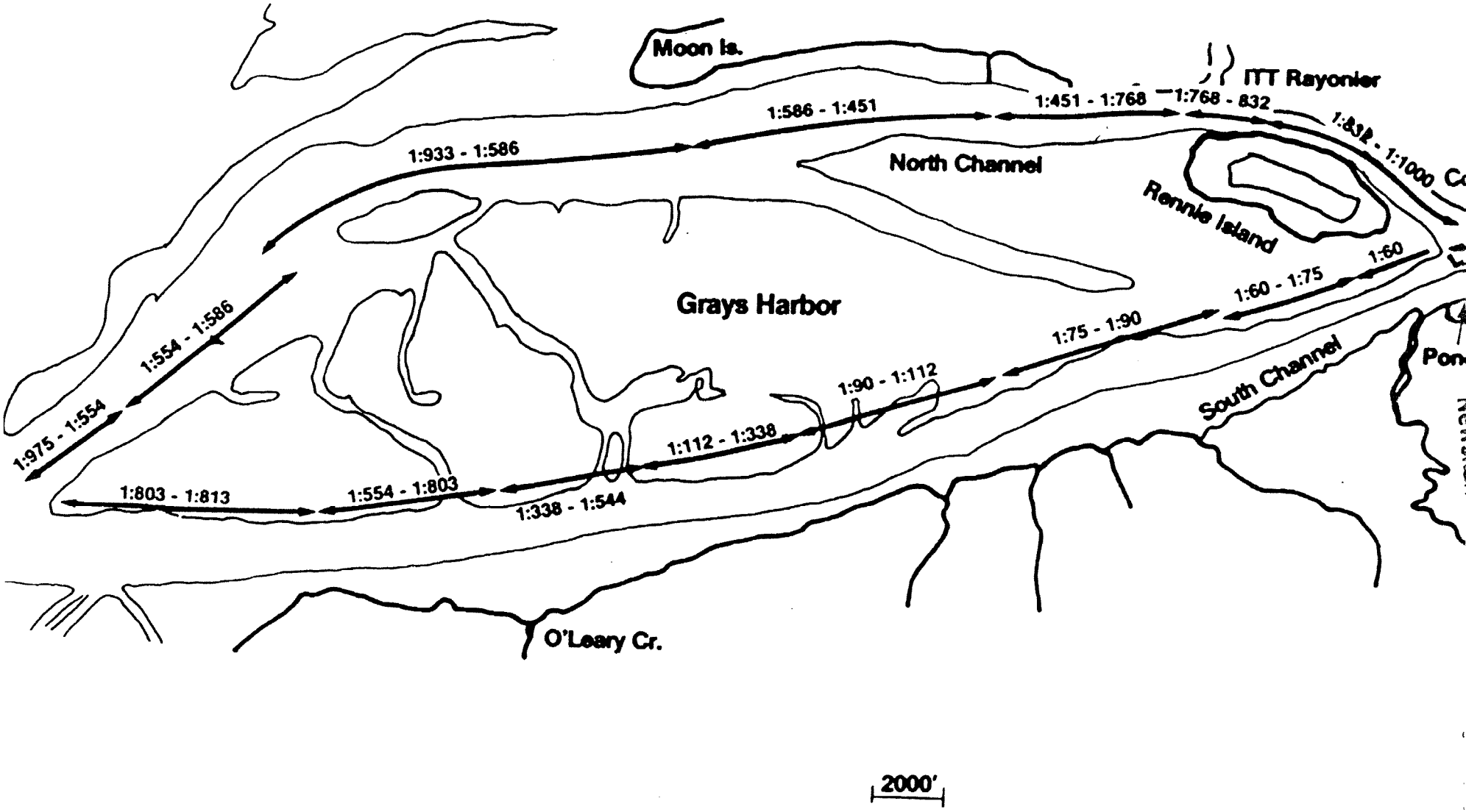


Figure 5 (from Weyerhaeuser Tech. Center, 1988)

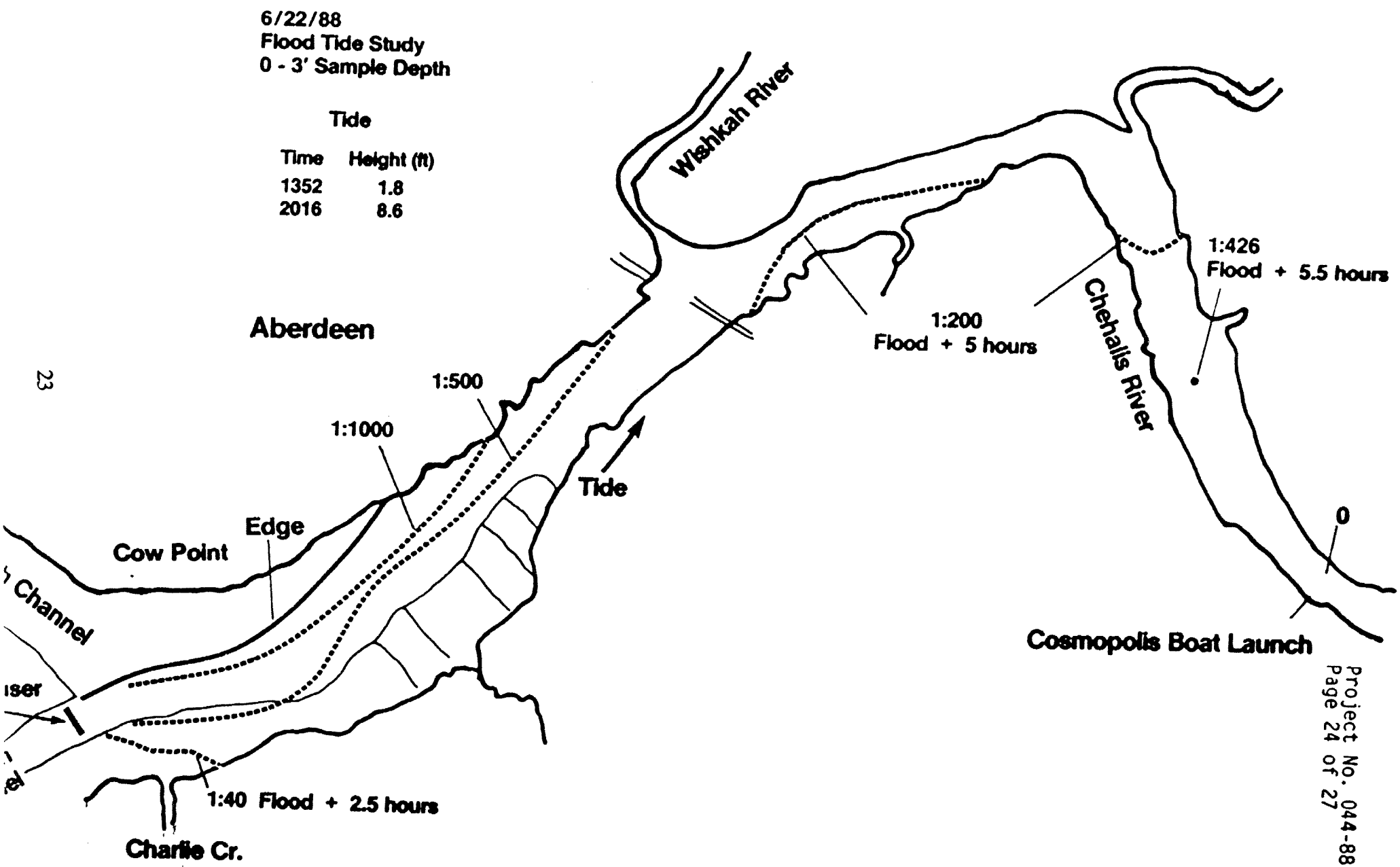
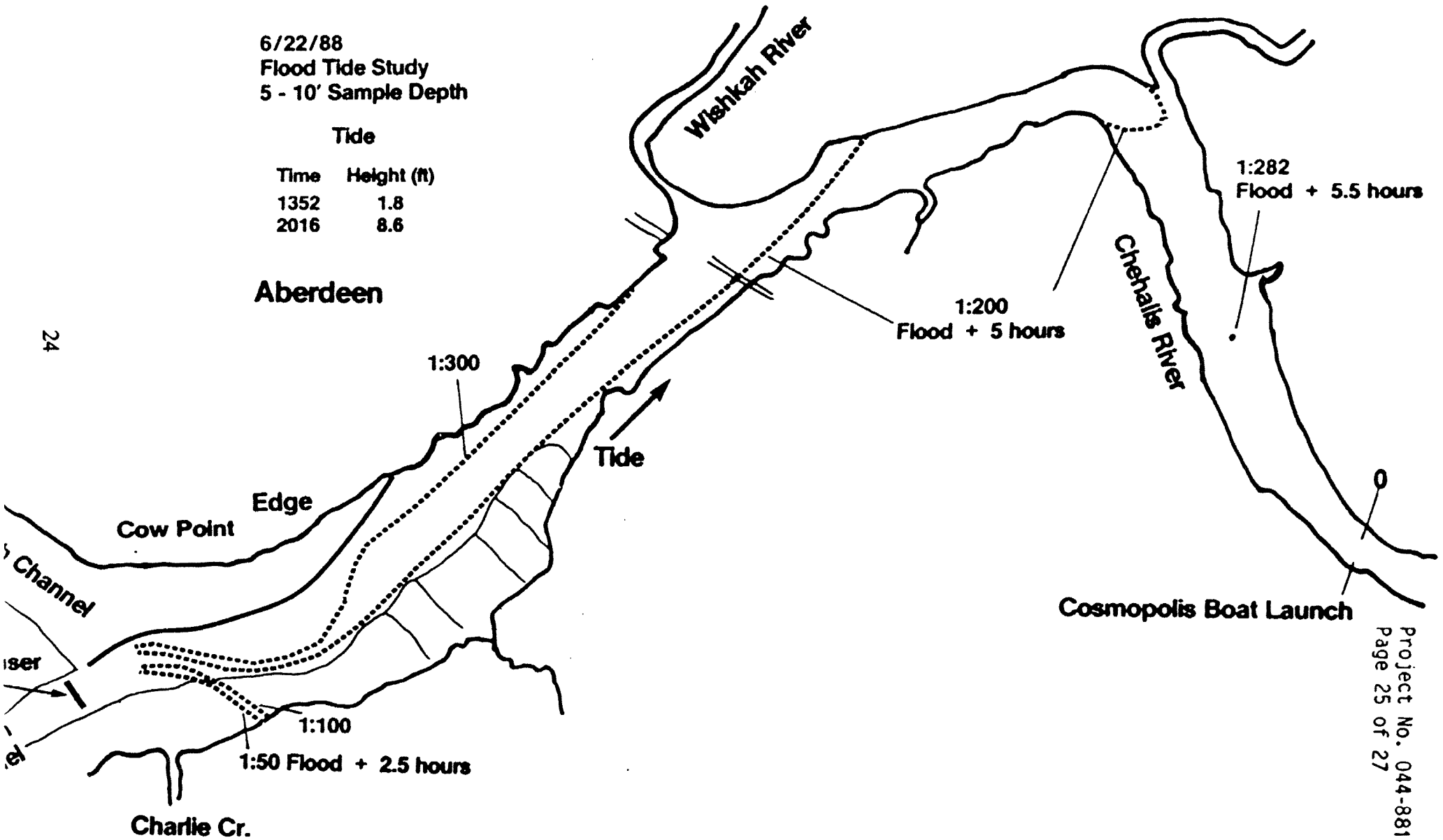


Figure 6 (from Weyerhaeuser Tech. Center, 1988)



None of the above takes ITT's discharge (which has greater toxicity to oyster larvae) into account, accumulation of effluent under conditions of long-term continuous discharge, or low flow conditions. Simultaneous discharge by both mills under conditions existing during the Weyerhaeuser dilution study would likely result in inadequate dilution (i.e., above the oyster and echinoderm NOEC) through most of the inner harbor (Rennie Island and above). A complicating factor in applying the bioassay results to the receiving waters is that salinities in inner Grays Harbor are sometimes below 20 ppt which is outside the acceptable range for the oyster and echinoderm tests. Also, Cardwell et al., (1976, 1979) have demonstrated that correlations between pulp mill effluent bioassays and receiving water toxicity can be poor.

Bioassay/Chemistry Correlations -- The Weyerhaeuser results were examined for links among effluent constituents and response of bioassay organisms using Spearman's rho, a non-parametric test of correlation. For this calculation, concentrations of individual organic compounds were summed for each class of chemicals analyzed (i.e., total volatiles, total phenols, etc.). The results are summarized in Table 9. Similar calculations were not done for ITT because of small sample size.

Significant correlations were almost exclusively confined to chemical constituents. Only one statistically significant correlation - total phenols and Microtox (r_s = 0.73, p = 0.05) - was found between chemical constituents and bioassays. Given the concentrations of toxic constituents analyzed in this discharge, the lack of correlation with bioassays is not unexpected. Table 10 summarizes relevant toxicity data for the bioassay organisms. Based on these data, the levels of metals and organic compounds measured in Weyerhaeuser and ITT effluents are one or more orders of magnitude below concentrations that produce adverse effects in these tests.

No significant correlation was found among the four bioassays. This suggests the test organisms were responding to different constituents and/or concentration levels. Although chlorinated resin acids and chlorophenols are widely considered to be major toxicants in pulp mill effluent (Leach, 1975; Leach and Thakore, 1977; Holmbom and Lehtinen, 1980; Oikari and Anas, 1985) their toxicity has primarily been demonstrated at relative high concentrations. Weyerhaeuser concluded resin acids, organic chlorides, metals, and other priority pollutants were not involved in rainbow trout toxicity of their effluent (Campbell, 1987). Sulfite, bisulfite, and surfactants were suggested as possible contributing factors in toxicity. These constituents were not analyzed during the present study due to lack of available analytical methods.

