



88e-21  
WA-22-0030

ANDREA BEATTY RINKER  
Director

STATE OF WASHINGTON  
DEPARTMENT OF ECOLOGY

7272 Cleanwater Lane, LU-11 • Olympia, Washington 98504-6611 • (206) 753-2353

TO: Art Johnson  
THROUGH: Lynn Singleton *LS*  
FROM: Joe Joy *J*  
SUBJECT: Chemical Characteristics of Three Wastewater Effluents Used  
in the Grays Harbor Bioassay Project: Spring 1987  
DATE: January 21, 1988

ABSTRACT

A pilot eight-day coho salmon smolt bioassay was performed on selected wastewater discharges to Grays Harbor to help identify the cause(s) of low out-migrant survival. Ecology participated in the project by analyzing the tested effluents and dilution water. Ten percent solutions of two pulp mill effluents and a municipal sewage effluent were collected at day one and again at day four when the solutions were renewed. All samples were analyzed for conventional, metal, volatile organic, semi-volatiles, resin acid, and guaiacol constituents. Analytical results indicated the effluents contained concentrations similar to those quantified in other studies. Recommendations for improvements in the bioassay procedure and analytical methods were made in anticipation of a full-scale bioassay.

INTRODUCTION

The Washington Department of Fisheries (WDF) has reported that Chehalis River basin salmon are contributing to the ocean fishery at reduced rates (Seiler, 1986). Seiler suggested that out-migrating salmon smolt populations may be undergoing severe losses in or near the Grays Harbor estuary. An interagency committee was formed in response to this report to coordinate investigative work performed by various local, state, and federal agencies and private industries attempting to determine the source and extent of the problem.

The committee recognized the need to assess the effects of Grays Harbor pulp mill and municipal sewage effluents on coho smolts using bioassay procedures. In pursuit of this assessment, they decided to run a renewal toxicity test pilot project before expending resources on full-scale bioassays. The pilot bioassay procedure was designed to:

1. Test the ability for various members to coordinate sub-tasks.

January 21, 1988

Page Two

2. Evaluate the bioassay procedures and analytical methods.
3. Collect preliminary chemical and bioassay data on the effects of these effluents on coho smolts.

The Department of Ecology Technical Services Program was assigned the task of analyzing effluent and control/dilution water used in the bioassay.

### The Bioassay

On April 30, 1987, the WDF delivered coho smolts (non-hatchery) to the Weyerhaeuser Company Research and Development staff at their mobile bioassay lab stationed at the company's Cosmopolis mill site. Concurrently, effluents arrived that had been collected that morning from the ITT sulfite pulp mill in Hoquiam, the Aberdeen wastewater treatment plant (WTP), and the Weyerhaeuser Cosmopolis (WEYCO) sulfite mill. Chlorinated water piped to WEYCO from Lake Aberdeen was used for the control tank and for dilutions. Staff from the Department of Ecology Water Quality Investigations Section (WQIS) arrived and obtained portions of each of the three effluents and the control/dilution water. These samples were transported to the Ecology Manchester Environmental Laboratory for analysis. WEYCO personnel conducted the bioassay over an eight-day period. Fresh solutions of effluent were used to renew the bioassay tanks on the fourth day, and Ecology WQIS personnel returned to repeat the sample collection and analysis procedures. The bioassay was terminated on the eighth day. The fish were transported to the U.S. Fish and Wildlife Service (USFWS) field station on Marrowstone Island, held in seawater, and observed for four months. USFWS personnel also performed periodic metabolic tests on the fish. At the end of the four months, some fish were held for tissue analysis by the U.S. Environmental Protection Agency (USEPA).

This report presents the analytical results of effluent and water samples taken during the bioassay. Recommendations are also made to improve some procedures and methods for the full-scale bioassay project tentatively scheduled for spring of 1988. The other agencies and industries involved in the pilot project will independently report the results of their sub-tasks.

### METHODS

A description of each sample collected for analysis by the Ecology lab at Manchester during the bioassay is presented in Table 1. All effluent samples were independently collected and delivered to the WEYCO mobile bioassay lab in plastic carboys provided by each of the facilities. Samples for laboratory analysis were taken from the carboys

January 21, 1988

Page three

after vigorous mixing. The control/dilution water samples were collected directly from the tap in the mobile lab. Most effluent and control/dilution water samples were analyzed in the field for pH and specific conductivity using field meters, and temperature using a mercury thermometer. The pH of a second set of resin acid, and guaiacol samples collected on May 4 was adjusted to 10 in the field using NaOH pellets. Volatile, semi-volatile, resin acid, and guaiacol samples were collected in priority-pollutant-cleaned glass jars and vials with teflon lids. Metals samples were collected in acid-cleaned, high-density polyethylene containers. All samples were stored on ice in the dark and were delivered to the Manchester Laboratory within three hours.

Table 2 lists the analytical methods used (Huntamer, 1986). The detection limits for the analyses can be found in Appendix I. Resin acid samples were extracted using the EPA Method 625 dichloromethane (methylene chloride) procedure and derivitized with diazomethane instead of the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) diethyl ether extraction and tri-ethyloxonium tetrafluoroborate derivitization procedure (NCASI, 1986) because of short lead time given to the lab (Huntamer, 1987). Both resin acid analysis procedures are outlined in Figure 1. The guaiacol samples were also extracted, derivitized, and analyzed using the modified EPA Method 625 outlined in Figure 1.

The following quality control and quality assurance (QA/QC) measures were taken:

- o A blind duplicate of one effluent sample was taken during the first collection and analyzed for all parameters.
- o A transport blank was analyzed for metals, semi-volatile, resin acid and guaiacol parameters during the second collection.
- o The second set of resin acid and guaiacol samples was analyzed both with and without pH adjustment.
- o Standard Manchester lab QA/QC procedures were followed; e.g., surrogate spikes on organic analyses, matrix spikes, replicate analyses, laboratory blanks, and internal and external standards.

## RESULTS and DISCUSSION

Analytical results from the two sets of samples are presented in Table 3. Included are the transport blank (#87-197479) and the blind duplicate (#87-187455) results. Tentatively identified compounds detected in the semi-volatile and methylated semi-volatile fractions of the samples are presented in Table 4.

### General Data Quality

The analytical results appear to be accurate, considering the methods used and analytical difficulties documented by the laboratory. The difficulties will be detailed below. The transport blank indicated quantifiable levels of four analytes: cadmium, mercury, and two phthalate esters. The results presented in Table 3 have not been corrected for the concentration of analytes detected in the transport blank. A volatile organics (VOA) transport blank should have been collected, and needs to be included in the full-scale project. The analytes of the duplicate samples for the first set of effluents appeared to be in general agreement. Standards and matrix spikes for the VOA samples were acceptable, and no problems were reported for the conventional and metal analyses.

The laboratory reported some difficulties with the semi-volatile, resin acid, and guaiacol analyses and results (Huntamer, 1987). One of the two control/dilutions water samples (#87-197478) was accidentally destroyed by the lab. However, since neither semi-volatiles, resin acid, nor guaiacols were detected in the one control/dilution sample, none of these compounds were expected in the other. Also, the dichloromethane extraction procedure failed to provide complete separation of the semi-volatiles, so that up to 50 percent of the neutral fraction was lost (Huntamer, 1987). Consequently, the concentrations of individual neutral compounds in the methylated acid fraction were quantified and were added to the results from the neutral-fraction analysis. Huntamer (1987) remarked that this was not a serious problem because of the small amounts of semi-volatile compounds in the samples.

There were also some problems with the resin acid procedure. Matrix spike recoveries were poor on the pH 10 adjusted sample (#87-197477Y), and in all spikes for levopimaric and neoabietic acids (Appendix II). Huntamer (1987) suggested the latter two compounds may have been rapidly degraded during or after the extraction procedure and may require special preservation techniques; he had no explanation for the poor spike recoveries on the pH 10 sample. Isomerization of neoabietic, levopimaric, and palustric acids has been noted in solutions stored at a pH of 2 (NCASI, 1983). For example, NCASI found 25 to 30 percent of the levopimaric acid converted to abietic acid under such conditions. However, they did not mention resin acid conversions or degradation in samples kept at pH 10.

Huntamer (1987) gave the following recommendations:

1. Give the laboratory ample lead time (2 weeks or more)
2. Strictly adhere to the NCASI method for resin acids extraction and analysis

January 21, 1988

Page five

3. Collect, preserve, and extract resin acid samples separate from semi-volatile samples

The full-scale project should incorporate these recommendations.

A high degree of variability is common in effluent grab samples unless, as may have been the case here, there is a daily periodicity in effluent treatment and control, and conditions influencing influent quantity and quality are stable. The second set of sample results showed few differences from the first (Table 3). This was surprising since the ITT and Aberdeen WTP samples were not 24-hour composites, but grabs. Ammonia concentrations in both the Aberdeen WTP and WEYCO mill effluents showed the greatest differences between sets. Despite the lack of significant problems with effluent variability during this bioassay, it may be better to collect 24-hour composite samples at all sites if a static re renewal bioassay is performed again.