Recent research with untreated kraft mill effluent has demonstrated that toxicity in a range of marine bioassays (English sole larvae - 96-hour lethality; California mussel larvae abnormality - 48-hour EC50; and sea urchin sperm cell - EC50) is primarily accounted for by a non-chlorinated, high molecular weight, water-soluble only fraction of the effluent (Cherr, 1990, personal communication). NCASI is currently conducting research to confirm these findings for a range of treated effluent types and determine the mechanism of toxicity. Preliminary tests using the echinoderm bioassay have shown similar but inconsistent results

Table 9. Correlations in chemistry and toxicity of Weyerhaeuser effluent. (Spearman's rho; significance level in parenthesis)

Positive Correlations between Chemistry and Toxicity	Negative Correlations between Chemistry and Toxicity
total phenols - Microtox .73 (.05)	chromium - Microtox .80(.03)
Positive Correlations among Bioassays	**Negative Correlations among Bioassays**
none	none
Positive Correlations among Chemical Constituents	**Negative Correlations among Chemical Constituents**
TSS - VOAs .89 (.02)	pH - total phenols .78 (.04)
t. rec. phenolics - total phenols .81 (.03)	pH - total guaiacols .74 (.05)
Pb - Zn .83 (.03)	TSS - total resin acids .74 (.05)
TOX - total catechols .86 (.02)	TOX - total cadmium .82 (.03)
TOX - total guaiacols .78 (.04)	
total guaiacols - total catechols .75 (.05)	
total resin acids - total fatty acids .81 (.03)	

Table 10. Toxicity of metals and organic compounds detected in effluents (μg/L).

Chemical	Concentrations Detected in Effluents	Rainbow Trout 48-96 Hr. LC50	Reference	Oyster Larvae Abnormality 48 Hr. EC50	48 Hr. NOEC	Reference	Microtox EC50	Reference
Metals								
cadmium	0.3 - 1.0	6 - 55	1	920	340-420	7	70,000	10
chromium	5.1 - 87	4,400 - 141,000	2,3	10,000	3,200	8	7,400 - 8,000	10
copper	3.9 - 16	150 - 500	2	32	10	8	38,000	11
lead	1.0 - 5.4	1,000 - 3,000	2				30,000	11
nickel	1.9 - 27	25,000 - 160,000	2,4				23,000	11
zinc	21 - 110	3,900 - 85,000	2	32,000	10,000	8	2,500 - 49,000	10
Volatiles								
chloroform	0.7 - 170	1,240 - 10,600	5	10,000	3,200	8	435,000	10
Phenols								
methylphenol	0.4 - 54	11,000	11				580 - 12,000	10,11
chlorophenol	0.1 - 0.9						1,500	10
dichlorophenol	0.2 - 5	2,800	6	Echinoderm Fertilization				
trichlorophenol	0.5 - 15	450 - 2,600	6	EC50	NOEC	Reference		
Guaiacols								
dichloroguaiacol	0.2 - 3	2,300	6	9,610	2,500	9		
trichloroguaiacol	0.1 - 3	700 - 1,000	6	2,010	1,000	9		
tetrachloroguaiacol	0.6 - 7	200 - 1,700	6					
Catechols								
dichlorocatechol	0.3 - 14	500 - 1,000	6					
trichlorocatechol	1 - 56	1,000 - 1,500	6					
tetrachlorocatechol	1 - 19	400 - 1,500	6					
Resin Acids								
abietic	3	700 - 1,500	6	3,710	2,500	9		
dehydroabietic	0.3 - 36	800 - 1,740	6	--	7,500	9		
chlorodehydroabietic	0.2 - 50	600 - 900	6	3,030	1,000	9		
dichlorodehydroabietic	1 - 27	600 - 1,200	6	870	500	9		
palustric	0.5 - 3	500 - 600	6					
isopimaric	2	400 - 1,000	6	2,030	1,000	9		
Fatty Acids								
oleic	1 - 97	3,500 - 8,200	6	--	<40,000	9		
linoleic	0.7 - 4	2,000 - 4,500	6	1,070	<1,000	9		
dichlorostearic	1 - 10	2,500	6	57	10	9		

References:
1 EPA (1985a)
2 NAS (1973)
3 EPA (1985b)
4 EPA (1980a)
5 EPA (1980b)
6 McLeary & Assoc. (1986)
7 Cardwell et al (1979)
8 Woelke (1972)
9 Cherr et al (1987)
10 Ribio & Kaiser(1987)
11 Bitton (1982)

for some other effluents including sulfite and oxygen delignification mills (Hall, 1990, personal communication). The NCASI data are not presently available.

Effluent Quality During Salmon Survival Experiments

A major objective of Ecology's monitoring effort was to determine if effluent quality during experiments conducted for the salmon study was typical of normal discharges. This concern is addressed below, drawing on data collected by Ecology, EPA, and industry.

Potentially Toxic Constituents -- Figures 7 and 8 compare the concentrations of metals and organic compounds measured in Weyerhaeuser and ITT effluent collected while the coho bioassay and/or live box experiments were underway (April 24 and May 17 samples), with similar data for the remainder of the monitoring period (March through June). The organics data were summed as described above.

For both Weyerhaeuser and ITT, comparable or higher metals concentrations were measured in effluent samples collected during the salmon study than in samples collected prior to and following the study. A similar conclusion holds for volatiles, guaiacols, and other chlorophenols concentrations in Weyerhaeuser samples. Some of the lower concentrations of phenols, catechols, resin acids, and fatty acids in Weyerhaeuser samples occurred during the salmon study, but only in one of the two collections. Levels of organic compounds in ITT effluent collected during the salmon study were at the upper end of the range observed during the four collections at that facility.

Bioassays -- Results of the oyster larvae and echinoderm bioassays - and, in the case of ITT, the rainbow trout and Microtox bioassays - indicate no appreciable changes in effluent toxicity occurred during the salmon study (Table 8). Rainbow trout and Microtox bioassays of Weyerhaeuser effluent, however, showed toxicity only prior to and after the study period.

Table 11 compares Ecology's rainbow trout data for Weyerhaeuser with results of rainbow trout bioassays conducted by the mill between January and September, 1989. When these data are considered together, the toxicity of Weyerhaeuser effluent to trout appears to vary from lethal to non-toxic over periods as short as one day and up to three days. Although Ecology results showed more frequent toxicity, it should be noted that the Ecology sample collected the day after Weyerhaeuser reported a bioassay failure (40% survival, March 6) had 100% survival.

Figure 9 summarizes Weyerhaeuser's rainbow trout data since 1986. Historically, there has been a general pattern of increased effluent toxicity during the spring and summer months and relative infrequent toxicity during fall and winter. As a result of the Weyerhaeuser bioassay failures in 1986, Ecology ordered the mill to conduct a study aimed at achieving compliance with the bioassay requirement in its NPDES permit. Control measures implemented as a result of this study (Campbell, 1987) have reduced the frequency of bioassay failures. Viewed in this light, the Weyerhaeuser bioassays in 1989 are consistent with the historical pattern of recent improvement in effluent toxicity since 1986. Ecology results, however, indicate that the effluent toxicity problem had not been solved.

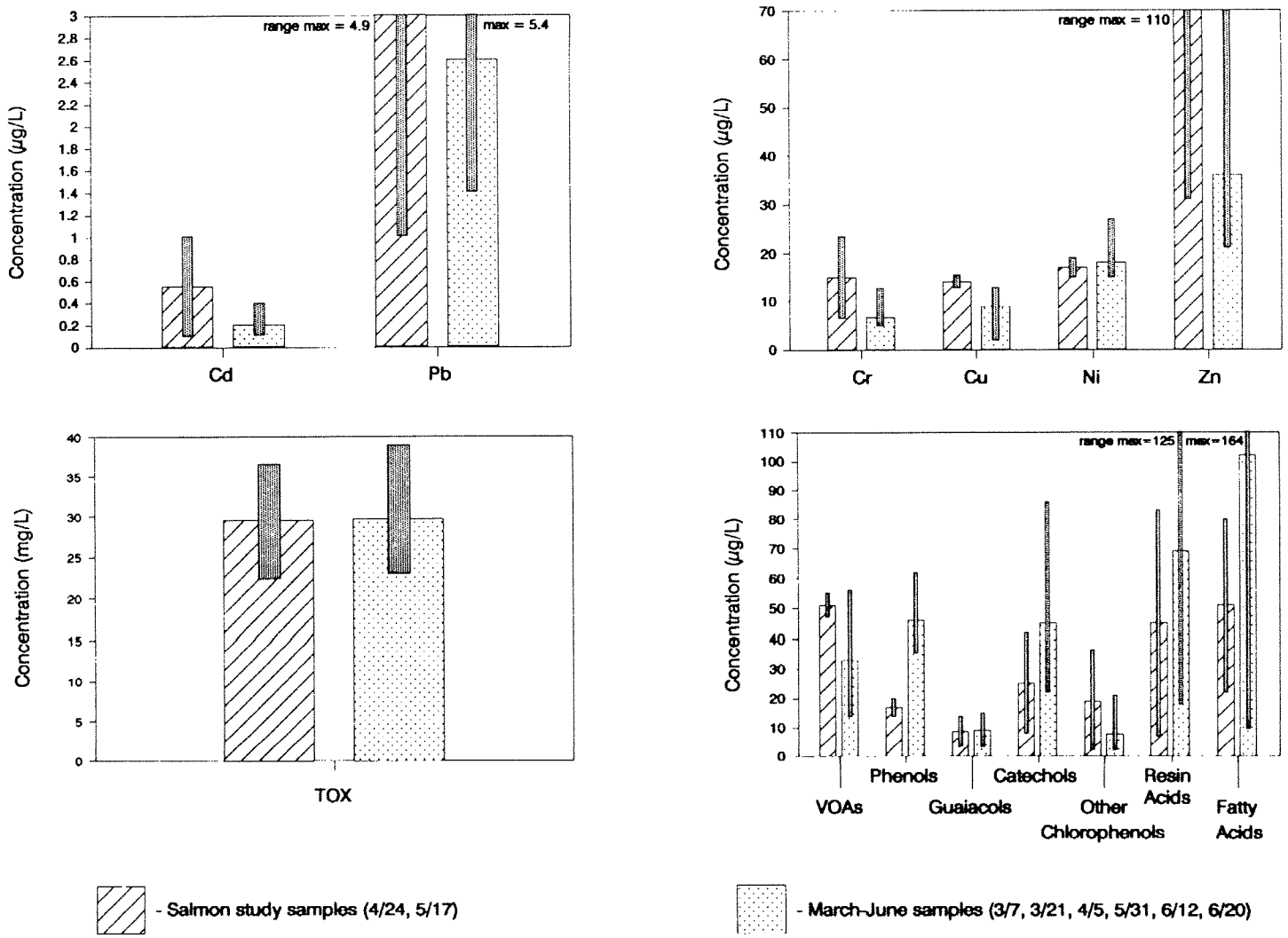


Figure 7. Toxic constituents in Weyerhaeuser effluent samples collected during salmon survival studies compared to other samples collected March - June 1989. Small bars within graphs represent data ranges.

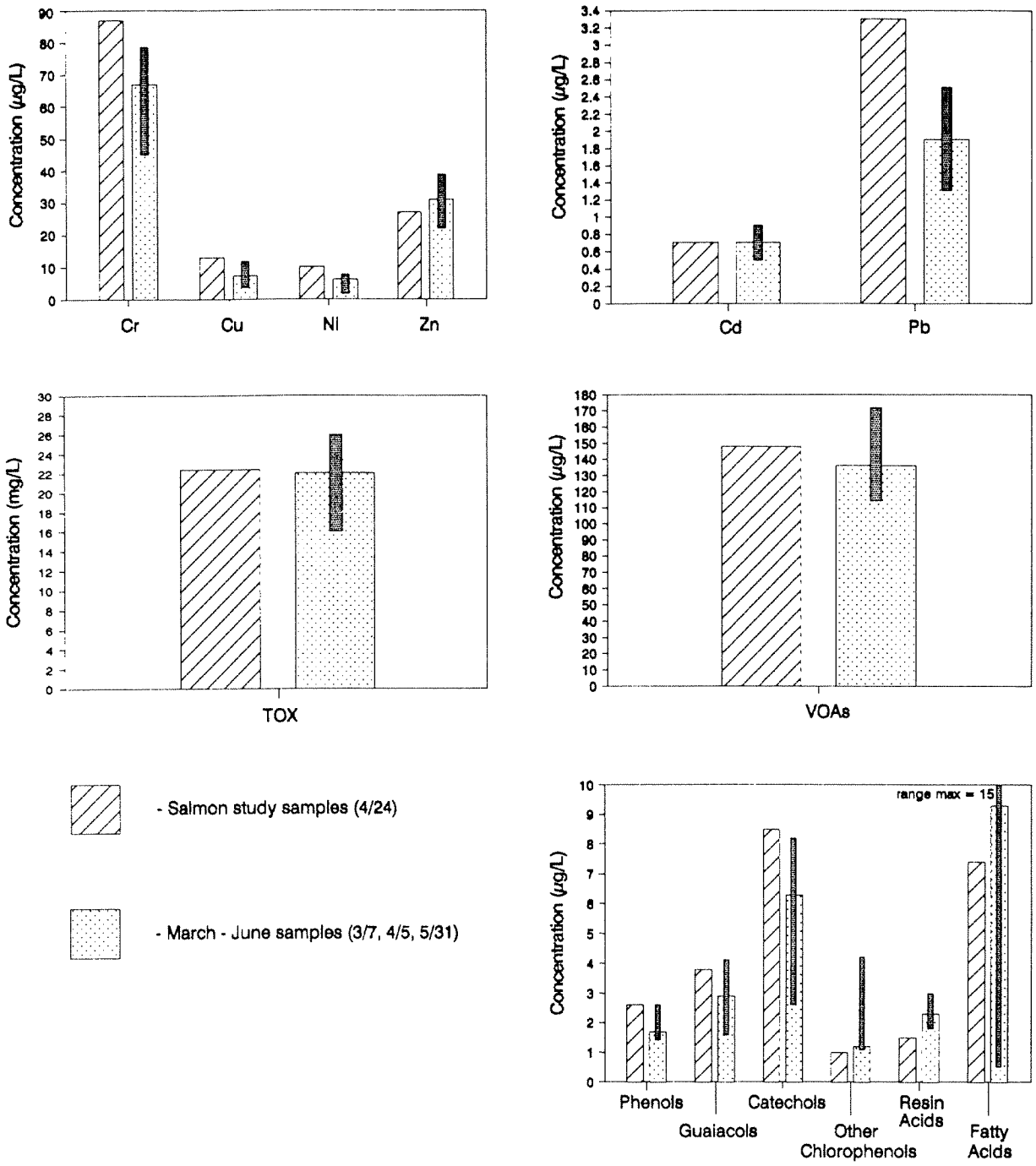


Figure 8. Toxic constituents in ITT effluent samples collected during salmon survival studies compared to other samples collected March - June 1989. Small bars within graphs represent data ranges.

Table 11. Comparison of rainbow trout effluent bioassays by Weyerhaeuser and Ecology during 1989 (% survival).

Date	Weyerhaeuser Data	Ecology Data
1/08	100%	--
1/22	100%	--
2/15	100%	--
2/26	100%	--
3/06	40%	--
3/07	--	100%
3/20	100%	--
3/21	--	13%
4/03	100%	--
4/05	--	100%
4/16	90%	--
4/21	--	100%
5/07	90%	--
5/17	--	100%
5/29	100%	--
5/31	--	3%
6/04	100%	--
6/12	--	100%
6/17	100%	--
6/20	--	0%
7/09	100%	--
7/23	100%	--
8/06	100%	--
8/20	100%	--
9/04	100%	--
9/17	100%	--

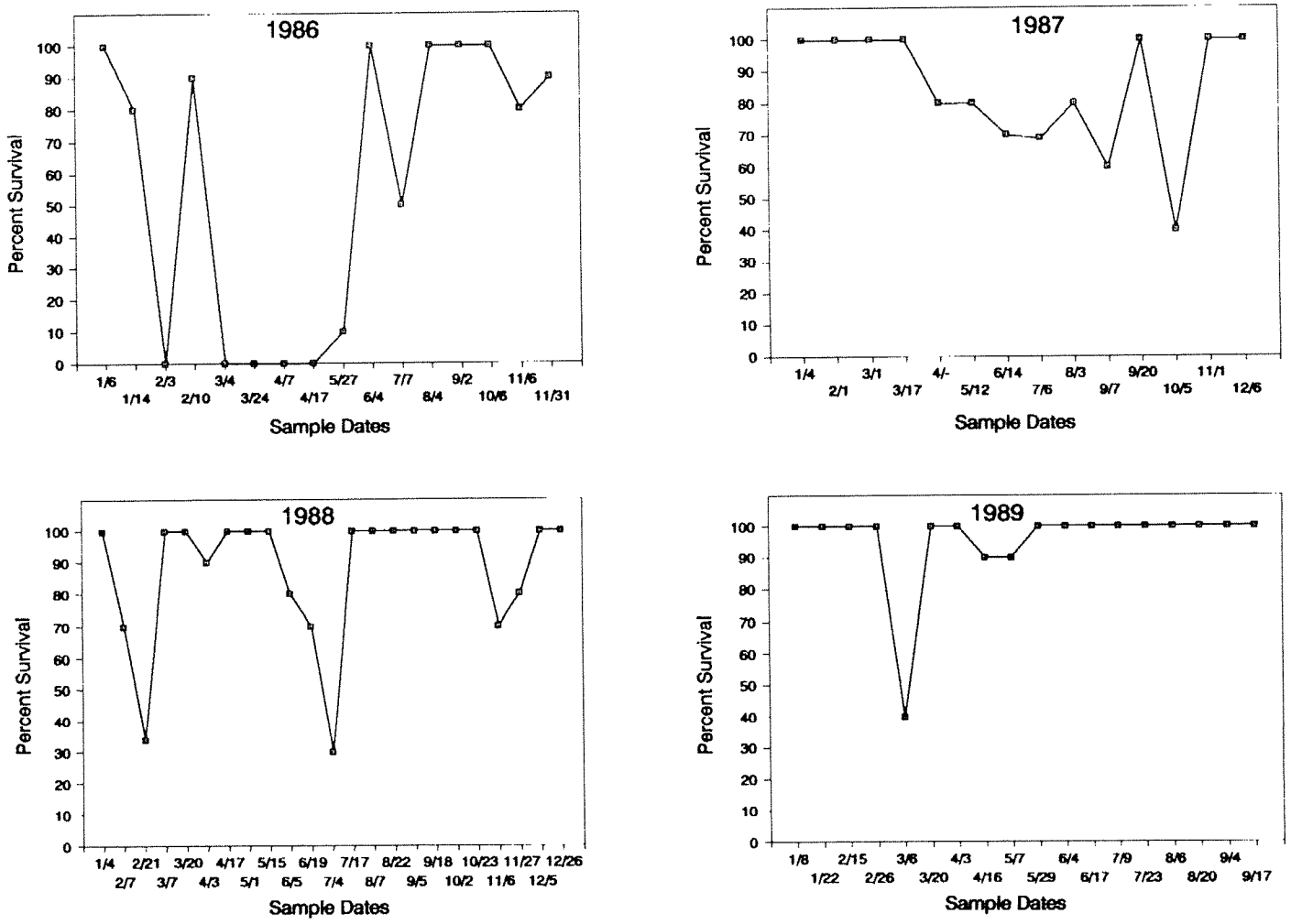


Figure 9. Historical record of Weyerhaeuser's rainbow trout bioassays 1986 - 1989.

The margin between toxic and non-toxic pulp mill effluent can be small. Acute lethality of mill effluents has been known to vary on a daily and even hourly basis (Walden and Howard, 1977; Chandrasekan, 1978). Relatively small increases in concentrations of effluent constituents can result in toxicity. For example, chlorodehydroabietic acid and tetrachloroguaiacol are toxic to rainbow trout at 750 μg/L and 350 μg/L, respectively, but non-toxic at 500 μg/L and 300 μg/L (Leach and Thakore, 1977).

Factors other than effluent quality potentially responsible for the greater number of failures in Ecology samples include sample collection and handling methods, and bioassay procedures. Weyerhaeuser samples are 24-hour composites (i.e., two discharge cycles sampled) in contrast to the single discharge sampled by Ecology. Time between sample collection and bioassay also can influence toxicity (Cardwell et al., 1976; Walden, 1976) and is not standardized.

Pulp mill effluent is much more toxic to salmonids at pH 6.7 than 7.4 (Walden, 1976). This may have been a contributing factor in the failure experienced in Ecology's July 20 sample at Weyerhaeuser which was the most toxic of the samples tested and, unlike other rainbow trout bioassays conducted for this study, drifted downward from an initial pH of 7.4 to a pH in the range of 6.5 - 6.8 midway through the test. Finally, Weyerhaeuser aerates the effluent mixture during their bioassays, while Ecology aerates only when necessary to maintain D.O. above minimum required saturation levels (>60% for the first 48 hours, >40% after 48 hours). In the upcoming NPDES permits, bioassay procedures will be standardized by stipulating the testing protocols following those described in Ecology (1980) or other protocols approved by Ecology.

Pulp Grades -- The schedule of pulp grades produced by Weyerhaeuser was examined to determine if there was a relationship with the bioassay failures or salmon study. Table 12 shows the results. Based on this information it appears that five of the six grades in largest production during March - June 1989 were being produced at one time or another during the salmon study. The remaining six grades were each in production for periods of one to three days only. Perhaps more significant is the fact that four separate pulp grades were in production during bioassay failures, and three of these were being made during the salmon study.

DMR Data -- Weyerhaeuser and ITT are required to submit monthly discharge monitoring reports (DMRs) to Ecology. Ecology assesses the accuracy of these data by monitoring the mill's analysis of EPA performance evaluation samples submitted annually, through annual sample splits and reviews of laboratory procedures, and with comprehensive inspections such as those conducted at the Grays Harbor mills in 1988 (Hallinan, 1989; Reif, 1989a). DMR data on flow, BOD, and TSS reported for March - June, 1989 are plotted in Figures 10 and 11. Based on these general indicators of plant performance and effluent quality, normal discharges were occurring during most of the salmon study.

Two significant effluent fluctuations, however, did take place over several days of the salmon study. The first was the interruption of Weyerhaeuser discharges in early May for annual

Table 12. Weyerhaeuser pulp grades in production during 1989 salmon survival experiments.

Weyerhaeuser Pulp Grade Code	Number of Days in Production During 1989 Salmon Survival Experiments		Total Number of Days in Production During March - June 1989
	April 21-May 7	May 12-28	
006[a]	11		35
096	2	8	23
094[b]			14
093[c]		2	12
029[d]	3		10
008	1	2	4
010			3
016			3
023			3
009			2
099			2
025			1

a - in production during rainbow trout bioassay failure (Weyerhaeuser March 6 sample)

b - in production during rainbow trout bioassay failure (Ecology March 27 sample)

c - in production during rainbow trout bioassay failure (Ecology May 31 sample)

d - in production during rainbow trout bioassay failure (Ecology June 20 sample)

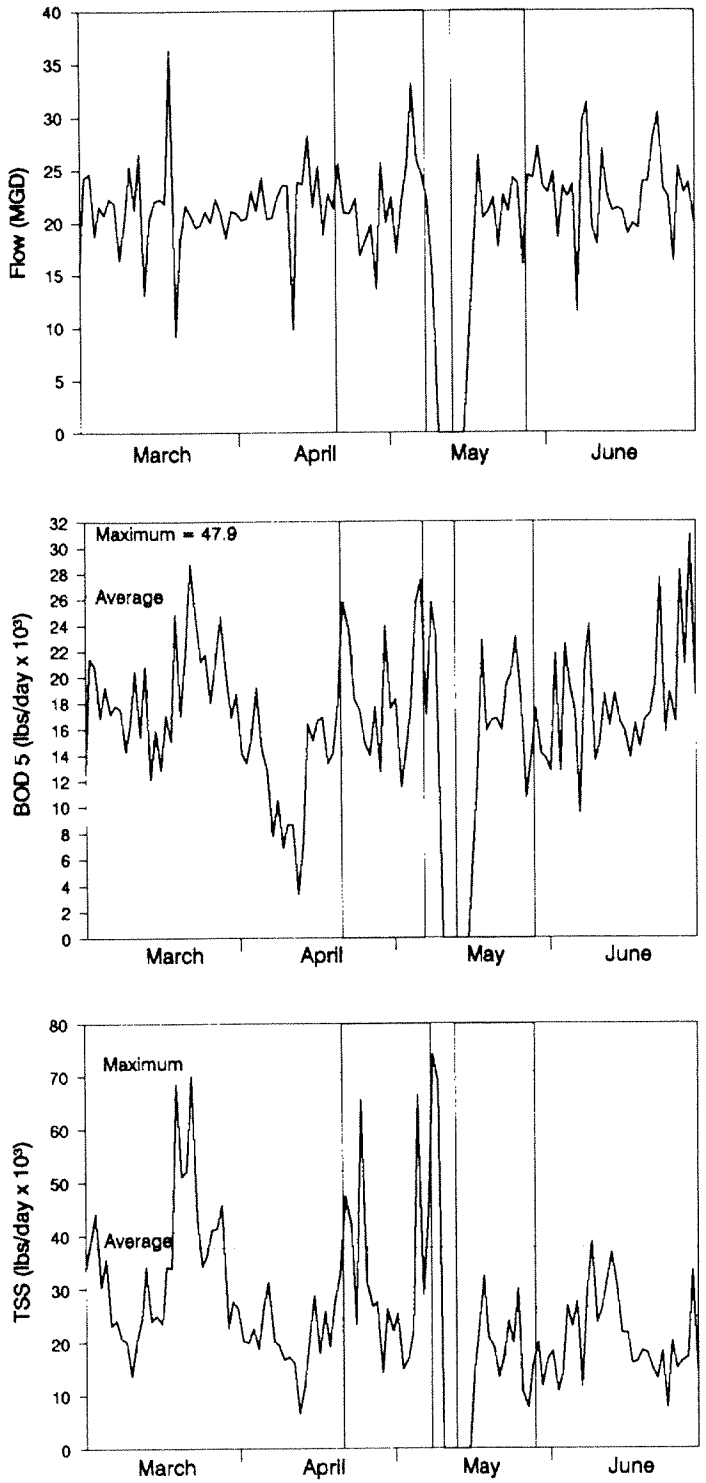


Figure 10. Weyerhaeuser discharge monitoring report data for March - June 1989. Periods of salmon survival studies (April 21 - May 7 and May 12 - May 28) indicated by vertical lines. Horizontal lines represent daily maximum and monthly average permit limits.