Resin acid and guaiacol samples at unadjusted and adjusted pH in the second set showed some differences (Table 3). The WEYCO effluent with a pH of 10 had a trichloroguaiacol concentration one fifth the pH 2.8 sample. Poor surrogate spike recovery in the ITT effluent with a pH of 10 prevented a useful comparison with the pH-unadjusted sample (Appendix II).

#### Effluent Quality

Most of the results look to be within the range of values commonly reported in other studies (Table 5). Of the chemicals detected or conditions recorded, only a portion are of particular interest to this project; i.e., those toxic to fish. The most commonly recognized fish toxicants in this set of pulp mill and municipal sewage effluents are:

- o Chlorinated compounds.
- o Ammonia.
- o pH.
- o Metals.
- o Chlorinated phenolics.
- o Resin acids.

Available USEPA aquatic life criteria are presented for these and other chemicals in Table 6.

The effluents were not tested in the field for residual chlorine. The control/dilution water from Lake Aberdeen is chlorinated, and most pulp mill effluents contain residual chlorine from bleaching processes. The Aberdeen WTP effluent sample was collected prior to chlorination. During the planned full-scale bioassay, the Aberdeen WTP sample should

January 21, 1988

Page six

be collected as chlorinated effluent since fish are exposed to chlorinated effluent in Grays Harbor. Residual chlorine field analyses should also be performed before and after mixing the effluent and dilution waters.

Chloroform was the most frequently detected chlorinated compound (Table 3). It was detected in all samples, which is not unusual (Table 5). Chloroform and bromodichloromethane are commonly detected in chlorinated domestic waters as well (Symons, et al., 1975). However, as mentioned above, a VOA transport blank should be included in the full-scale bioassay. This is to ensure that chloroform is not being introduced in some part of the sample collection, transport, or analysis. The chloroform concentrations were not at levels considered toxic to aquatic life (Table 6). However, chloroform is a suspected carcinogen and mutagen (USEPA, 1986).

Ammonia concentrations were within the range of values normally found in pulp mill effluents (Table 5). The estimated total ammonia concentration in the 10 percent dilution of the Aberdeen WTP effluent (2.5 mg/L) was at or near the USEPA freshwater chronic (4-day) limit for salmonids (USEPA, 1986). This potentially toxic condition was unknown at the time of the bioassay, but there was some concern whether the fish would become stressed as a result of excreted ammonia building up in the tanks over the four days. So at the time of the effluent changeover, a sample was taken for ammonia analysis from the Aberdeen WTP effluent fish tank. The ammonia concentration in the sample was 9.4 mg/L--an increase of approximately 6.9 mg/L (25 mg/L times 0.1 = 2.5 mg/L; 9.4 mg/L minus 2.5 mg/L = 6.9 mg/L). According to USEPA criteria, this ammonia concentration could have been acutely toxic to the fish in freshwater at pH levels above 7.7 and temperatures greater than 5 to 10°C.

A constant feed, flow-through bioassay would remove ammonia built up from wastes excreted by the fish, while allowing effluent ammonia stress to be observed. The pH, temperature, and ammonia levels should be monitored in future bioassays.

The pH values of the WEYCO mill effluent reveals a problem in the bioassay procedure. The WEYCO mill adjusts its final effluent pH to 3 to control coliform levels; ITT does not. The 2.7 to 3.1 pH of the WEYCO mill effluent would probably have been toxic to the bioassay fish at full strength. The buffering capacity of the dilution water may have kept the pH above 5.0 in the 10 percent WEYCO effluent solutions, but as a precaution the team performing the bioassays adjusted the pH of the fish tank; their report should be consulted on this detail.

A pH below 5 is toxic for most fish primarily because of the CO<sub>2</sub> concentration (Doudoroff and Katz, 1950; Alabaster and Lloyd, 1982). However, the buffering capacity of brackish water is generally better

January 21, 1988

Page seven

than freshwater, so that common brackish conditions in Grays Harbor when WEYCO discharges are not as influenced by severely low pH as may occur in a freshwater bioassay. Therefore, if higher strength solutions of the effluents are used in the full-scale bioassay, the WEYCO effluent may create pH-related mortalities unless: (a) the effluent pH is artificially adjusted in the bioassay tanks, or (b) a brackish water solution is used to dilute the effluents. Perhaps an artificial seawater solution could be added to the primary freshwater dilution source to alleviate the problem.

Seven metals were detected in the samples (Table 3). Copper and cadmium were detected in all samples, although cadmium was also detected in the transport blank. Zinc was detected in all test solutions except the second control/dilution sample. Lead is generally present in municipal wastewater effluents, but was not detected in any sample. Perhaps a lead-spiked sample is warranted as a QA/QC check. Copper and cadmium concentrations in some of the full-strength effluents were at USEPA criteria levels (Table 6). Since the toxicities of these metals are hardness- and pH-dependent, these parameters should be monitored in the fish tanks during the full-scale project bioassay. If analytical costs become an issue, the following metals can probably be eliminated from the analysis: antimony, beryllium, selenium, silver, and thallium. They do not appear to be common in either type of effluents (Table 5).

A few chlorinated phenolics including chlorinated guaiacols, were detected in the samples in minor amounts (Table 3). These compounds were detected only in the pulp mill effluents, and are not uncommon in mill and municipal treatment effluents (Table 5). Trichlorophenol and trichloroguaiacol were the predominant compounds detected. The concentrations of the phenolic compounds detected may be affected by pH adjustments of the samples. The pH 10-adjusted WEYCO and ITT samples of the second collection showed distinctly lower concentrations of chlorinated guaiacols than the non-adjusted samples (Table 3). According to a NCASI study, chlorinated guaiacols and catechols may degrade in samples preserved and extracted at pH 10 (NCASI, 1983). NCASI (1983) also states that derivitization with diazomethane converts both chlorinated guaiacols and chlorinated catechols into chlorinated veratroles. Therefore, the two original analytes become indistinguishable, and the reported results here are probably the sum of those two compounds. Considering these findings, the pH 10 adjustment for preservation of the samples should be reserved only for the resin acid analysis, and a better guaiacol and catechol method should be found.

The toxicity of chlorinated phenolic compounds to aquatic life has not been thoroughly investigated. Table 7 lists the toxicity data that could be located. It is interesting to note the similarities in toxicity for the more chlorinated phenolic compounds. For example,

January 21, 1988

Page eight

Hutchins (1979) presents work performed by Leach and Thakore (1977) showing tri- and tetrachlorinated guaiacols acutely toxic to rainbow trout at 0.1 to 1 mg/L. A similar range is reported by USEPA (1980) and Buccafusco, Ells, and LeBlanc (1981) for tri- and tetrachlorinated phenol toxicities. Only the sum of chlorinated phenols and guaiacols in the second, full-strength, WEYCO sample had a concentration within this range. Chloroguaiacols and chlorophenols are reported to be lipophilic and accumulative in fish lipid tissue, but they are also relatively rapidly depurated (Bjorseth, et al., 1981).

Resin acids were not detected to the degree usually found in pulp mill effluents (Table 5). As mentioned earlier, extraction and analytical problems may have interfered with accurate quantification of these compounds. The toxicity data found for resin acids are presented in Table 7. Although they and chlorinated phenols have long been identified as some of the most toxic components of pulp mill effluents, there have not been many published toxicity studies. The data reported in Hutchins (1979) from work performed by Leach and Thakore (1977) indicate individual compounds are acutely toxic to coho at 0.2 to 0.8 mg/L, and mixtures of resin acid are toxic at 0.3 to 0.5 mg/L (Table 7).

A large number of other organic compounds were tentatively identified (Table 4). Many of these are similar to compounds reported in kraft mill bleachery effluents (Kringstad and Lindstrom, 1984; Lindstrom and Osterberg, 1986; Voss, 1983). They are generally described as chlorinated and unchlorinated components of wood lignins. Current research is centered on their mutagenicity and toxicity to bacteria. Further research of the importance of these compounds and techniques for their positive identification may be useful before the full-scale bioassay is undertaken.

There are other compounds that might be considered for analysis during the full-scale bioassay that were not tested in the pilot. For example, Hutchins (1979) mentions the following toxic pulp effluent components: eugenol, jvabiones, fatty acids, and diterpene alcohols. Under certain effluent conditions, sulfite and bisulfite may be toxic (Hutchins, 1979; Seeley, 1987). Other individual toxic components of pulp mill effluent, accounting for over 40 percent of the total sulfite effluent toxicity, remain unidentified (Hutchins, 1979). Also, although municipal effluent toxicity may be related primarily to ammonia and chlorine compounds, there can be pesticides and other unidentified toxic compounds as well. It may be prudent to perform a more thorough literature search on the toxic components in these effluents before the list of analyses in full-scale bioassay plan is finalized.