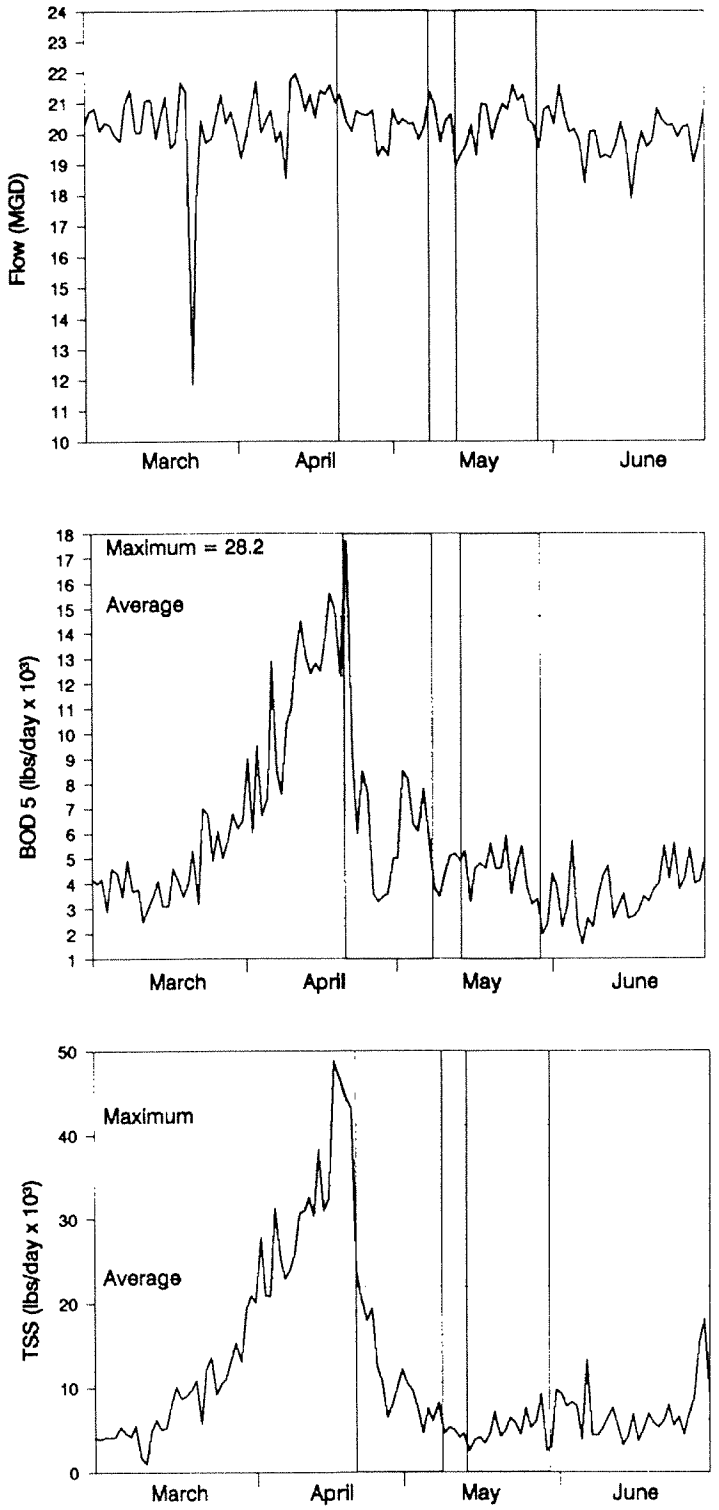


Figure 11. ITT discharge monitoring report data for March - June 1989. Periods of salmon survival studies (April 21 - May 7 and May 12 - May 28) indicated by vertical lines. Horizontal lines represent daily maximum and monthly average permit limits.

plant maintenance. This began May 9 and extending into the first four days of the second round of live box experiments begun May 12. Study participants were warned of the shutdown in advance. The second fluctuation was the large increase in BOD and TSS loads from ITT prior to start of the coho smolt bioassay. This occurred due to an upset in the wastewater treatment system. In ITT's opinion, a series of BOD shocks resulted in dispersed floc conditions and poor settling of sludge in the clarifiers (Schaaf, 1989). Reduction in BOD loading eventually brought about return to normal treatment, although there were elevated TSS discharges during the first days of the bioassay. Excursions above NPDES limits at Weyerhaeuser and ITT during March - June 1989 and actions taken by Ecology are summarized in Table 13.

Fisheries' Effluent Samples -- A final concern with regard to the salmon study was the quality of effluent samples collected by Fisheries for the coho smolt bioassay. To determine if these were representative, grab samples were taken every other day from tanker truck loads of effluents used in the test. The samples were analyzed by Ecology for specific conductance, color, TSS, total recoverable phenolics, and TOX (Appendix G). Figures 12 and 13 compare these results with the mean, standard deviation, and range of values measured in samples collected by Ecology at the mill outfalls between March and June.

Fisheries' samples of Weyerhaeuser effluent collected during the bioassay period were within ranges observed by Ecology for specific conductance, color, TSS, and total recoverable phenolics - although highly colored effluent samples were collected early in the bioassay. TOX concentrations in all Fisheries samples, however, were consistently higher (50.1 - 80.8 mg/L) than Ecology measurements at the mills (22.5 - 39.0 mg/L) and appeared to increase as the bioassay progressed.

Samples of ITT effluent collected by Fisheries were also, on average, within ranges predicted by Ecology results for specific conductance, color, TSS, and total recoverable phenolics, although occasional outliers occurred for each of these variables. High TSS concentrations in the initial sample analyzed probably reflect the treatment plant upset described above. TOX concentrations in Fisheries' ITT samples were initially within the range of Ecology results but, like Weyerhaeuser samples, increased with successive samples to levels above those measured during Ecology's monitoring at the mills.

The reason for generally elevated TOX in Fisheries' bioassay samples is not known. TOX in pulp mill effluent often correlates with TSS, but a concomitant increase in TSS was not observed. The fact that there was a coincident increase in TOX for both mills' effluent suggests it may have been an artifact of sampling or sample handling methods by Fisheries and/or Ecology.

During April 22 - 24, EPA analyzed Fisheries' effluent samples as part of an independent study of toxicity in Grays Harbor estuary (Hornig, unpublished data). In this study a continuous flow centrifuge coupled to XAD resin columns was used for collection of suspended particulate matter (SPM) and soluble components. Target chemicals included

Table 13. NPDES permit exceedences during March - June 1989.

Date	Excursion	Ecology Action
Weyerhaeuser		
3/06[a]	40% survival in rainbow trout bioassay	$10,000 penalty
3/21[b]	13% survival in rainbow trout bioassay	$10,000 penalty
5/08[a]	daily maximum TSS load 74,100 lbs/day (permit 70,700 lbs/day)	mill contacted for explanation of problem
5/31[b]	3% survival in rainbow trout bioassay	$10,000 penalty
6/20[b]	0% survival in rainbow trout bioassay	$10,000 penalty
ITT		
4/18-21[a]	four daily maximum TSS loads 43,300-48,800 lbs/day; monthly average 26,000 lbs/day (permit 40,800 lbs/day maximum, 21,900 lbs/day monthly average)	$5,000 penalty

a - reported by industry Discharge Monitoring Report

b - Ecology sample, present study

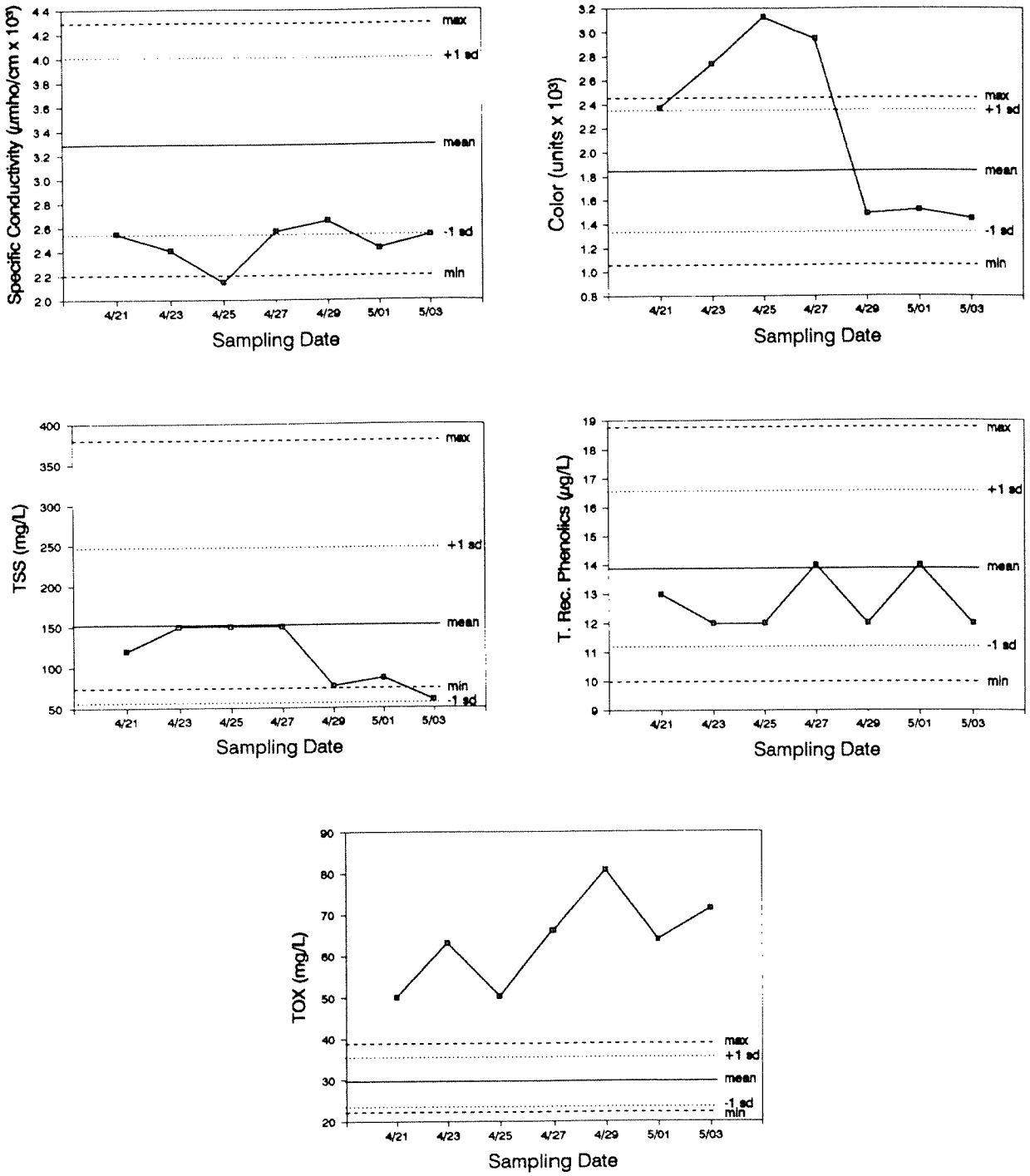


Figure 12. Quality of Fisheries' Weyerhaeuser effluent samples collected for coho smolt bioassay (line graphs) compared to results of Ecology's March - June 1989 monitoring program (represented by data means ±1 sd and ranges).

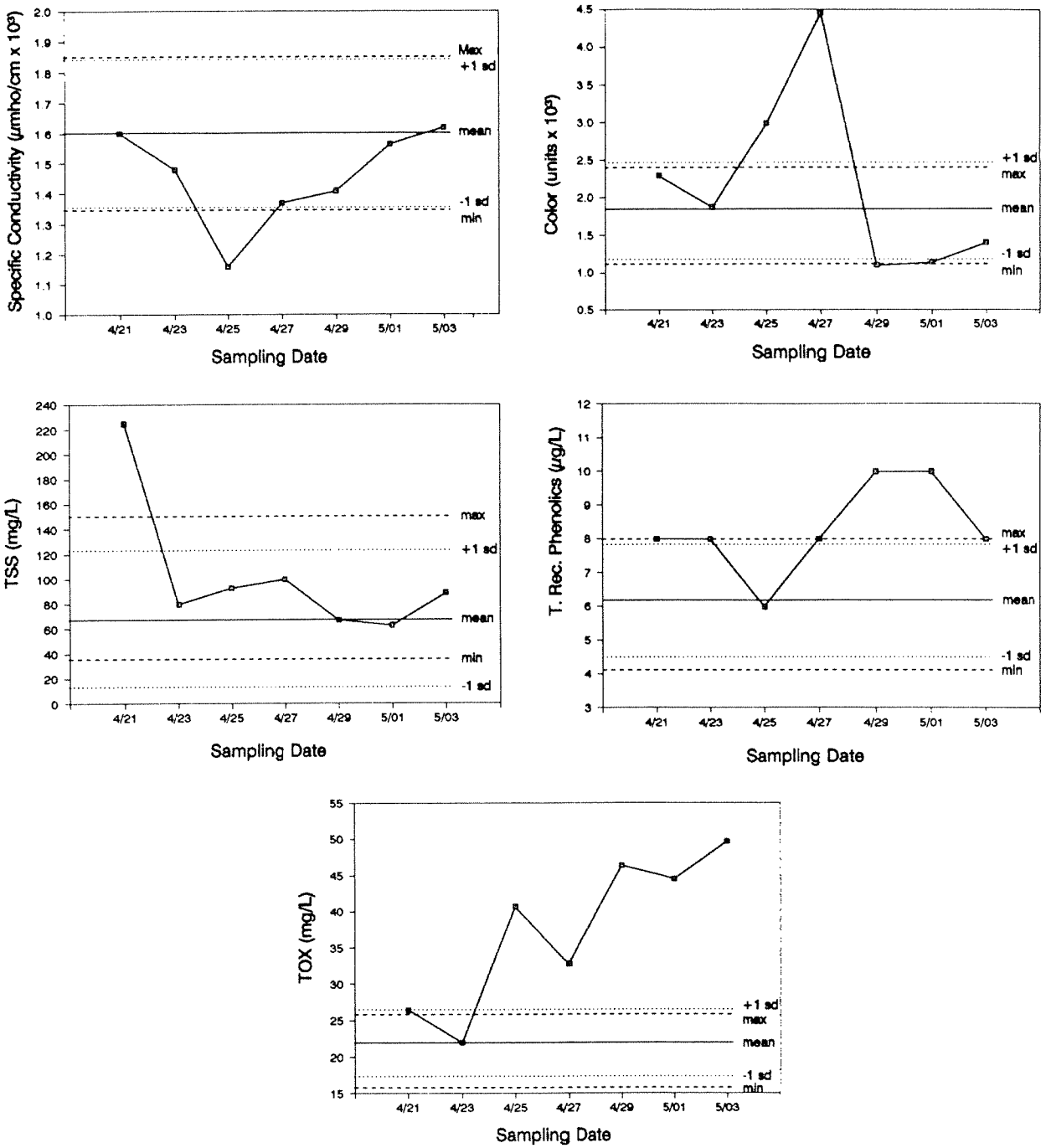


Figure 13. Quality of Fisheries' ITT effluent samples collected for coho smolt bioassay (line graphs) compared to results of Ecology's March - June 1989 monitoring program (represented by data means ± 1 sd and ranges).

the same metals and organic compounds analyzed during Ecology's monitoring program (Table 1); TOX was not analyzed. Ecology's Compliance Monitoring Section provided technical support for the EPA study.

Tables 14 and 15 compare EPA results with Ecology's data for effluent collected at the mill outfalls during the same period (April 24). EPA and Ecology samples of whole effluent agreed closely in concentrations of the majority of metals and volatile compounds. EPA results showed zinc concentrations two to three times higher than measured in Ecology samples. EPA also detected a much higher concentration of chloroform in Weyerhaeuser effluent than Ecology (130 vs. 16 μg/L).

Most phenols, guaiacols, catechols, resin acids, and fatty acids were detected in common by EPA and Ecology. EPA results show phenols, guaiacols, and catechols were effectively absorbed by XAD resin; resin and fatty acids were primarily associated with SPM. Total concentrations (SPM + XAD) of phenols, guaiacols, and catechols were in good agreement with concentrations measured in Ecology's whole water samples. EPA, however, measured somewhat higher concentrations of chlorinated resin acids and fatty acids.

CONCLUSIONS

Constituents of pulp mill effluents to which studies have commonly attributed toxic properties, are present at low levels in Weyerhaeuser and ITT effluents. These and other potentially toxic chemicals analyzed during the present study do not explain adverse effects observed in effluent bioassays with rainbow trout, Microtox (except perhaps phenols), oyster larvae, and echinoderm sperm cells. Furthermore, they constitute a minor loading to the inner harbor relative to the total discharge of halogenated material. The most significant difference in effluent quality between the two mills appears to be continued sporadic toxicity of Weyerhaeuser effluent to rainbow trout. Effluent dilution may not be adequate in inner Grays Harbor, based on results of the oyster larvae and echinoderm bioassays.

The weight of evidence provided by chemical and bioassay data collected by Ecology, EPA, and industry show pulp mill effluent quality during experiments conducted for the 1989 Grays Harbor salmon survival study was generally typical of normal discharges. Ecology's rainbow trout bioassays at Weyerhaeuser are not in agreement with industry data showing a general absence of toxicity. The Ecology results suggest a toxic property of this effluent may have been absent, or present at reduced levels, during the salmon study experiments. However, short-term effluent variability, sample collection, sample handling, and bioassay protocols are all potentially important contributing factors in this apparent discrepancy.

Conducting this sampling program without announcing to the mills when collections would occur did not result in delays in obtaining samples and was met with cooperation by mill personnel. A useful data set was obtained which has the additional benefit of objectivity and impartiality imparted by doing unannounced sampling.

Table 14. Comparison of Ecology and EPA analysis of Weyerhaeuser effluent during 1989 coho smolt bioassays (μg/L).

Effluent Source:	Weyerhaeuser				
Investigator:	Ecology	EPA			
Date:	4/24	4/22	4/23-24	4/23-24	SPM +
Matrix:	whole water	whole water	SPM	XAD Resin	XAD
Metals					
cadmium	0.2 U	0.2	NA	NA	--
chromium	6.9	6.5	NA	NA	--
copper	13	12	NA	NA	--
lead	1.0	3.0	NA	NA	--
nickel	15	18	NA	NA	--
zinc	31	85	NA	NA	--
Volatiles					
chloroform	16	130	NA	NA	--
2-butanone	36	42	NA	NA	--
toluene	2.6	2	NA	NA	--
bromodichloromethane	0.3 U	5 U	NA	NA	--
1,2-dichloropropane	0.7 U	5 U	NA	NA	--
Phenols					
4-methylphenol	10	NA	0.8	9.7	10
2,4-dimethylphenol	0.3	NA	0.03 U	0.04	0.04
2-chlorophenol	0.2	NA	0.03 U	0.1 U	ND
2,4-dichlorophenol	2	NA	0.2	2.1	2.3
2,4,6-trichlorophenol	8	NA	0.7	6.0	6.7
Guaiacols					
guaiacol	2	NA	0.1	1.9	2.0
4-allylguaiacol	0.9	NA	0.03	0.4	0.4
4-chloroguaiacol	0.4	NA	0.03	0.2	0.2
4,5-dichloroguaiacol	2	NA	0.1	1.3	1.4
4,5,6-trichloroguaiacol	2	NA	0.2	1.3	1.5
tetrachloroguaiacol	7	NA	0.5	2.6	3.1
Catechols					
4-chlorocatechol	0.5	NA	0.04	0.4	0.4
4,5-dichlorocatechol	4	NA	0.6	5.3	5.9
3,4,5-trichlorocatechol	26	NA	6.7	18	25
tetrachlorocatechol	12	NA	1.2	3.9	5.1
Other Chlorophenols					
trichlorosyringol	35	NA	1.4	12	13
6-chlorovanillin	0.5 U	NA	0.03 U	0.7	0.7
5,6-dichlorovanillin	1	NA	0.03 U	0.1	0.1
Resin Acids					
abietic	0.4 U	NA	0.2	0.2 U	0.2
dehydroabietic	1	NA	0.7	0.2 U	0.7
12-chlorodehydroabietic	1	NA	6.7	2.3	9.0
14-chlorodehydroabietic	0.5	NA	2.4	1.1	3.5
dichlorodehydroabietic	1	NA	5.0	2.4	7.4
palustric	0.4 U	NA	ND	0.2 U	ND
isopimaric	0.4 U	NA	0.4	0.2 U	0.4

Table 14. (Continued)

Effluent Source:	Weyerhaeuser				
Investigator:	Ecology	EPA			
Date:	4/24	4/22	4/23-24	4/23-24	SPM +
Matrix:	whole water	whole water	SPM	XAD Resin	XAD
Fatty Acids					
oleic	**1**	NA	**17**	0.2 U	**17**
linoleic	**0.7**	NA	**14**	0.2 U	**14**
octadecanoic	**3**	NA	**13**	**5.9**	**19**
hexadecanoic	**5**	NA	**23**	0.2 U	**23**
palmitoleic	**3**	NA	**23**	0.2 U	**23**
9,10-dichlorostearic	**9**	NA	**0.7**	**4.5**	**5.2**
Miscellaneous					
a-terpineol	0.5 U	NA	0.03 U	0.1 U	ND

U = not detected at detection limit shown
NA = not analyzed
ND = not detected

Table 15. Comparison of Ecology and EPA analysis of ITT effluent during 1989 coho smolt bioassays (μg/L).

Effluent Source:	ITT				
Investigator:	Ecology	EPA			
Date:	4/24	4/23	4/23-24	4/23-24	SPM +
Matrix:	whole water	whole water	SPM	XAD Resin	XAD
Metals					
cadmium	0.7	1.2 NA	NA	--	
chromium	87	146	NA	NA	--
copper	13	17	NA	NA	--
lead	3.3	4.2 NA	NA	--	
nickel	10	6.3 NA	NA	--	
zinc	27	54	NA	NA	--
Volatiles					
chloroform	140	95	NA	NA	--
2-butanone	6.2	10 U	NA	NA	--
toluene	0.8	0.4	NA	NA	--
bromodichloromethane	1.1	0.5	NA	NA	--
1,2-dichloropropane	0.7 U	0.5 U	NA	NA	--
Phenols					
4-methylphenol	0.7	NA	25	0.08	25
2,4-dimethylphenol	0.5 U	NA	0.05 U	0.07 U	ND
2-chlorophenol	0.5 U	NA	0.05 U	0.07 U	ND
2,4-dichlorophenol	0.4	NA	0.3	0.3	0.6
2,4,6-trichlorophenol	1	NA	0.5	1.0	1.5
Guaiacols					
guaiacol	0.6	NA	2.8	0.1	2.9
4-allylguaiacol	0.5 U	NA	0.2	0.07 U	0.2
4-chloroguaiacol	0.5 U	NA	0.05 U	0.07 U	ND
4,5-dichloroguaiacol	0.4	NA	0.1	0.2	0.3
4,5,6-trichloroguaiacol	0.3	NA	0.05 U	0.1	0.1
tetrachloroguaiacol	2	NA	0.3	1.1	1.4
Catechols					
4-chlorocatechol	0.1	NA	0.04	0.07 U	0.04
4,5-dichlorocatechol	0.4	NA	0.2	0.08	0.3
3,4,5-trichlorocatechol	4	NA	0.7	0.7	1.4
tetrachlorocatechol	4	NA	0.2	0.5	0.7
Other Chlorophenols					
trichlorosyringol	0.5 U	NA	0.05 U	0.07 U	ND
6-chlorovanillin	0.4	NA	0.05 U	0.3	0.3
5,6-dichlorovanillin	0.4	NA	0.05 U	0.2	0.2
Resin Acids					
abietic	0.4 U	NA	0.9	0.1 U	0.9
dehydroabietic	0.4 U	NA	1.2	0.1 U	1.2
12-chlorodehydroabietic	0.3	NA	2.3	0.1 U	2.3
14-chlorodehydroabietic	0.4 U	NA	0.8	0.1 U	0.8
dichlorodehydroabietic	0.4 U	NA	0.6	0.1 U	0.6
palustric	0.4 U	NA	ND	0.1 U	ND
isopimaric	0.4 U	NA	ND	0.1 U	ND

Table 15. (Continued)

Effluent Source:	ITT				
Investigator:	Ecology	EPA			
Date:	4/24	4/22	4/23-24	4/23-24	SPM +
Matrix:	whole water	whole water	SPM	XAD Resin	XAD
Fatty Acids					
oleic	0.4 U	NA	**8.8**	0.1 U	**8.8**
linoleic	0.4 U	NA	**0.3**	0.1 U	**0.3**
octadecanoic	**2**	NA	**13**	**3.2**	**15**
hexadecanoic	**2**	NA	**26**	B	**26**
palmitoleic	**1**	NA	**29**	0.1 U	**29**
9,10-dichlorostearic	**2**	NA	**0.6**	**1.7**	**2.3**
Miscellaneous					
a-terpineol	0.5 U	NA	0.05 U	0.07 U	ND

U = not detected at detection limit shown
NA = not analyzed
ND = not detected
B = blank contamination

RECOMMENDATIONS

1. Ecology should assure that approved protocols are being followed during rainbow trout bioassays by the Grays Harbor mills. Ecology should conduct periodic effluent collections and sample splits for trout assay. Weyerhaeuser should maintain or increase its twice monthly schedule of trout bioassays until it is demonstrated the toxicity problem no longer exists.

2. The possible role of surfactants, sulfite/bisulfite, and especially the water soluble, high molecular weight fraction in toxicity of Grays Harbor pulp mill effluents should be further investigated.

3. The toxicity of the inner Grays Harbor water column should be assessed by direct measurements employing oyster larvae and echinoderm sperm cell bioassays or comparably sensitive tests. This would ideally be scheduled to include periods of maintenance shutdown at the pulp mills.

4. Effluent collection and analysis during unannounced inspections should become a routine part of Ecology's compliance monitoring program.

Acknowledgements -- The authors appreciate the courtesy shown by Weyerhaeuser and ITT personnel during effluent collections at their facilities. We also thank Nancy Eller of USFWS for collecting during the coho smolt bioassay. The work of the Ecology/EPA Manchester laboratory in analyzing the samples for this study is very much appreciated. Sonya Kirkendall and Kelly Carruth did the word processing for this report.

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APPENDIX A

Ecology Analysis of Water Samples
During 1988 Grays Harbor Salmon Survival Study

Table A-1. Metals Concentrations in Water Samples Collected by Ecology during Coho Smolt Bioassay, Aberdeen, May 26-30, 1988 (μg/L; ppb-total recoverable metal).

Sample Type	Chehalis River Water		Weyerhaeuser Effluent		
Collection Date	5/27	5/30	5/28	-- 5/30 --	
Collection Time at Facility	0830	0855	1305	1225	
Time Subsample Collected	1610	1325	1510*	1630	1645
Sample Number (22-)	8234	8242	8257	8236	8237
Antimony	0.1 U	0.1 U	0.1 U	1 U	1 U
Arsenic	1 U	0.30	2 UJ	2 UJ	2 UJ
Cadmium	0.08	0.06	0.22	0.18	0.15
Chromium	0.6	0.9	1 U	5.7	5.2
Copper	1.3 B	1.4 B	6.8	8.4	8.4
Lead	2.2 J	1.2 J	2.0	1.7	1.8
Mercury	0.1 U	0.1 U	0.1 U	0.26	0.14
Nickel	1 U	1.0	6.6	6.0	5.8
Selenium	0.5 U	0.5 U	1 U	1 U	1 U
Silver	0.2	0.19	0.1 UJ	0.1 UJ	0.1 UJ
Thallium	0.1 U	0.1 U	1 U	1 U	1 U
Zinc	13 BJ	10 BJ	133 J	93 J	91 J

* Subsample was collected 5/29

Sample Type	ITT Effluent		Aberdeen STP Effluent		
Collection Date	5/27	5/30	5/27	----5/30----	
Collection Time at Facility	1500	1410	0852	1200	
Time Subsample Collected	1625	1510	1545	1610	1620
Sample Number (22-)	8231	8238	8232	8239	8240
Antimony	1 U	1 U	0.29	0.27	0.58
Arsenic	2 UJ	2 UJ	0.58	0.87	0.84
Cadmium	0.64	0.9	0.20	0.24	0.38
Chromium	486	227	1.4	1.2	1.7
Copper	5.8	8.6	8.7	8.7	5.6
Lead	4.3	5.9	2.4 J	3.3 J	1.4 J
Mercury	0.1 U	0.1 U	0.1 U	0.1	0.1 U
Nickel	7.2	6.2	2.2	2.2	2.1
Selenium	1 U	1 U	0.5 U	0.5 U	0.5 U
Silver	0.1 UJ	0.1 UJ	0.7	0.8	0.3
Thallium	1 U	1 U	0.1 U	0.1 U	0.1 U
Zinc	49 J	52 J	38	32	22