January 21, 1988

Page nine

#### CONCLUSIONS AND RECOMMENDATIONS

Two sets of full-strength effluent and dilution water samples were analyzed for conventional, metal, volatile, semi-volatile, resin acid, and guaiacol components. The analytical results appeared to be accurate. For example, the semi-volatile and resin acid extractions with dichloromethane were not entirely successful. Some chlorinated phenolic components and guaiacols may have been degraded because of sample preservation at pH 10.

Effluent and dilution water results appeared to be within the range reported in other studies. Some components potentially toxic to aquatic life were detected. Ammonia may have built up in the bioassay tanks to levels stressful to fish as a result of initial diluted effluent ammonia and fish-excreted ammonia. The extremely low pH of the WEYCO mill effluent also could stress fish in the low-alkalinity dilution water. Aquatic toxicity criteria were exceeded for cadmium, copper, and total chlorinated phenolics in some full-strength effluents. They did not appear high enough to cause toxicity in a 10 percent solution. Unchlorinated and chlorinated compounds tentatively identified in the effluents were similar to those reported in the literature, and may require further investigation.

The following improvements to the bioassay procedures and analytical techniques are recommended:

- o Collect 24-hour composite samples to minimize effluent quality variability.
- o Collect chlorinated rather than unchlorinated Aberdeen WTP effluent for the bioassay, and consider using a brine solution for dilution water. Both may more accurately portray environmental conditions in Grays Harbor, and the brine solution may buffer pH of the WEYCO effluent.
- o Consider using a flow-through toxicity testing scheme rather than a static or renewal scheme to prevent build-up of ammonia.
- o Field test for residual chlorine and hydrogen sulfide in the effluents prior to addition to the bioassay tanks.
- o Monitor pH, temperature, ammonia, and hardness in the bioassay tanks to help evaluate metal or other component toxicity.
- o Notify lab chemists well in advance of the bioassay so they can have all analytical materials at hand.
- o Collect volatile organics transport and transfer blank samples to ensure the quality of the effluent analyses.

January 21, 1988

Page ten

- o Analyze a spiked lead sample for QA.
- o Use NCASI resin acid method of extraction and analysis.
- o Preserve, store, and extract resin acid samples separate from semi-volatile and guaiacol samples.
- o Do not adjust the pH of the guaiacol samples to 10 or derivitize the sample with diazomethane. Research a better method for their analysis.
- o Antimony, beryllium, selenium, silver, and thallium can probably be dropped from the list of analyses.
- o Because many may be toxic, a more thorough evaluation of the tentatively identified compounds detected in the pilot study should be performed prior to finalization of the full-scale bioassay analysis list.
- o The efficacy of adding eugenol, juvabionones, diterpene alcohols, catechols, bisulfite, and other compounds to the list of analyses should be investigated.

JJ:cp

Attachment

cc: George Houck, Industrial Section  
Don Kjosness, Industrial Section  
Gary Bailey, SWRO  
Mike Morhous, SWRO  
Dick Huntamer, Lab

## REFERENCES

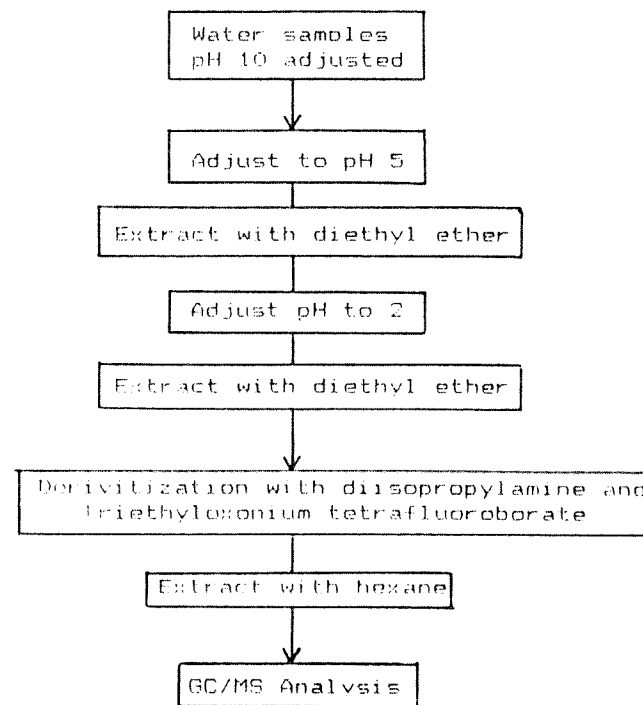
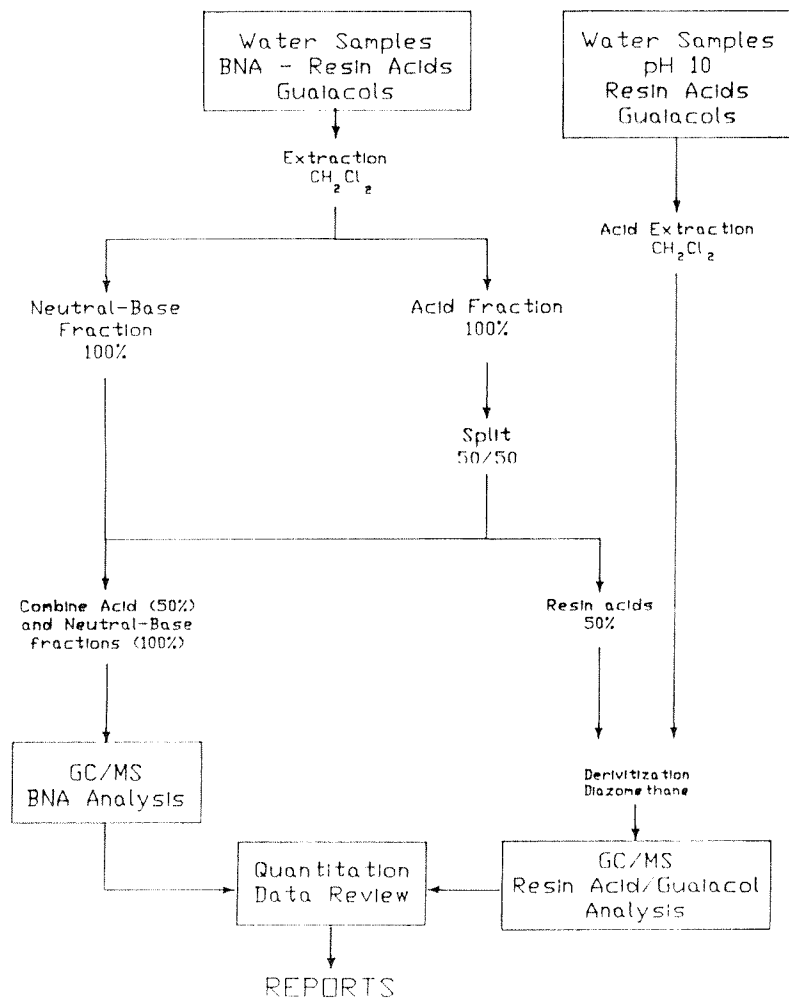
- Alabaster, J. and R. Lloyd, 1982. Water Quality Criteria for Freshwater Fish, 2nd Edition. Butterworths Publishing, Boston, MA. 361 pp.
- Albright, R., 1987. "Priority pollutant scans of Grays Harbor pulp mill effluents." Memorandum from USEPA Region 10, Office of Water Plng. to Grays Harbor Committee. Sept. 5, 1987. 1 pp.
- AWWA, WPCF, APHA, 1985. Standard Methods for the Analysis of Water and Wastewater. 16th Edition. American Water Works Assn., Washington DC.
- Bjorseth, A., G. Carlberg, N. Gjos, M. Moller, G. Tveten, 1981. "Halogenated organic compounds in spent bleach liquors: Determination, mutagenicity testing and bioaccumulation." pgs. 1119-1130, in: Advances in the Identification and Analysis of Organic Pollutants in Water, edited by L. Keith. Ann Arbor Science Press, Ann Arbor, MI.
- Buccafusco, R., S. Ellis, and G. LeBlanc, 1981. "Acute toxicity of priority pollutants to bluegill (Lepomis macrochirus). Bulletin Envir. Contam. and Toxicol. v. 26, pg. 446-452.
- Doudoroff, P. and M. Katz, 1950. "Critical review on the toxicity of industrial wastes and their components to fish." Sew. Indust. Wastes 22(11): 1432-1458 pp.
- Federal Register, 1984. "Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act." Federal Register v. 49(209), October 26, 1984. pgs. 1-210.
- Huntamer, D., 1986. Dept. of Ecology Laboratory Users' Manual, Manchester, WA, December 8, 1986. 139 pp.
- Huntamer, D., 1987. "Semi-volatile and resin acid/guaiacol analysis of Grays Harbor effluent samples." Dept. of Ecology memo. to L. Singleton, Ecology Water Quality Invest. Section, August 20, 1987, Olympia, WA. 3 pp.
- Hutchins, F., 1979. Toxicity of Pulp and Paper Mill Effluent: A Literature Review, Corvallis Environmental Research Laboratory, USEPA Doc. 600/3-79-013, Corvallis, OR. 44 pp.
- Kjosness, D., 1987. Pulp mill, refinery and smelter data. Dept. of Ecology, Industrial Section, Olympia, WA. 1 pp.
- Kringstad, K. and K. Lindstrom, 1984. "Spent liquors from pulp bleaching." Envir. Sci. and Tech. vol. 18(8): 236A-248A.
- Leach, J. and A. Thakore, 1977. "Compounds toxic to fish in pulp mill waste streams." Prog. Water Tech., vol. 9:787
- Lindstrom, K. and F. Osterberg, 1986. "Chlorinated carboxylic acids in softwood kraft pulp spent bleach liquors." Envir. Sci. and Tech. vol. 20(2):133-138