U = not detected at detection limit shown
J = an estimated value due to low matrix spike recoveries (75%)
B = detected value is 5 times reagent blank

Table A-1. (continued)

Sample Type	Hoquiam STP Effluent		Dilution Water
Collection Date	5/27	5/30	5/27
Collection Time at Facility	0802	1308	-
Time Subsample Collected	1530	1450	1445
Sample Number (22-)	8233	8241	8235
Antimony	1.3	1.0	0.1 U
Arsenic	1.2	1.6	0.23
Cadmium	0.21	0.18	0.17
Chromium	2.2	1.6	0.8
Copper	6.1	6.9	1.2 B
Lead	5.8 J	2.0 J	0.9 J
Mercury	0.1 U	0.1	0.1 U
Nickel	2.3	2.0	1 U
Selenium	0.5 U	0.5 U	0.5 U
Silver	0.1	0.15	0.1
Thallium	0.1 U	0.1 U	0.1 U
Zinc	50 J	42 J	8 BJ

Sample Type	Transfer Blank	Transport Blank	Reference Toxicant	
Collection Date	5/30	-	5/27	5/30
Time Subsample Collected	-	-	1045	1335
Sample Number (22-)	8245	8246	8247	8263
Antimony	0.1 U	0.1 U	NA	NA
Arsenic	0.15	.18	NA	NA
Cadmium	0.05	0.05	NA	NA
Chromium	0.5 U	0.5 U	NA	NA
Copper	0.7 B	0.6 B	13	13
Lead	0.47 J	0.54 J	NA	NA
Mercury	0.1 U	0.1	NA	NA
Nickel	1 U	1 U	NA	NA
Selenium	0.5 U	0.5 U	NA	NA
Silver	0.18	0.20	NA	NA
Thallium	0.1 U	0.1 U	NA	NA
Zinc	4.2 BJ	5.3 BJ	NA	NA

U = not detected at detection limit shown
J = an estimated value due to low matrix spike recoveries (75%)
B = detected value is 5 times reagent blank
NA = not analyzed

Table A-2. Organic Priority Pollutants/Hazardous Substances List Compounds Detected in Water Samples Collected by Ecology During Large-scale Smolt Bioassay, Aberdeen, May 26-30, 1988 (μg/L;ppb)

Sample Type	Chehalis River Water		Weyerhaeuser Effluent			ITT Effluent	
Collection Date	5/27	5/30	5/28	--5/30--		5/27	5/30
Collection Time at Facility	0830	0855	1305	--1225--		1500	1410
Time Subsample Collected	1610	1325	1510*	1630	1645	1625	1510
Sample No. (22-)	8234	8242	8257	8236	8237	8231	8238
Volatile Organics							
Chloroform	5 U	5 U	140	180 J	170 J	220	190 J
Bromodichloromethane	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Styrene	5 U	5 U	5 U	0.9 J	5 U	5 U	5 U
Carbon disulfide	5 U	5 U	0.5 J	0.3 J	0.3 J	5 U	5 U
Toluene	5 U	5 U	0.5 J	0.5 J	0.6 J	5 U	5 U
Acetone	3 U	10 U	30 B	29 U	35 U	3 U	2 U
2-Butanone	2 U	10 U	25 B	17 BJ	11 U	10 BU	10 U
Low Molecular Weight PAH							
Naphthalene	1 U	0.9 U	0.3 J	0.9 U	1 U	0.4 J	0.5 J
Acenaphthylene	1 U	0.9 U	1 U	0.9 U	1 U	0.1 J	0.9 U
Acenaphthene	1 U	0.9 U	1 U	0.9 U	1 U	0.7 J	0.9 U
Fluorene	1 U	0.9 U	1 U	0.9 U	1 U	0.06J	0.9U
Phenanthrene	1 U	0.9 U	1 U	0.9 U	1 U	1	0.9 U
High Molecular Weight PAH							
Fluoranthene	1 U	0.9 U	1 U	0.9 U	1 U	0.8	0.9 U
Pyrene	1 U	0.9 U	1 U	0.9 U	1 U	1.1	0.9 U
Benzo(a)anthracene	1 U	0.9 U	1 U	0.9 U	1 U	0.2 J	0.9 U
Chrysene	1 U	0.9 U	1 U	0.9 U	1 U	0.3 J	0.9 U
Benzo(b)fluoranthene	1 U	0.9 U	1 U	0.9 U	1 U	0.2 J	0.9 U
Benzo(k)fluoranthene	1 U	0.9 U	1 U	0.9 U	1 U	0.3 J	0.9 U
Chlorinated Organics							
bis(2-Chloroethyl)ether	1 U	0.9 U	1 U	0.9 U	1 U	5 J	0.9 U
1,4-Dichlorobenzene	1 U	0.9 U	1 U	0.9 U	1 U	0.9 U	0.9 U
Phthalates							
Dimethylphthalate	1 U	0.9 U	1	1	1 U	2	0.9 U
Di-n-butylphthalate	0.07BJ	0.9 BU	1 BU	0.9 BU	1 BU	0.9 BU	0.9BU
Butylbenzylphthalate	1 BU	0.9 BU	1 BU	0.9 BU	1 BU	0.5 BJ	1 B
bis(2-Ethylhexyl)phthalate	4 B	1 B	1 BU	0.7 BJ	1 BU	2 B	1 B
Di-n-octylphthalate	0.3 J	0.9 U	1 U	0.9 U	1 U	0.6 J	0.9 U
Phenols							
Phenol	0.5 U	0.9 U	1 U	0.9 U	1 U	0.9 U	0.9 U
4-Methylphenol	0.5 U	0.9 U	37	0.9 U	19	0.9 U	0.9 U
2,4-Dichlorophenol	0.5 U	0.9 U	1 U	2	1 U	0.9 U	0.9 U
2,4,6-Trichlorophenol	0.5 U	0.9 U	8	5	7	4 J	6
Miscellaneous Extractables							
Benzoic acid	2.5 U	5 U	5 U	5 U	11	5 U	4 U
Dibenzofuran	1 U	0.9 U	1 U	0.9 U	1 U	0.07J	0.9 U
N-Nitrosodiphenylamine	1 U	0.9 U	1 U	0.9 U	1 U	0.9 U	0.9 U
Organochlorine Pesticides	ND	ND	ND	ND	ND	ND	ND
Polychlorinated Biphenyls	ND	ND	ND	ND	ND	ND	ND

* = subsample was collected 5/29
U = not detected at detection limit shown
J = an estimated concentration
B = also detected in method blank
ND = not detected

Table A-2. (continued)

Sample Type	Aberdeen STP Effluent			Hoquiam STP Effluent		Dilution Water	Transfer Blank	Transport Blank
Collection Date	5/27	--5/30--		5/27	5/30	5/27	5/30	--
Collection Time at Facility	0852	--1200--		0802	1308	--	--	--
Time Subsample Collected	1545	1610	1620	1530	1450	1445	--	--
Sample No. (22-)	8232	8239	8240	8233	8241	8235	8245	8246
Volatile Organics								
Chloroform	3 J	7 J	8 J	3 U	3 J	3 J	5 U	5 U
Bromodichloromethane	5 U	1 J	1 J	5 U	0.8 J	5 U	5 U	5 U
Styrene	2 J	1 J	1 J	5 U	5 U	5 U	5 U	5 U
Carbon disulfide	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Toluene	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Acetone	6 U	5 U	5 U	2 U	1 U	2 U	3 U	3 U
2-Butanone	46 B	10 BJ	13 BJ	1 U	10 U	10 U	10 U	1 U
Low Molecular Weight PAH								
Naphthalene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Acenaphthylene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Acenaphthene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Fluorene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Phenanthrene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
High Molecular Weight PAH								
Fluoranthene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Pyrene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Benzo(a)anthracene	1 U	1 U	1 U	0.9 U	0.04J	0.9 U	1 U	2 U
Chrysene	1 U	1 U	1 U	0.9 U	0.9 U	0.08J	1 U	2 U
Benzo(b)fluoranthene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Benzo(k)fluoranthene	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Chlorinated Organics								
bis(2-Chloroethyl)ether	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
1,4-Dichlorobenzene	0.3 J	0.3 J	0.3 J	0.9 U	0.9 U	0.9 U	1 U	2 U
Phthalates								
Dimethylphthalate	1	1 J	1 U	2	0.2 J	0.9 U	1 U	2 U
Di-n-butylphthalate	0.7 BJ	0.5 BJ	0.3 BJ	0.4 BJ	0.3 BJ	0.1 BJ	0.2 BJ	2 BU
Butylbenzylphthalate	0.3 BJ	0.3 BJ	1 BJ	0.3 BJ	0.1 BJ	0.2 BJ	1 BU	2 BU
bis(2-Ethylhexyl)phthalate	4 B	4 B	4 B	7 B	3 B	1 B	1 B	0.9 BJ
Di-n-octylphthalate	0.6 J	0.6 J	0.5 J	0.3 J	0.1 J	0.2 J	0.2 J	2 U
Phenols								
Phenol	0.5 J	1 J	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
4-Methylphenol	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
2,4-Dichlorophenol	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
2,4,6-Trichlorophenol	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
Miscellaneous Extractables								
Benzoic acid	2 J	0.5 J	6 U	0.5 J	5 U	0.9 U	5 U	10 U
Dibenzofuran	1 U	1 U	1 U	0.9 U	0.9 U	0.9 U	1 U	2 U
N-Nitrosodiphenylamine	5 U	1 U	1 U	0.9 U	0.1 J	0.9 U	1 U	2 U
Organochlorine Pesticides	ND	ND	ND	ND	ND	ND	ND	ND
Polychlorinated Biphenyls	ND	ND	ND	ND	ND	ND	ND	ND

* = subsample was collected 5/29
U = not detected at detection limit shown
J = an estimated concentration
B = also detected in method blank
ND = not detected

Table A-3. Pesticides Detected in Water Samples Collected by Ecology During Coho Smolt Bioassay, Aberdeen, May 26-30, 1988 (μg/L; ppb)

Sample Type	Chehalis River Water		Weyerhaeuser Effluent			ITT Effluent	
Collection Date	5/27	5/30	5/28	--5/30--		5/27	5/30
Collection Time at Facility	0830	0855	1305	--1225--		1500	1410
Time Subsample Collected	1610	1325	1510*	1630	1645	1625	1510
Sample No. (22-)	8234	8242	8257	8236	8237	8231	8238
Pentachlorophenol	0.002	0.004	NA	NA	NA	NA	NA
2,3,4,5-Tetrachlorophenol	0.002 U	0.002 U	NA	NA	NA	NA	NA
Diuron	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U

Sample Type	Aberdeen STP Effluent			Hoquiam STP Effluent		Dilution Water	Transfer Blank	Transport Blank
Collection Date	5/27	--5/30--		5/27	5/30	5/27	5/30	--
Collection Time at Facility	0852	--1200--		0802	1308	--	--	--
Time Subsample Collected	1545	1610	1620	1530	1450	1445	--	--
Sample No. (22-)	8232	8239	8240	8233	8241	8235	8245	8246
Pentachlorophenol	0.40	0.068	0.12	0.002 M	0.28	0.002 M	0.002 M	0.005
2,3,4,5-Tetrachlorophenol	0.066	0.032	0.08	0.002 U	0.01 M	0.002 U	0.002 U	0.005 U
Diuron	0.4 M	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U	0.4 U

* = subsample was collected 5/29
M = presence of material verified but not quantified
NA = not analyzed

Table A-4. Chlorophenols, Resin Acids, and Fatty Acids Detected in Water Samples Collected by Ecology During Coho Smolt Bioassay, Aberdeen, May 26-30, 1988 (μg/L; ppb)

Sample Type	Weyerhaeuser Effluent			ITT Effluent		Transfer Blank	Transport Blank
Collection Date	5/28	--5/30--		5/27	5/30	--	--
Collection Time at Mill	1305	--1225--		1500	1410	--	--
Time Subsample Collected	1510*	1630	1645	1625	1510	--	--
Sample No. (22-)	8257	8236	8237	8231	8238	8245	8246
Guaiacols							
Guaiacol	5	0.5 U	0.5 U	0.5 U	0.7 J	0.4 U	1 U
4,5,6-Trichloroquaiacol	4	12	12	6	7	0.4 U	1 U
Tetrachloroquaiacol	8	9	0.5 U	5	7	0.4 U	1 U
Other Chlorophenols							
Trichlorosyringol	5	18	20	0.5 U	0.5 J	0.4 U	1 U
Resin Acids							
Abietic	0.4 U	0.5 U	0.5 U	0.5 U	0.3 J	0.4 U	1 U
Dehydroabietic	6	0.5 U	2 J	2 J	2 J	0.4 U	1 U
Dichlorodehydroabietic	4	3 J	0.5 U	5	10	0.4 U	0.1 J
Isopimaric	1 J	0.5 U	0.5 U	0.5 U	0.6 U	0.4 U	1 U
Fatty Acids							
Oleic Acid	2 J	0.5 U	0.5 U	32	35	0.4 U	1 U
Linoleic	2 J	0.5 U	0.5 U	0.5 U	0.6 U	0.4 U	1 U

* = collected 5/29
U = not detected at detection limit shown
J = an estimated concentration

Note: Sample preservation and analysis methods used to obtain the above data where modified in 1989; the two data sets are not strictly comparable.