- Mills, W.B., D. Porcella, M. Unga, S. Gherni, K. Sommers, et al., 1985. Water Quality Assessment vol. 1. USEPA report EPA 600/6-85-002a, Athens, GA.
- NCASI, 1983. A Comparison of Results from the Analysis of Pulp Mill Effluent for Compounds of Pulpmill and Bleach Plant Origin. National Council of the Paper Industry for Air and Stream Improvement, Inc. Bulletin 397, April 1983, New York, NY. 271 pp.
- NCASI, 1986. Procedures for the Analysis of Resin and Fatty Acids in Pulp Mill Effluents. National Council of the Paper Industry for Air and Stream Improvement, Inc. Bulletin 501, August 1986, New York, NY. 32 pp.
- Seely, T.L., 1987. Memorandum to R. Burkhalter, Ecology Industrial Section, Olympia, WA. from Weyerhaeuser Paper Co. Cosmopolis Mill Vice President/ Mill Manager, July 30, 1987.
- Seiler, D., 1986. "Grays Harbor, its impact on salmon production." Washington Dept. of Fisheries Harvest Mgmt. Div., memorandum to E. Manary and G. DiDonato, Olympia, WA. February 4, 1986, 3 pp.
- Symons, J., T. Bellar, J. Carswell, et al., 1975. "National organics reconnaissance survey for halogenated organics." Journ. AWWA: Nov. (634-647).
- USEPA, 1980a. Ambient Water Quality Criteria for Chlorinated Phenols. U.S. Environmental Protection Agency, Office of Water Regulations and Standards. Doc. EPA 440/5-80-032, Washington DC, 161 pp.
- USEPA, 1980b. Development Document for Effluent Limitation Guidelines and Standards for the Pulp, Paper and Paperboard, Builders Paper and Board Mills (proposed). USEPA report EPA 440/1-80/025b, Washington DC.
- USEPA, 1983. Methods for the Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency Support Laboratory, Cincinnati, OH.
- USEPA, 1985. Contract Laboratory Program Statement of Work (SOW), Inorganic Analysis, Multi-media, Multi-concentration. SOW No. 785. U.S. Environmental Protection Agency, Washington DC.
- USEPA, 1986. Quality Criteria for Water 1986. U.S. Environmental Protection Agency, EPA 440/5-86-001, Office of Water Regulations and Standards, Washington DC.
- Voss, R., 1983. "Chlorinated neutral organics in biologically treated bleached kraft mill effluents." Envir. Sci. and Tech. vol. 15(9) 530-537.

Figure 1. A comparison of Ecology (Huntamer, 1987) and NCASI (NCASI, 1986) methods for resin acid analysis.

ECOLOGY MANCHESTER LABORATORY RESIN ACID / GUAIACOL ANALYTICAL METHOD

NCASI RESIN AND FATTY ACID ANALYTICAL METHOD 85.01\*



\* National Council of the Paper Industry for Air and Stream Improvement Technical Bulletin 501 (NCASI, 1986)

Table 1. Descriptions and analytical tests performed on samples collected as part of the Grays Harbor pilot bioassay project, April - May, 1987.

Ecology Sample	Sample Description	Field/Laboratory Activities
WEYCO	Meyerhaeuser Co. Cosmopolis sulfite pulp mill effluent; a 24 hr. composite sample collected after secondary treatment at Pond 'D'.	Temperature, pH, conductivity/ pH, conductivity, solids(4), alkalinity, hardness, chemical oxygen demand, ammonia, priority pollutant metals, semi-volatiles, volatile organics, resin acids, guaiacols.
ITT	ITT Hoquiam sulfite pulp mill effluent collected as a grab sample from the secondary effluent line at 8:30 A.M. on 4/30/87, and 9:00 A.M. on 5/4/87.	Temperature, pH, conductivity/ pH, conductivity, solids(4), alkalinity, hardness, chemical oxygen demand, ammonia, priority pollutant metals, semi-volatiles, volatile organics, resin acids, guaiacols.
Aberdeen WTP	Aberdeen municipal wastewater treatment plant effluent collected as a grab sample after secondary treatment but before chlorination at 8:30 A.M. on 4/30/87, and 9:00 A.M. on 5/4/87.	Temperature, pH, conductivity/ pH, conductivity, solids(4), alkalinity, hardness, chemical oxygen demand, ammonia, priority pollutant metals, semi-volatiles, volatile organics, resin acids, guaiacols.
Control	Chlorinated Lake Aberdeen water used by the WEYCO Cosmopolis mill, the City of Aberdeen, and as bioassay dilution water in the pilot project; collected as a grab sample from a faucet inside the WEYCO mobile bioassay trailer at 3:30 P.M. on 4/30/87, and 1200 P.M. on 5/4/87.	Temperature, pH, conductivity/ pH, conductivity, solids(4), alkalinity, hardness, chemical oxygen demand, ammonia, priority pollutant metals, semi-volatiles, volatile organics, resin acids, guaiacols.
Duplicate	The Aberdeen WTP sample selected at random from a choice of the three effluent samples on 4/30/87.	Temperature, pH, conductivity/ pH, conductivity, solids(4), alkalinity, hardness, chemical oxygen demand, ammonia, priority pollutant metals, semi-volatiles, volatile organics, resin acids, guaiacols, metals(6)
Transport Blank	Carbon free water from the Ecology Manchester Environmental Laboratory carried to the Cosmopolis site and back in standard sample containers on 5/4/87.	None/ priority pollutant metals, semi-volatiles
Fish tank Aber'n,eff.	Bioassay solution from the Aberdeen WTP fish tank after four days of exposure to the fish collected on 5/4/87 at 1230 P.M.	None/ Ammonia
pH Adjusted	Samples collected from the WEYCO, ITT, and Aberdeen WTP effluents and adjusted to pH 10 in the field on 5/4/87.	pH/ resin acids, guaiacols

Table 2. Analytical procedures for samples taken during the Grays Harbor effluent pilot bioassay, April- May 1987 (Huntamer, 1986).

Analysis	Method #	COMPOUND	Method #	COMPOUND
Conventionals		Semi-volatiles (continued)	EPA 625	Semi-volatiles (continued)
pH	SM 423	Pentachlorophenol	"	3,3'-dichlorobenzidine
Total Alkalinity	SM 403	bis(2-chloroethyl) ether	"	2-methylphenol
Total Hardness	SM 314B	bis(2-chloroisopropyl) ether	"	4-methylphenol
Total Solids	SM 209A	bis(2-chloroethoxy)methane	"	Benzyl alcohol
Total Non-Vol. Solids	SM 209D	4-chlorophenyl phenyl ether	"	4-bromophenyl phenyl ether
Total Suspended Solids	SM 205C	1,3-dichlorobenzene	"	4-chloroaniline
T. Non-Vol. Sus. Solids	SM 209D	1,4-dichlorobenzene	"	Dibenzofuran
COD	SM 508C	1,2-dichlorobenzene	"	n-nitroso-di-n-propylamine
NH3-N	EPA 350.1	1,2,4-trichlorobenzene	"	Volatiles
Metals	CLP 785	Hexachloroethane	"	Chloromethane
Arsenic	"	Nitrobenzene	"	Bromomethane
Beryllium	"	Hexachlorobenzene	"	Vinylchloride
Cadmium	"	2,6-dinitrotoluene	"	Chloroethane
Chromium	"	2,4-dinitrotoluene	"	Methylene chloride
Copper	"	Isophorone	"	1,1-dichloroethylene
Lead	"	Nitrosodiphenylamine	"	1,1-dichloroethane
Thallium	"	Hexachlorobutadiene	"	1,2-dichloroethane
Nickel	"	Hexachlorocyclopentadiene	"	Trichloroethene
Silver	"	2-chloronaphthalene	"	Chloroform
Zinc	"	Acenaphthene	"	1,1,1-trichloroethane
Antimony	"	Acenaphthylene	"	1,1,2-trichloroethane
Selenium	"	Fluorene	"	Carbon tetrachloride
Mercury	"	Naphthalene	"	Bromodichloromethane
Resin Acid/ Guaiacols	Special -	Phenanthrene	"	1,2-dichloropropane
Guaiacol	see text	Anthracene	"	cis-1,3-dichloropropene
4,5,6-trichloroguaiacol	and	Fluoranthene	"	trans-1,3-dichloropropene
Tetrachloroguaiacol	Figure 1	Pyrene	"	Total Xylenes
Retene	"	Benzo(a)anthracene	"	Benzene
Isopimaric Acid	"	Chrysene	"	Chlorodibromomethane
Levopimaric Acid	"	Benzo(b)fluoranthene	"	Bromoform
Dehydroabietic Acid	"	Benzo(k)fluoranthene	"	1,1,2,2-tetrachloroethane
Abietic Acid	"	Benzo(a)pyrene	"	Tetrachloroethene
Neobietic Acid	"	Dibenzo(a,h)anthracene	"	Toluene
Dichlorodehydroabietic acid	"	Indeno-1,2,3-c,d-pyrene	"	Chlorobenzene
Semi-volatiles	EPA 625	Benzo(g,h,i)perylene	"	Ethylbenzene
Phenol	"	Diethylphthalate	"	Acetone
2-chlorophenol	"	Di-n-butylphthalate	"	2-butanone
2-nitrophenol	"	Benzyl butylphthalate	"	2-chloroethylvinyl ether
2,4-dimethylphenol	"	bis(2-ethylhexyl)phthalate	"	Carbon disulfide
2,4-dichlorophenol	"	Di-n-octyl phthalate	"	Vinyl acetate
4-chloro-3-methylphenol	"	Dimethylphthalate	"	4-methyl-2-pentanone
2,4,6-trichlorophenol	"	Benzoic acid	"	2-hexanone
2,4,5-trichlorophenol	"	2-nitroaniline	"	Styrene
2,4-dinitrophenol	"	3-nitroaniline	"	trans-1,2-dichloroethene
4-nitrophenol	"	4-nitroaniline	"	2-hexanone
4,6-dinitro-o-cresol	"	2-methylnaphthalene	"	

\* Methods are noted from the following references:

SM = Standard Methods (AWWA,WPCF,APHA, 1985)

EPA = U. S. Environmental Protection Agency (Federal Register, 1984) for Methods 624 & 625.

EPA = U. S. Environmental Protection Agency (USEPA, 1983) for Method 350.1.

CLP = U. S. Environmental Protection Agency, Contract Laboratory Program (USEPA, 1985)

Table 3. Analytical data for the effluent and control water used in the April, 1987 fish bioassay.  
All values µg/L unless otherwise noted.

Station	WEYCO EFF. POND D	WEYCO EFF. POND D	WEYCO EFF. POND D	ITT EFF	ITT EFF	ITT EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	CONTROL-LK ABERDEEN	CONTROL-LK ABERDEEN	TRANSPORT BLANK	FISH TANK ABERDEEN EFF
Date	4/30	5/04	5/04	4/30	5/04	5/04	4/30	4/30	5/04	5/04	4/30	5/04	5/04	5/04
Collection time	14:45:00	11:05:00	11:06:00	08:30:00	08:10:00	08:10:00	08:30:00	08:30:00	09:00:00	09:00:00	14:30:00	12:03:00		
Sample Number	87-187451	87-197475	87-197475	87-187452	87-197476	87-197476	87-187453	87-187455	87-197477	87-197477	87-187454	87-197478	87-197479	87-197480
Sample type *	24HR	24HR	24HR	GRAB	GRAB	GRAB	GRAB	DUP	GRAB	GRAB	GRAB	GRAB	GRAB	GRAB
FIELD CONVENTIONAL														
Field Temp. (deg C)	15.5	19.0	19.0	17.0	21.0	21.0	14.8	14.8	17.0	17.0				14.6
Field pH (s.u.)	3.1	2.7	2.8	6.5	6.4	6.4	7.4	7.4	7.1	7.1				6.7
Field Cond. (µmhos/cm)	2000	2000	2000	1200	1450	1450	420	420	325	325				60
LAB CONVENTIONAL														
Lab Cond. (µmhos/cm)	2140	2710	2710	1360	1550	1550	428	443	362	362	56	56		
pH adjusted for Resin Acids:	NO	NO	YES	NO	NO	YES	NO	NO	NO	YES	NO	NO		
Laboratory pH (s.u.)	2.9	2.8	10.0	6.3	6.4	10.0	7.2	7.2	7.4	10.0	6.7	6.6		
Total Alkalinity as CaCO <sub>3</sub>	--	--		39	74		110	120	210		21	38		
Total Hardness as CaCO <sub>3</sub>	400	550		280	310		92	75	86		36	47		
Total Solids	1800	2100		1500	1700		240	260	290		61	65		
Total Non-Vol. Solids	880	1100		760	860		160	170	140		43	43		
Total Suspended Solids	220	160		63	61		9	9	6		10	13		
Total Non-Vol. Susp. Solids:	14	16		6	11		2	3	2		4	8		
COD	800	800		870	1000		41	37	33		25	12		
NH <sub>3</sub> -N	0.72	4.8		7.2	9.5		25	23	8.0		0.24	0.21		9.4
METALS														
Arsenic	--	--		0.0040	--		--	0.002	0.002		--	--		--
Beryllium	--	--		--	--		--	--	--		--	--		--
Cadmium	0.0034	0.0023		0.0008	0.0015		0.0005	0.0007	0.0007		0.0004	0.0004		0.0003
Chromium	0.053	0.031		0.068	0.124		--	0.003	--		--	--		--
Copper	0.031	0.081		0.013	0.010		0.010	0.007	0.011		0.002	0.004		--
Lead	--	--		--	--		--	--	--		--	--		--
Thallium	--	--		--	--		--	--	--		--	--		--
Nickel	0.062	0.009		0.116	0.011		--	--	0.004		--	--		--
Silver	--	--		--	--		--	--	--		--	--		--
Zinc	0.181	0.162		0.032	0.075		0.021	0.014	0.021		0.004	--		--
Antimony	--	--		--	--		--	--	--		--	--		--
Selenium	--	--		--	--		--	--	--		--	--		--
Mercury	0.00014	0.00007		0.00007	--		0.0001	0.00004	--		0.00007	--		0.00007
VGA AND BNA COMPOUNDS														
Acetone	--	0.0073J		--	--		--	--	--		--	--		--
Chloroform	0.0073	0.0031J		0.1100	0.190		0.0023J	0.0019J	0.0023J		0.022	0.018		--
Benzene	--	--		--	--		--	--	--		--	--		--
Bromodichloromethane	--	--		0.00042J	0.00018J		--	--	--		0.0027J	0.0031J		--
Hylenes	--	--		--	0.00068J		--	--	--		--	--		--
Ethylbenzene	--	--		--	0.00011J		--	--	--		--	--		--
Toluene	0.001J	0.001J		--	0.000056J		--	--	--		--	--		--
Benzoic acid	--	0.003J		--	--		--	--	--		--	--		--
di-n-butylphthalate	--	--		--	--		0.0003J	0.0002J	0.0003J		--	LAC		0.0002J
bis(2-ethylhexyl)phthalate	--	--		--	--		--	--	--		--	LAC		--
di-n-octylphthalate	--	--		--	--		--	--	--		--	LAC		0.0007J
2,4,6-trichlorophenol	--	0.011		0.0009J	--		--	--	--		--	LAC		--
2,4,5-trichlorophenol	0.011	--		--	--		--	--	--		--	LAC		--
Naphthalene	0.0002J	0.0003J		--	--		--	--	--		--	LAC		--
1,2-dichlorobenzene	--	--		--	--		--	--	0.0003J		--	LAC		--
1,4-dichlorobenzene	--	--		--	--		0.0002J	0.0002J	0.0003J		--	LAC		--
4-methylphenol	0.047	0.035		0.0005J	--		--	--	--		--	LAC		--
Phenol	--	0.0007J		--	--		--	--	--		--	LAC		--
bis(2-chloroethyl)ether	--	--		--	0.0009J		--	--	--		--	LAC		--
2,4-dichlorophenol	0.002	0.003J		--	--		--	--	--		--	LAC		--
RESIN ACIDS / GUAIACOLS														
4,5,6-trichloroguaiacol	0.046	0.09100	0.01600	--	0.00610	--	--	--	--		--	LAC		--
Tetrachloroguaiacol	0.015	0.01900	0.00670	0.0056	0.00740	--	--	--	--		--	LAC		--
Dehydroabiatic acid	0.015	0.01800	0.02300	0.0019J	--		--	--	--		--	LAC		--
Dichlorodehydroabiatic acid	0.013	0.05700	0.04700	0.0082	0.00500	--	--	--	--		--	LAC		--

\* Sample either a 24-hr. composite or a single event grab. DUP is a field duplicate.  
 -- Denotes value below detection limit. Blank spaces indicate analysis was not performed.  
 J Value is estimated; analyte present but not quantifiable.  
 LAC Sample accidentally destroyed at the laboratory.