Table A-5. Conventional Water Quality Data for Samples Collected by Ecology during Coho Smolt Bioassay, Aberdeen, May 26-30, 1988

WEYERHAEUSER EFFLUENT						
Collection Date	5/26	5/27	5/28	5/29	---5/30---	
Time Effluent Collected at Mill	0800	1140	1305	1135	1225	
Time Subamples Collected	2020	1415*	1635	1510	1630	1645
Sample Number (22-)	8246	8230	8251	8249	8236	8237
pH (units)	6.3	6.3	6.7	6.4	6.3	6.5
Specific Conductance (umhos/cm)	2070	2050	2070	2090	2070	2070
Color (units)	2600	2800	2000	2800	2800	2800
Turbidity (NTU)	10	10	15	15	15	10
Total Suspended Solids (mg/L)	60	58	120	100	96	100
Total Hardness (mg/L as $CaCO_3$)	310	300	310	300	310	300
Free Chlorine (mg/L)	NA	NA	NA	NA	NA	NA
Chloramines (mg/L)	NA	NA	NA	NA	NA	NA
Total Sulfides (mg/L)	0.1 U	0.1 U	3.6	0.9	0.1U	0.1U
Total Organic Carbon (mg/L)	270	290	280	260	290	300
Total Recoverable Phenolics (μg/L)	21	14	12	12	10	12

ITT EFFLUENT					
Collection Date	5/26	5/27	5/28	5/29	5/30
Time Effluent Colected at Mill	1200	1500	1450	1320	1410
Time Subsamples Collected	2030	1625	1620	1500	1510
Sample Number (22-)	8247	8231	8252	8258	8238
pH (units)	6.7	6.7	6.6	6.6	6.8
Specific Conductance (umhos/cm)	1540	1550	1590	1600	1610
Color (units)	1600	1800	2000	2100	2000
Turbidity (NTU)	15	20	25	25	25
Total Suspended Solids (mg/L)	77	84	120	110	120
Total Hardness (mg/L as $CaCO_3$)	340	330	330	310	300
Free Chlorine (mg/L)	NA	NA	NA	NA	NA
Chloramines (mg/L)	NA	NA	NA	NA	NA
Total Sulfides (mg/L)	0.1 U	0.1 U	0.5	0.9	0.3
Total Organic Carbon (mg/L)	270	320	300	300	290
Total Recoverable Phenolics (μg/L)	6	8	7	6	5 U

* = Collected 5/28
NA = Not analyzed
U = Not detected at detection limit shown

Table A-5. (continued)

ABERDEEN STP EFFLUENT						
Collection Date	5/26	5/27	5/28	5/29	---5/30---	
Time Effluent Collected at STP	**	0852	1350	1348	1200	
Time Samples Collected	2055	1545	1630	1445	1610	1620
Sample Number (22-)	8248	8232	8253	8259	8239	8240
pH (units)	7.1	7.3	7.2	7.2	7.0	7.0
Specific Conductance (umhos/cm)	364	381	316	327	337	337
Color (units)	42	29	55	50	46	42
Turbidity (NTU)	4	4	4	4	4	4
Total Suspended Solids (mg/L)	8	6	9	11	12	10
Total Hardness (mg/L as $CaCO_3$)	64	71	64	60	66	64
Free Chlorine (mg/L)	0.1	0.05 U	0.05	0.1	0.15	--
Chloramines (mg/L)	0.6	0.45	0.4	0.6	0.95	--
Total Sulfides (mg/L)	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U	--
Total Organic Carbon (mg/L)	11	16	18	19	19	16
Total Recoverable Phenolics (μg/L)	5 U	6	5 U	26	12	12

HOQUIAM STP EFFLUENT					
Collection Date	5/26	5/27	5/28	5/29	5/30
Time Effluent Collected at STP	**	0802	1208	1231	1308
Time Samples Collected	2050	1530	1355	1430	1450
Sample Number (22-)	8249	8233	8254	8260	8241
pH (units)	7.1	7.1	7.1	7.2	7.4
Specific Conductance (umhos/cm)	586	540	532	543	572
Color (units)	88	92	59	55	21
Turbidity (NTU)	4	4	3	2	2
Total Suspended Solids (mg/L)	9	2	6	6	6
Total Hardness (mg/L as $CaCO_3$)	67	66	65	71	70
Free Chlorine (mg/L)	0.05 U	0.05 U	0.05 U	0.05 U	0.05U
Chloramines (mg/L)	0.1	0.05	0.1	0.1	0.1
Total Sulfides (mg/L)	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Total Organic Carbon (mg/L)	11	14	10	10	12
Total Recoverable Phenolics (μg/L)	5 U	5 U	5 U	5 U	5 U

** = Not Available
NA = Not analyzed
U = Not detected at detection limit shown

Table A-5. (continued)

CHEHALIS RIVER WATER					
Collection Date	5/26	5/27	5/28	5/29	5/30
Time Sample Collected	0900	0830	1012	0825	0855
Time Subsamples Collected	2035	1610	1420	1300	1325
Sample Number (22-)	8250	8234	8255	8261	8242
pH (units)	7.4	7.4	7.5	7.6	7.1
Specific Conductance (umhos/cm)	74	78	72	69	71
Color (units)	21	38	17	25	--
Turbidity (NTU)	2	1	2	2	1
Total Suspended Solids (mg/L)	1	2	3	5	2
Total Hardness (mg/L as $CaCo_3$)	26	27	24	27	25
Free Chlorine (mg/L)	0.05 U	0.05 U	0.05 U	0.05 U	0.05 U
Chloramines (mg/L)	0.05 U	0.05 U	0.05 U	0.05 U	0.05 U
Total Sulfides (mg/L)	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Total Organic Carbon (mg/L)	2.3	3.6	3.8	5.7	3.8
Total Recoverable Phenolics (μg/L)	5 U	5 U	5 U	5 U	5 U

DILUTION WATER					
Collection Date	5/26	5/27	5/28	5/29	5/30
Time Samples Collected	1830	1445	1425	1305	1315
Sample Number (22-)	8251	8235	8256	8262	8243
pH (units)	7.5	7.4	7.3	7.4	7.5
Specific Conductance (umhos/cm)	53	54	54	69	54
Color (units)	4	4	8	17	NA
Turbidity (NTU)	1 U	1 U	1 U	2	1 U
Total Suspended Solids (mg/L)	1	2	1	4	2
Total Hardness (mg/L as $CaCO_3$)	20	18	27	23	18
Free Chlorine (mg/L)	0.05 U	0.05 U	0.05 U	0.05 U	0.05U
Chloramines (mg/L)	0.1	0.05	0.05	0.1	0.1
Total Sulfides (mg/L)	0.1 U	0.1 U	0.1 U	0.1 U	0.1 U
Total Organic Carbon (mg/L)	2 U	2 U	2.7	2.8	2.2
Total Recoverable Phenolics (μg/L)	NA	5 U	NA	NA	5 U

NA = Not analyzed
U = Not detected at detection limit shown

Appendix B. Sample containers and handling.

Analysis	Sample Volume	Container	Preservation
specific conductance, color, TSS	2 liter	polyethylene	cool to 4° C
total recoverable phenolics	1 quart	glass with teflon lid liner	phosphoric acid, copper sulfate, ferrous sulfate; cool to 4° C
TOX	1 liter	amber glass with teflon lid liner	cool to 4° C
metals	1 quart	polyethylene cubitainer with teflon lid liner	adjust pH to ≤ 2 with H_2SO_4; cool to 4° C
volatiles	40 mL	glass with teflon septum	cool to 4° C
phenols, guaiacols, catechols	1 gallon	glass with teflon lid liner	adjust pH to 2.0 with H_2SO_4; cool to 4° C
resin and fatty acids	1 gallon	glass with teflon lid liner	adjust pH to 10 with NaOH; cool to 4° C
rainbow trout bioassay	10 gallons	polyethylene cubitainer	cool to 4° C
microtox bioassay	8 ounce	glass with teflon lid liner	cool to 4° C
oyster larvae bioassay	2 gallons	glass with teflon lid liner	cool to 4° C
echinoderm sperm cell bioassay	½ gallon	glass with teflon lid liner	cool to 4° C

Appendix C. Matrix and surrogate spike recoveries in pulp mill effluent samples (%).

1. Matrix Spike Recoveries

Metals	Mean ± sd
cadmium (n=14)	95 ± 26
chromium (n=2)	94 ± 4
copper (n=14)	88 ± 34
lead (n=14)	94 ± 12
mercury (n=15)	80 ± 16
nickel (n=2)	102 ± 1
silver	NA
zinc (n=12)	96 ± 8
Volatiles (n=8)	
1,1-dichloroethene	109 ± 11
trichloroethene	101 ± 2
benzene	106 ± 8
toluene	111 ± 7
chlorobenzene	89 ± 12
Guaiacols/Catechols (n=8)	
4-chloro-3-methylphenol	95 ± 7
pentachlorophenol	82 ± 22
2,4,6-trichlorophenol	99 ± 7
2-nitrophenol	94 ± 17
guaiacol	89 ± 11
2-methylphenol	81 ± 14
2-chlorophenol	83 ± 11
2,4,5-trichlorophenol	100 ± 9
4-allylguaiacol	88 ± 33
4-propenylguaiacol	88 ± 29
acetophenone	73 ± 13
4-nitrophenol	99 ± 18
2,4-dimethylphenol	86 ± 16
4-methylphenol	98 ± 21
phenol	80 ± 9

Guaiacols/Catechols (n=8)	Mean ± sd
2,4-dichlorophenol	97 ± 3
tetrachloroguaiacol	96 ± 16
tetrachlorocatechol	100 ± 24
4-chlorocatechol	98 ± 11
4,5-dichloroguaiacol	95 ± 21
trichlorosyringol	97 ± 12
4,5-dichlorocatechol	107 ± 10
a-terpineol	84 ± 9
4-chloroguaiacol	98 ± 7
3,4,5-trichlorocatechol	125 ± 18
6-chlorovanillin	45 ± 41
5,6-dichlorovanillin	70 ± 56
4,5,6-trichloroguaiacol	98 ± 11
Resin/Fatty Acids (n=8)	
hexadecanoic (n=6)	120 ± 93
octadecanoic (n=6)	100 ± 76
linoleic	81 ± 58
oleic (n=6)	85 ± 82
pimaric	67 ± 44
palmitoleic (n=6)	114 ± 68
sandaracopimaric	70 ± 45
neoabietic	23 ± 21
retene	86 ± 9
abietic	55 ± 33
dehydroabietic	84 ± 48
eicosatrienoic (n=6)	52 ± 40
palustric	32 ± 24
isopimaric	65 ± 37
9,10-dichlorostearic	70 ± 46
dichlorodehydroabietic	69 ± 32
14-chlorodehydroabietic	65 ± 42
12-chlorodehydroabietic	78 ± 51

2. Surrogate Spike Recoveries

Volatiles (n=16)	
D8-toluene	101 ± 4
bromofluorobenzene	97 ± 2
D4-1,2-dichlorobenzene	95 ± 3
Resin/Fatty Acids (n=16)	
methyl-o-methylpodocarp.	41 ± 36
heptadecanoic acid	53 ± 54
1-fluorenecarboxy.	57 ± 50

Guaiacols/Catechols (n=16)	
2-ethoxyphenol	70 ± 23
2,4,6-tribromophenol	82 ± 32
D6-resorcinol	53 ± 7
2-fluorobiphenol	103 ± 42
2-fluorophenol	67 ± 12
D5-nitrobenzene	75 ± 17
D5-phenol	62 ± 14
D3-alpha-terpineol (n=7)	39 ± 7
2,6-dibromophenol	85 ± 11

NA = not analyzed

Appendix D. Results of field duplicates (μg/L, except as indicated).

Mill:	WEYCO		ITT		WEYCO		WEYCO		WEYCO	
Date:	3/07	3/07	4/05	4/05	5/31	5/31	6/12	6/12	6/20	6/20
Sample No.:	8020	8021	8015	8016	8000	8001	8000	8001	8005	8006
sp. cond. (umhos/cm)	2200	2200	1400	1500	3570	3790	NA	NA	3360	3390
color (units)	1870	1860	2330	2350	1210	1200	NA	NA	1770	2010
TSS (mg/L)	140	120	150	680	71	76	NA	NA	100	104
t. rec. phenolics	12	12	5.6	5.6	12	12	NA	NA	16.0	16.0
TOX (mg/L)	35.0	43.0	26.3	22.6	NA	28.6	23.2	23.4	27.7	34.3
cadmium	0.2 U	0.2 U	0.8	1	0.2 U	0.2 U	NA	NA	0.2 U	0.2 U
chromium	10 U	10 U	52	100	4.6	6.5	NA	NA	5.7	7.0
copper	9.6 B	6.5 B	12 B	12 B	9.2 B	11 B	NA	NA	4 BU	4 BU
lead	1.9	1.1	2.0	1.6	1.4	1.4	NA	NA	1.9	2.6
nickel	29	25	4.9	12	10	20	NA	NA	27	20 U
zinc	33 B	25 B	36 B	42 B	21 B	21 B	NA	NA	32 B	36 B
chloroform	27	8.4	170	170	NA	17	9.8	10	11	11
2-butanone	16	13	1.0 U	1.0 U	NA	6.2 U	19	19	1.0 U	1.0 U
toluene	1.4 B	1.5 B	0.6 B	0.6 B	NA	4.3 B	3.0 B	3.0 B	2.3 B	2.4 B
4-methylphenol	24 BJ	26 B	0.3 BJ	0.5 BJ	24 B	28 B	NA	NA	27 B	33 B
2,4-dimethylphenol	1 U	1 U	0.5 U	0.8 U	0.5 U	0.8 U	NA	NA	0.1 J	0.8 U
2-chlorophenol	1 U	1 U	0.5 U	0.8 U	0.1 J	0.1 J	NA	NA	0.1 J	0.1 J
2,4-dichlorophenol	4 J	3 J	0.6 J	0.5 J	2 J	2 J	NA	NA	3 J	4 J
2,4,6-trichlorophenol	13 J	13	0.9 J	0.8 J	7	7	NA	NA	12	12
guaiacol	2 J	2 J	0.2 J	0.3 J	1 J	2 J	NA	NA	3 J	3 J
4-allylguaiacol	1 U	1 U	0.5 U	0.8 U	0.3 J	0.8 U	NA	NA	0.5 J	0.8 U
4-chloroguaiacol	0.5 J	0.6 J	0.5 U	0.8 U	0.2 J	0.8 U	NA	NA	0.5 U	0.8 U
4,5-dichloroguaiacol	2 J	2 J	2 J	2 J	1 J	1 J	NA	NA	2 J	2 J
4,5,6-trichloroguaiacol	1 J	1 J	0.6 J	0.6 J	1 J	1 J	NA	NA	2 J	2 J
tetrachloroguaiacol	3 J	3 J	0.7 J	0.8 J	4	4 J	NA	NA	3 J	3 J
4-chlorocatechol	2 J	2 J	0.2 J	0.2 J	0.5 U	0.5 J	NA	NA	1 J	1 J
4,5-dichlorocatechol	14 J	14	1 J	1 J	0.9 J	3	NA	NA	10	9
3,4,5-trichlorocatechol	48	47	5 J	5 J	12 J	17 J	NA	NA	56 J	56
tetrachlorocatechol	12 J	12	2 J	3 J	6 J	7 J	NA	NA	18	20
trichlorosyringol	1 U	1 U	0.5 U	0.8 U	0.4 J	0.5 J	NA	NA	2 J	2 J
6-chlorovanillin	2 J	2 J	2 J	2 J	0.8 J	0.9 J	NA	NA	1 J	1 J
5,6-dichlorovanillin	1 J	1 J	1 J	2 J	1 J	1 J	NA	NA	1 J	0.8 U
abietic acid	0.6 U	0.5 U	0.5 U	0.5 U	0.6 U	0.7 U	NA	NA	6	0.5 U
dehydroabietic acid	3 B	2 B	0.1 BJ	0.5 BU	20 B	24 B	NA	NA	27 B	12 B
12-chlorodehydroabietic	8	6	3 J	0.3 J	42	58	NA	NA	59	19
14-chlorodehydroabietic	4	3	0.5 U	0.5 J	19	25	NA	NA	25	9
dichlorodehydroabietic	5	3	0.5 U	0.5 U	21	33	NA	NA	30	8
palustric acid	0.6 U	0.5 U	0.5 U	0.5 U	0.6 U	0.7 U	NA	NA	5	0.5 U
isopimaric acid	0.6 U	0.5 U	0.5 U	0.5 U	3 J	2 J	NA	NA	3 J	2 J
oleic acid	11 B	7 B	2 B	4 B	36 B	61 B	NA	NA	36 B	16 B
linoleic acid	1 B	0.7 B	0.5 BU	0.5 BU	4 BJ	4 B	NA	NA	0.5 BU	0.5 BU
hexadecanoic acid	NA	NA	3 B	4 B	43 B	60 B	NA	NA	71 B	24 B
octadecanoic acid	NA	NA	2 B	2 B	61 BJ	78 BJ	NA	NA	55 B	21 B
palmitoleic acid	NA	NA	2	4	14	17	NA	NA	11 J	0.5 U
9,10-dichlorostearic acid	NA	NA	3 J	3 J	5	5 J	NA	NA	6	6
a-terpineol	1 UJ	1 U	0.5 U	0.8 U	0.5 U	0.8 U	NA	NA	0.5 U	1 J