Table 4. Tentatively identified compounds detected in the semi-volatile and methylated semi-volatile fractions of effluent and control/ dilution water samples collected during the Grays Harbor renewal bioassay pilot project, April-May, 1987. All values are mg/L unless otherwise noted.

Station	WEYCD EFF POND D	WEYCD EFF POND D	WEYCD EFF POND D	ITT EFF	ITT EFF	ITT EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	ABERDEEN WTP EFF	CONTROL-LK ABERDEEN	CONTROL-LK ABERDEEN	TRANSPORT BLANK
Date	4/30	5/04	5/04	4/30	5/04	5/04	4/30	4/30	5/04	5/04	4/30	5/04	5/04
Collection time	14:45:00	11:05:00	11:06:00	08:30:00	08:10:00	08:10:00	08:30:00	08:30:00	09:00:00	09:00:00	14:30:00	12:03:00	
Sample Number	87-187451	87-197475	87-197475	87-187452	87-197476	87-197476	87-187453	87-187455	87-197477	87-197477	87-187454	87-197478	87-197479
Sample type *	24HR	24HR	24HR	GRAB	GRAB	GRAB	GRAB	DUP	GRAB	GRAB	GRAB	GRAB	GRAB
1,1,1,3,3-pentachloro-2-propanone	0.069	0.044											
2-methyl hexanoic or pentanoic acid	0.007												
2-methyl hexanoic acid or related compound	0.012												
1,1,3,3-tetrachloro-2-propanone	0.012	0.008											
2,5-dimethylbenzene butanoic acid	0.066	0.082											
Hexadecanoic acid	0.230												
Isoquinoline							0.015	0.013					
2-butoxyethanol phosphate							0.014	0.007				0.260J	
3-ethylphenol acetate	0.01J												
2-furan carboxaldehyde		0.890											
5-methyl-2-furan carboxaldehyde		0.030											
Cyclohexanone		0.003											
METHYLATED BNA													
12-(acetyloxy)-9-octadecanoic acid [ME]*	0.085J	0.590J	0.220J	0.083J			0.051J	0.065J		0.029J	0.023J	0.092J	
9-octadecanoic acid [ME]								0.035J					
a-methyl-4(2-methylpropyl)benzetic acid [ME]							0.0087J					0.0086J	
1,4-dichloro-2,5-dimethoxybenzene				0.060J		0.010J							
1,2,3,4-tetrachloro-5,6-dimethoxybenzene				0.075J									
Dichloro-dimethoxybenzene						0.0051J							
8-methyl decanoic acid [ME]			0.092J										
10-octadecanoic acid [ME]		0.740J	0.360J										
16-methyl-heptadecanoic acid [ME]		0.410J	0.180J									0.071J	
1,1,2,2-tetrachloroethane									0.057J		0.0091J	0.014J	
Heptadecanoic acid [ME]		0.240J											
4-(1-methylethyl)benzoic acid [ME]		0.0098J											
4-(1,5-dimethyl-3-oxohexyl)cyclohexane carboxylic acid [ME]		0.990J											
4-methyl-benzenesulfonic acid [ethyl ester]					0.055J								
n-4-dimethyl-n-propyl benzenesulfonamide					0.110J								

\* [ME] denotes methyl ester form

J value estimated

Table 5. Data from other studies investigating municipal wastewater (POTW) and public utility effluent characteristics. ALL VALUES ARE U.S.

Compound	USEPA Guidelines Study *			Ecology Database **		USEPA 1986 Studies**		POTW Effluents***	
	Mean	Min.	Max.	Low	High	Min	Max	Min	Max
Conventional	:	:	:	:	:	:	:	:	:
DOC	1242	690 to	2070	:	:	:	:	:	:
NH <sub>2</sub> -N	21	7 to	48	:	:	:	:	:	:
Metals	:	:	:	:	:	:	:	:	:
Arsenic	:	:	:	--	0.421	0.004	:	0.001	0.072
Beryllium	:	:	:	--	0.001	:	:	:	:
Cadmium	:	:	:	--	0.030	0.004	0.001	0.002	0.082
Chromium	0.006	0.003 to	0.016	--	0.710	0.005	0.003	0.002	0.759
Copper	0.033	0.008 to	0.100	+	0.137	0.009	0.009	0.002	0.255
Lead	0.011	-- to	0.042	--	0.301	:	:	0.020	0.217
Thallium	:	:	:	--	0.060	0.002	0.005	:	:
Nickel	0.009	-- to	0.018	--	0.150	0.007	0.002	0.007	0.279
Silver	:	:	:	--	0.141	:	:	0.011	0.030
Zinc	0.116	0.025 to	0.420	0.006	1.261	0.007	0.006	0.016	0.181
Antimony	:	:	:	--	0.007	:	:	0.001	0.069
Selenium	:	:	:	--	0.090	:	:	0.001	0.150
Mercury	0.001	-- to	0.002	--	0.002	:	0.000	0.000	0.001
Resin Acid Sulfonates	:	:	:	:	:	:	:	:	:
4,5,6-trichloroparacetic acid	0.001	-- to	0.002	:	:	:	:	:	:
Isoparacetic Acid	0.017	-- to	0.084	:	:	:	:	:	:
Dehydroacetic Acid	0.246	-- to	0.950	:	:	:	:	:	:
Abietic Acid	0.076	0.008 to	0.340	:	:	:	:	:	:
Dichlorodehydroabietic acid	0.001	-- to	0.003	:	:	:	:	:	:
Chlorodehydroabietic Acid	0.039	-- to	0.093	:	:	:	:	:	:
Pimaric Acid	0.017	-- to	0.052	:	:	:	:	:	:
Diacetic Acid	0.081	0.031 to	0.120	:	:	:	:	:	:
Linoleic Acid	0.034	-- to	0.160	:	:	:	:	:	:
Epoxy stearic Acid	0.007	-- to	0.020	:	:	:	:	:	:
Semi-volatiles	:	:	:	:	:	:	:	:	:
Phenol	0.041	-- to	0.250	--	0.020	0.004	:	0.001	0.089
2-chlorophenol	0.027	0.021 to	0.050	:	:	:	:	:	:
4-methylphenol	:	:	:	--	0.09	:	:	:	:
2,4-dimethylphenol	:	:	:	--	+	:	:	:	:
2,4-dichlorophenol	0.053	-- to	0.130	--	0.021	:	:	:	:
2,4,6-trichlorophenol	0.106	0.002 to	0.270	--	0.087	0.008	:	:	:
4-nitrophenol	:	:	:	--	+	:	:	:	:
Pentachlorophenol	0.001	0.001 to	0.001	--	0.010	+	:	0.001	0.440
Hexachloroethane	:	:	:	--	+	:	:	:	:
Acenaphthene	:	:	:	--	+	:	:	:	:
Fluorene	:	:	:	--	+	:	:	:	:
Naphthalene	0.036	0.007 to	0.088	--	+	+	:	:	:
Phenanthrene	:	:	:	--	+	:	:	:	:
Anthracene	:	:	:	--	+	:	:	:	:
Fluoranthene	:	:	:	--	+	:	:	:	:
Pyrene	:	:	:	--	+	:	:	:	:
Benzo(a)anthracene	:	:	:	--	+	:	:	:	:
Chrysene	:	:	:	--	+	:	:	:	:
Benzo(b)fluoranthene	:	:	:	--	+	:	:	:	:
Benzo(k)fluoranthene	:	:	:	--	+	:	:	:	:
Benzo(a)pyrene	:	:	:	--	+	:	:	:	:
Dibenz(a,h)anthracene	:	:	:	--	+	:	:	:	:
Indeno(1,2,3-c,d)pyrene	:	:	:	--	+	:	:	:	:
Benzo(g,h,i)perylene	:	:	:	--	+	:	:	:	:
Diethylphthalate	0.014	0.014 to	0.014	--	0.021	:	:	0.001	0.007
Di-n-butylphthalate	:	:	:	--	0.005	:	:	0.001	0.097
Benzyl butylphthalate	:	:	:	--	0.012	:	:	0.001	0.034
bis(2-ethylhexyl)phthalate	0.010	-- to	0.091	--	0.140	:	:	0.001	0.370
Di-n-octyl phthalate	:	:	:	--	+	:	:	:	:
Dimethylphthalate	:	:	:	--	0.001	:	:	:	:
Volatile organic compounds	:	:	:	--	:	:	:	:	:
Chloroethane	:	:	:	--	0.018	:	:	:	:
Methylene chloride	0.271	0.002 to	3.100	--	0.062	:	:	0.001	62.000
1,2-dichloroethane	:	:	:	--	0.002	:	:	:	:
Trichloroethene	:	:	:	--	+	:	:	0.001	0.230
Chloroform	0.433	0.120 to	1.200	--	37.000	0.170	:	0.001	0.087
1,1,1-trichloroethane	0.007	0.006 to	0.008	--	0.014	:	:	0.001	3.500
Bromodichloroethane	0.002	-- to	0.005	--	+	:	:	0.001	0.006
Benzene	0.016	-- to	0.096	--	0.015	:	:	0.001	0.072
Tetrachloroethene	0.003	-- to	0.006	--	+	+	:	0.001	1.200
Toluene	0.014	-- to	0.066	--	0.041	+	:	0.001	1.100
Chlorobenzene	:	:	:	--	0.001	:	:	:	:
Ethylbenzene	:	:	:	--	0.046	:	:	0.001	0.049
Dichlorofluoroethane	:	:	:	--	+	:	:	:	:

\* Taken from Table 4-31 of reference USEPA, 1980b. Four sulfite paper mills - total 12 samples.

\*\* Washington Dept. of Ecology Industrial Section data for 6 sulfite mills - 12 samples total (Kjosness, 1987)

+ Compound detected but not quantified.

\*\* Sample results from Grays Harbor testing June 17, 1986 (Albright, 1987)

-- Compound not detected.

\*\*\* Data from 40 municipal plants for pollutants detected in greater than 10% of the samples. Table III-39 in Mills, et al., 1986.

Table 6. USEPA criteria for the protection of aquatic life for organic compounds and metals detected in the Grays Harbor effluent samples. All values are  $\mu\text{g/L}$ .

ORGANIC COMPOUNDS

COMPOUND	USEPA LOWEST OBSERVED EFFECTS LEVELS *			
	FRESHWATER		MARINE	
	Acute	Chronic	Acute	Chronic
Chloroform	28.90	1.24	--	--
Benzene	5.30	--	5.10	0.70
Bromodichloromethane	11.00	--	12.00	6.40
Xylenes	--	--	--	--
Ethylbenzene	32.00	--	0.43	--
Toluene	17.50	--	6.30	5.00
Benzoic acid	--	--	--	--
di-n-butylphthalate	--	--	--	--
bis(2-ethylhexyl)phthalate	--	--	--	--
di-n-octylphthalate	--	--	--	--
2,4,6-trichlorophenol	--	0.97	--	--
2,4,5-trichlorophenol	--	--	--	--
Naphthalene	2.30	0.62	2.35	--
1,2-dichlorobenzene	1.12	0.76	1.97	--
1,4-dichlorobenzene	1.12	0.76	1.97	--
4-methylphenol	--	--	--	--
Phenol	10.20	2.56	5.80	--
bis(2-chloroethyl)ether	--	--	--	--
2,4-dichlorophenol	2.02	0.37	--	--
4,5,6-trichloroquaiacol	--	--	--	--
Tetrachloroquaiacol	--	--	--	--
Dehydroabiatic acid	--	--	--	--
Dichlorodehydroabiatic acid	--	--	--	--

\* None of the compounds listed above have sufficient data to establish firm criteria for the protection of aquatic life, so the USEPA has given lowest observed effect level (LOEL) data until criteria can be established.  
 -- Insufficient data to establish a LOEL.

METALS

Site	Date	Hardness	USEPA FRESHWATER CRITERIA FOR AQUATIC LIFE													
			Cadmium		Chromium +3		Copper		Nickel		Zinc		Arsenic +3		Mercury	
			acute	chronic	acute	chronic	acute	chronic	acute	chronic	acute	chronic	acute	chronic	acute	chronic
WEYCO	4/30	400	18.7	3.4	5405	644	65	39	4582	509	379	343	360	190	2.4	0.012
ITT	4/30	280	12.5	2.5	4036	481	47	29	3389	377	280	254	360	190	2.4	0.012
ABERDEEN	4/30	92	3.6	1.1	1622	193	16	11	1322	147	109	99	360	190	2.4	0.012
ABERDEEN	4/30	75	2.8	0.9	1372	164	14	9	1112	124	92	83	360	190	2.4	0.012
CONTROL	4/30	36	1.2	0.5	752	90	7	5	598	66	49	45	360	190	2.4	0.012
WEYCO	5/04	550	26.8	4.3	7015	836	88	51	5999	667	496	449	360	190	2.4	0.012
ITT	5/04	310	14.1	2.8	4386	523	51	31	3694	411	305	276	360	190	2.4	0.012
ABERDEEN	5/04	86	3.3	1.0	1535	183	15	10	1248	139	103	93	360	190	2.4	0.012
CONTROL	5/04	47	1.7	0.6	936	112	9	6	749	83	62	56	360	190	2.4	0.012
TRANS BLNK	5/04															

acute: 1 hr. average concentration, once in three years  
 chronic: 4 day average concentration

Table 7. Data for resin acids, guaiacols, chlorophenols and related compounds toxicity to freshwater fish. All values mg/L.

Compound	Species	Method	Duration	Effect	Concentration	Reference
Abietic acid	coho	static *	96-hr	LC 50	0.41	Leach and Thakore, 1977**
Dehydroabietic acid	coho	static *	96-hr	LC 50	0.75	Leach and Thakore, 1977**
Chlorodehydroabietic acid	rainbow tr	static	96-hr	LC 50	0.60	Leach and Thakore, 1977**
Dichlorodehydroabietic acid	rainbow tr	static	96-hr	LC 50	0.60	Leach and Thakore, 1977**
Isopimaric acid	coho	static *	96-hr	LC 50	0.22	Leach and Thakore, 1977**
Palustric acid	coho	static *	96-hr	LC 50	0.55	Leach and Thakore, 1977**
Pimaric acid	coho	static *	96-hr	LC 50	0.32	Leach and Thakore, 1977**
Sandaracopimaric acid	coho	static *	96-hr	LC 50	0.36	Leach and Thakore, 1977**
Epoxy stearic acid	rainbow tr	static	96-hr	LC 50	1.50	Leach and Thakore, 1977**
Dichlorostearic acid	rainbow tr	static	96-hr	LC 50	2.50	Leach and Thakore, 1977**
Trichloroguaiacol	rainbow tr	static	96-hr	LC 50	0.75	Leach and Thakore, 1977**
Tetrachloroguaiacol	rainbow tr	static	96-hr	LC 50	0.32	Leach and Thakore, 1977**
2,4,6-trichlorophenol	fathd minnow	static	96-hr	LC 50	0.60	USEPA, 1972 ***
2,4,6-trichlorophenol	bluegill	static	96-hr	LC 50	0.32	USEPA, 1978 ***
2,4,6-trichlorophenol	fathd minnow	ELS	96-hr	chronic	0.72	USEPA, 1978 ***
2,4,6-trichlorophenol	bluegill	static	24-hr	LC 50	0.72	Buccafusco, Ellis & LeBlanc, 1981
2,4,6-trichlorophenol	bluegill	static	96-hr	LC 50	0.32	Buccafusco, Ellis & LeBlanc, 1981
2,4,5-trichlorophenol	bluegill	static	96-hr	LC 50	0.45	USEPA, 1978 ***
2,4,5-trichlorophenol	rainbow tr	static	48-hr	LC 50	1.00	Shumway & Palensky, 1973
2,4,5-trichlorophenol	bluegill	static	24-hr	LC 50	0.61	Buccafusco, Ellis & LeBlanc, 1981
2,4,5-trichlorophenol	bluegill	static	96-hr	LC 50	0.45	Buccafusco, Ellis & LeBlanc, 1981
2,3,4,6-tetrachlorophenol	bluegill	static	24-hr	LC 50	0.19	Buccafusco, Ellis & LeBlanc, 1981
2,3,4,6-tetrachlorophenol	bluegill	static	96-hr	LC 50	0.14	Buccafusco, Ellis & LeBlanc, 1981
2,3,4,6-tetrachlorophenol	bluegill	static	96-hr	LC 50	0.14	USEPA, 1978 ***
2,3,4,6-tetrachlorophenol	bluegill	static	96-hr	LC 50	0.17	USEPA, 1978 ***
2,3,4,6-tetrachlorophenol	goldfish	static	24-hr	LC 50	0.75	Kobayashi, et al., 1979 ***
Pimarol	rainbow tr	static	96-hr	LC 50	0.30	Leach and Thakore, 1977**
Isopimarol	rainbow tr	static	96-hr	LC 50	0.30	Leach and Thakore, 1977**
Dehydroabietol	rainbow tr	static	96-hr	LC 50	0.80	Leach and Thakore, 1977**
Abietol	rainbow tr	static	96-hr	LC 50	1.80	Leach and Thakore, 1977**
Juvabione	rainbow tr	static *	96-hr	LC 50	1.50	Leach and Thakore, 1977**
Juvabiol	rainbow tr	static *	96-hr	LC 50	1.80	Leach and Thakore, 1977**
4'-dehydrojuvabione	rainbow tr	static *	96-hr	LC 50	0.80	Leach and Thakore, 1977**
Dehydrojuvabione	rainbow tr	static *	96-hr	LC 50	2.00	Leach and Thakore, 1977**
Resin acid mixture	coho	static	96-hr	LC 50	0.3 - 0.5	Leach and Thakore, 1977**

\* Static bioassay with toxicant solution renewal every 4 to 8 hours.