U = not detected at detection limit shown
J = estimated value
B = also detected in transfer and/or method blanks
NA = not analyzed

Appendix E. Chemical data for Weyerhaeuser effluent (μg/L, except as indicated).

Date:	3/07	3/21	4/05	4/24	5/17	5/31	6/12	6/20
Sample No.:	8020/21*	8013	8018	8020	8000	8000/01*	8000	8005/06*
flow (MGD)	22.3	18.4	21.2	22.3	18.9	23.5	27.0	23.9
temp. (°C)	NA	17.4	17.7	23.4	16.2	22.9	23.2	22.8
pH (units)	2.7	2.3	2.2	2.4	3.0	2.8	2.7	2.4
spec. conduct. (μmho/cm)	2200	4200	4300	3010	3110	3680	2470	3380
color (units)	1860	1070	1680	2450	2460	1200	2140	1890
TSS (mg/L)	130	380	120	170	125	74	120	100
t. rec. phenolics	12.2	18.8	15.0	10.0	13.1	12.3	14.0	16.0
TOX (mg/L)	39.0	26.5	29.8	36.7	22.5	28.6	23.3	31.0
cadmium	0.2 U	0.23	0.3	0.2 U	1.0	0.2 U	0.4	0.2 U
chromium	10 U	10 U	13	6.9	23	5.6	5.1	6.3
copper	8.1 B	11 B	13 B	13 B	16 B	10 B	9.5 B	4 BU
lead	1.5	3.5	5.4	1.0	4.9	1.4	1.4	2.2
nickel	27	23	16	15	19	15	17	18
zinc	28 B	36 B	70 B	31 B	110 B	21 B	24 B	34 B
chloroform	18	16	14	16	0.7 J	17	9.9	11
2-butanone	14	27	19	36	39	6.2 U	19	2.0 U
toluene	1.4 B	13 B	2.7 B	2.6 B	7.3 B	4.3 B	3.0 B	2.4 B
bromodichloromethane	0.2 U	0.4 J	0.2 U	0.3 U	0.3 U	0.3 U	0.3 U	0.2 U
4-methylphenol	25 BJ	54 BJ	28 B	10 B	11 B	26 B	37 BJ	30 B
2,4-dimethylphenol	1 U	1 U	0.1 J	0.3 J	0.1 J	0.5 U	0.1 J	0.1 J
2-chlorophenol	1 U	1 U	0.1 J	0.2 J	0.5 U	0.1 J	0.1 J	0.9 J
2,4-dichlorophenol	4 J	1 J	5	2 J	0.6 J	2 J	1 J	4 J
2,4,6-trichlorophenol	13 J	6 J	15	8	2 J	7	6	12
guaiacol	2 J	5 J	3	2 J	0.5 J	2 J	1 J	3 J
4-allylguaiacol	1 U	1 U	0.5 J	0.9 J	0.2 J	0.3 J	0.5 U	0.5 U
4-chloroguaiacol	0.6 J	1 U	0.3 J	0.4 J	0.5 U	0.2 J	0.1 J	0.5 U
4,5-dichloroguaiacol	2 J	1 J	3 J	2 J	0.2 J	1 J	1 J	2 J
4,5,6-trichloroguaiacol	1 J	1 U	3 J	2 J	0.3 J	1 J	0.8 J	2 J
tetrachloroguaiacol	3 J	1 J	5 J	7	2 J	4 J	4	3 J
4-chlorocatechol	2 J	1 J	1 J	0.5 J	0.5 U	0.4 J	0.7 J	1 J
4,5-dichlorocatechol	14 J	5 J	6	4 J	1 J	2 J	3 J	10
3,4,5-trichlorocatechol	48	23	28 J	26 J	5 J	14 J	15	56 J
tetrachlorocatechol	12 J	11	6 J	12 J	2 J	6 J	8	19
trichlorosyringol	1 U	5 J	7	35	2 J	0.4 J	20	2 J
6-chlorovanillin	2 J	1 U	2 J	0.5 U	0.5 U	0.8 J	0.5 U	1 J
5,6-dichlorovanillin	1 J	1 U	2 J	1 J	0.5 U	1 J	0.5 U	0.9 J
abietic acid	0.5 U	1 U	0.4 U	0.4 U	0.5 U	0.6 U	0.5 U	3
dehydroabietic acid	2 B	16 B	3 B	1 B	36 B	23 B	20 B	20 B
12-chlorodehydroabietic	7	26	4	1	28 J	50	41	39
14-chlorodehydroabietic	4	12	8	0.5	10	22	4 J	17
dichlorodehydroabietic	4	12	3	1	8	27	14	19
palustric acid	0.5 U	1 U	0.4 U	0.4 U	0.5 U	0.6 U	0.5	3
isopimaric acid	0.5 U	2	0.4 U	0.4 U	0.5 U	2 J	0.5 U	2 J
oleic acid	9 B	97 B	0.4 BU	1 B	15 B	48 B	42 B	26 B
linoleic acid	0.8 B	1 BU	0.4 BU	0.7 B	0.5 BU	4 BJ	0.5 BU	0.5 BU
hexadecanoic acid	NA	NA	5 B	5 B	27 B	52 B	64 B	48 B
octadecanoic acid	NA	NA	4 B	3 B	35 B	70 BJ	41 B	38 B
palmitoleic acid	NA	NA	0.4 U	3	0.5 U	16	12	6 J
9,10-dichlorostearic acid	NA	NA	10	9	2 J	5 J	5 J	6
a-terpineol	NA	1 U	0.4 U	0.5 U	0.5 U	0.5 U	0.5 U	0.6 J

* = duplicate sample; data are mean of duplicates
U = not detected at detection limit shown
J = estimated value
B = also detected in transfer and/or methods blanks
NA = not analyzed

Appendix F. Chemical data for ITT effluent (μg/L, except as indicated).

Date:	3/07		4/05		4/24		5/31	
Sample No.:	8023		8015/16*		8021		8003	
flow (MGD)	20.0		20.0		20.8		20.9	
temp. (°C)	18.4		19.6		23.4		24.9	
pH (units)	7.0		6.9		6.8		7.5	
spec. conductance (μmho/cm)	1850		1450		1350		1760	
color (units)	2420		2340		1470		1130	
TSS (mg/L)	37		150		40		43	
t. rec. phenolics	4.1		5.6		8.0		7.0	
TOX (mg/L)	26.0		24.4		22.4		16.0	
cadmium	0.5		0.9		0.7		0.6	
chromium	58		79		87		45	
copper	3.9	B	12	B	13	B	6.2	B
lead	2.5		1.8		3.3		1.3	
nickel	20	U	8.4		10		1.9	
zinc	22	B	39	B	27	B	31	B
chloroform	120		170		140		110	
2-butanone	1.0	U	1.0	U	6.2	U	6.2	U
toluene	0.6	BU	0.6	B	0.8	BU	0.8	BU
bromodichloromethane	0.9		0.2	U	1.1		0.5	J
1,2-dichloropropane	0.5	J	0.6	U	0.7	U	0.7	U
4-methylphenol	1	BU	0.4	BJ	0.7	BJ	0.2	BJ
2,4-dimethylphenol	1	U	0.5	U	0.5	U	0.5	U
2-chlorophenol	1	U	0.5	U	0.5	U	0.5	U
2,4-dichlorophenol	1	U	0.6	J	0.4	J	0.2	J
2,4,6-trichlorophenol	1	U	0.8	J	1	J	0.5	J
guaiacol	1	U	0.2	J	0.6	J	0.1	J
4-allylguaiacol	1	U	0.5	U	0.5	U	0.5	U
4-chloroguaiacol	1	U	0.5	U	0.5	U	0.5	U
4,5-dichloroguaiacol	0.6	J	2	J	0.4	J	0.3	J
4,5,6-trichloroguaiacol	0.3	J	0.6	J	0.3	J	0.1	J
tetrachloroguaiacol	0.7	J	0.8	J	2	J	0.6	J
4-chlorocatechol	1	U	0.2	J	0.1	J	0.5	U
4,5-dichlorocatechol	0.6	J	1	J	0.4	J	0.3	J
3,4,5-trichlorocatechol	4		5	J	4	J	1	J
tetrachlorocatechol	3		2	J	4	J	1	J
trichlorosyringol	1	U	0.5	U	0.5	U	0.5	U
6-chlorovanillin	0.8	J	2	J	0.4	J	0.5	J
5,6-dichlorovanillin	1	J	2	J	0.4	J	0.4	J
abietic acid	0.5	U	0.5	U	0.4	U	0.5	U
dehydroabietic acid	0.3	BJ	0.1	BJ	0.4	BU	0.5	BU
12-chlorodehydroabietic	0.5		1.6		0.3	J	0.5	U
14-chlorodehydroabietic	0.2	J	0.5	U	0.4	U	0.5	U
dichlorodehydroabietic	0.5	U	0.5	U	0.4	U	0.5	U
palustric acid	0.5	U	0.5	U	0.4	U	0.5	U
isopimaric acid	0.5	U	0.5	U	0.4	U	0.5	U
oleic acid	0.5	BU	3	B	0.4	BU	4	JB
linoleic acid	0.5	BU	0.5	BU	0.4	BU	0.5	BU
hexadecanoic acid	NA		4	B	2	B	5	B
octadecanoic acid	NA		2	B	2	B	2	BJ
palmitoleic acid	NA		3		1		0.5	U
9,10-dichlorostearic acid	NA		3	J	2	J	1	J
a-terpineol	1	U	0.5	U	0.5	U	0.5	U

* = duplicate sample; data are mean of duplicates
U = not detected at detection limit shown
J = estimated value
B = also detected in transfer and/or methods blanks
NA = not analyzed

Appendix G. Quality of Fisheries samples of pulp mill effluents for 1989 coho smolt bioassay.

WEYERHAEUSER EFFLUENT

Date:	4/21	4/21*	4/23	4/25	4/27	4/29	5/01	5/01*	5/03
Sample No.:	8022	8023*	8080	8082	8084	8086	8088	8089*	8092
sp. conduct. (μmho/cm)	2600	2500	2410	2150	2570	2660	2520	2340	2540
color (units)	2410	2340	2740	3130	2950	1490	1520	1520	1450
TSS (mg/L)	130	110	150	150	150	77	94	79	60
t. rec. phenolics (μg/L)	12	14	12	12	14	12	16	12	12
TOX (mg/L)	50.1	50.2	63.2	50.5	66.3	80.8	65.9	62.2	71.5

ITT EFFLUENT

Date:	4/21	4/21*	4/23	4/25	4/27	4/29	5/01	5/01*	5/03
Sample No.:	8024	8025*	8081	8083	8085	8087	8090	8091*	8093
sp. conduct. (μmho/cm)	1600	1600	1480	1160	1370	1410	1560	1570	1620
color (units)	2310	2270	1870	2990	4450	1100	1140	1140	1400
TSS (mg/L)	230	220	80	93	100	67	70	56	89
t. rec. phenolics (μg/L)	8	8	8	6	8	10	8	12	8
TOX (mg/L)	26.7	26.3	22.0	40.7	32.8	46.4	35.9	53.1	49.7

* = duplicate sample