\*\* Referenced and listed in Hutchins (1979)

\*\*\* Referenced and listed in USEPA (1980)

ELS Early life-stage test

APPENDIX I.

Detection limits for parameters analyzed in the Grays Harbor effluent pilot bioassay, April-May, 1987. All values ug/L.

Detection limits for parameters analyzed in the Grays Harbor effluent pilot bioassay, April-May, 1987. All values ug/L.

COMPOUND	Detection Limits	COMPOUND	Detection Limits	COMPOUND	Detection Limits
Total Alkalinity	1000	bis(2-chloroisopropyl)ether	1-9	3,3'-dichlorobenzidine	2-17
Total Hardness	1000	bis(2-chloroethoxy)methane	1-9	2-methylphenol	1-9
Total Solids	1000	4-chlorophenyl phenyl ether	1-9	4-methylphenol	1-9
Total Non-Vol. Solids	1000	1,3-dichlorobenzene	1-9	Benzyl alcohol	1-9
Total Suspended Solids	1000	1,4-dichlorobenzene	1-9	4-bromophenyl phenyl ether	1-9
T. Non-vol. Sus. Solids	1000	1,2-dichlorobenzene	1-9	4-chloroaniline	1-9
ODD	4000	1,2,4-trichlorobenzene	1-9	Dibenzofuran	1-9
NH3-N	10	hexachloroethane	1-9	n-nitroso-di-n-propylamine	1-9
Arsenic	1	Nitrobenzene	1-9	Chloroacetane	10
Ferrous	0.2	hexachlorobenzene	1-9	Bromoacetane	10
Manganese	0.3	2,6-dinitrotoluene	1-9	Vinylchloride	10
Chromium	1	2,4-dinitrotoluene	1-9	Chloroethane	10
Copper	1	Isophorone	1-9	Methylene chloride	5
Lead	1	Nitrosodiphenylamine	1-9	1,1-dichloroethane	5
Thallium	1	Hexachlorobutadiene	1-9	1,1-dichloroethane	5
Nickel	1	Hexachlorocyclopentadiene	1-9	1,2-dichloroethane	5
Silver	0.2	2-chloronaphthalene	1-9	Trichloroethene	5
Zinc	1	Acenaphthene	1-9	Chloroform	10
Antimony	1	Acenaphthylene	1-9	1,1,1-trichloroethane	5
Selenium	1	Fluorene	1-9	1,1,2-trichloroethane	5
Mercury	0.07	Naphthalene	1-9	Carbon tetrachloride	5
Guaiacol	5-15	Phenanthrene	1-9	Bromodichloroethane	5
4,5,6-trichloroguaiacol	5-15	Anthracene	1-9	1,2-dichloropropane	5
Tetrachloroguaiacol	5-15	Fluoranthene	1-9	cis-1,3-dichloropropene	5
Retene	3-15	Pyrene	1-9	trans-1,3-dichloropropene	5
Isopimaric Acid	3-15	Benzo(a)anthracene	1-9	Total xylenes	5
Devoipimaric Acid	3-15	Chrysene	1-9	Benzene	5
Dehydroabiatic Acid	3-15	Benzo(b)fluoranthene	1-9	Chlorodibromoethane	5
Abietic Acid	3-15	Benzo(k)fluoranthene	1-9	Bromoform	5
Neoadietic Acid	6-30	Benzo(a)pyrene	1-9	1,1,2,2-tetrachloroethane	10
Dichlorodihydroabiatic acid	5-15	Dibenz(a,h)anthracene	1-9	Tetrachloroethene	5
Phenol	1-9	Indeno-1,2,3-c-d-pyrene	1-9	Toluene	5
2-chlorophenol	1-9	Benzo(g,h,i)perylene	1-9	Chlorobenzene	5
2-nitrophenol	1-9	Diethylphthalate	1-9	Ethylbenzene	5
2,4-dimethylphenol	1-9	Di-n-butylphthalate	1-9	Acetone	10
2,4-dichlorophenol	1-9	Benzyl butylphthalate	1-9	2-butanone	5
4-chloro-3-methylphenol	1-9	bis(2-ethylhexyl)phthalate	1-9	2-chloroethylvinyl ether	10
2,4,6-trichlorophenol	1-9	Di-n-octyl phthalate	1-9	Carbon disulfide	5
2,4,5-trichlorophenol	4-9	Dimethylphthalate	1-9	Vinyl acetate	5
2,4-dinitrophenol	4-43	Benzoic acid	23-43	4-methyl-2-pentanone	10
4-nitrophenol	4-43	2-nitroaniline	4-43	2-hexanone	10
4,6-dinitro-o-cresol	4-43	3-nitroaniline	4-43	Styrene	5
Pentachlorophenol	4-43	4-nitroaniline	4-43	trans-1,2-dichloroethene	5
bis(2-chloroethyl)ether	1-2	2-methylnaphthalene	1-9	2-hexanone	10

Appendix II. Semi-volatile surrogate spike recoveries and resin acid/guaiacol blanks and matrix spike data for Grays harbor effluent samples collected in April and May 1987.

Semivolatile Surrogate Spike Recoveries.

Compound	Sample Identification							
	187451	187452	187453	187454	187455	187455Y	187455YJ	BN7127W
	%	%	%	%	%	%	%	%
2 fluorophenol	91	50	67	62	72	90	94	82
Phenol-d5	97	44	65	34	64	87	85	70
Nitrobenzene-d5	79	52	57	79	69	72	80	71
2-fluorobiphenyl	84	58	80	81	51	76	76	72
Pyrene-d10	103	66	86	81	99	84	89	85
Terphenyl-d14	65	68	110	79	88	91	103	109

Compound	197475	197476	197477	197478	197479	BN7131W	QA/QC
	%	%	%	%	%	%	Limits %
2 fluorophenol	58	53	55	↑	46	84	23-121
Phenol-d5	51	23	34	↓	23	68	15-103
Nitrobenzene-d5	70	45	73	↓	39	64	41-120
2 fluorobiphenyl	66	55	68	↓	66	67	44-119
Pyrene-d10	71	63	90	↓	88	80	--
Terphenyl-d14	43	70	104	↓	116	103	38-128

Resin Acid/Guaiacol Laboratory Blanks and Matrix Spike Analyses

CAS #	Compound	LAB BLANKS			MATRIX SPIKES			
		Units	SAMPLE ID 1874 - 27W 31W	Units	SAMPLE ID 1874 - 55Y 55YJ	Units	SAMPLE ID 1974 - 77Y 77YJ	
90-05-1	Guaiacol	ug/L	10u 10u	%	144 69	49 9		
	4,5,6 Trichloroguaiacol*	ug/L	10u 10u	%	138 145	-- 188		
944-31-6	Tetrachloroguaiacol*	ug/L	10u 10u	%	121 106	1 149		
4833-65-8	Retene	ug/L	10u 10u	%	90 95	183 117		
1686-62-0	Isopimaric Acid*	ug/L	20u 20u	%	88 82	2 107		
3513-69-7	Levopimaric Acid*	ug/L	20u 20u	%	-- --	13 --		
1235-74-1	Dehydroabietic Acid*	ug/L	10u 10u	%	94 90	4 145		
127-25-3	Abietic Acid*	ug/L	10u 10u	%	89 83	1 39		
3310-97-2	Neoabietic Acid*	ug/L	20u 20u	%	1 0.1	2 0.1		
	Dichlorodehydroabietic Acid*	ug/L	10u 10u	%	51 56	1 96		
2459-25-8	2-Napthoic Acid* (surrogate spike)	%	90 85	%	93 95	13 118		
	Sample pH	pH	-- --	pH	7.2 7.2	10 10		

\* Measured as the Methylene Ester  
 \*\* Sample Preserved at pH 10 at Time of Collection  
 Analyzed for Resin Acids/Guaiacols Only