ENVIRONMENT CANADA
CONSERVATION AND PROTECTION
ENVIRONMENTAL PROTECTION
PACIFIC AND YUKON REGION

ASSESSMENT OF STORM WATER RELATED CHLOROPHENOL RELEASES FROM WOOD PROTECTION FACILITIES IN BRITISH COLUMBIA

Regional Program Report 87-14

By

P.K. Krahn
J.A. Shrimpton
R.D. Glue

AUGUST 1987

ABSTRACT

This report documents the contamination of storm water runoff with chlorophenols leached from surface treated lumber in British Columbia. Storm water runoff from sawmills and lumber export terminals was suspected as a significant source of chlorophenols to adjacent water courses based on a 1978 Environment Canada Study. During 1986 and 1987, a four month field study was conducted at five sawmills and two lumber export terminals. The sites represented typical lumber handling and treatment methods including dip tanks, low pressure and high pressure spray systems. Leachate dripping directly from the wood and yard runoff was analyzed for 2,3,4,6-tetrachlorophenol and pentachlorophenol using a gas chromatography method.

It was found that leaching from treated lumber began after 1.0 to 1.5 mm of continuous rainfall. Dip treated lumber leached up to 158 000 parts per billion (ppb) and generated runoff with up to 6 600 ppb total chlorophenols. Low pressure sprayed lumber leached up to 576 000 ppb total chlorophenols. High pressure sprayed lumber leached up to 9 800 ppb and generated average yard runoff up to 1 968 ppb total chlorophenols. Chlorophenols were found to leach from treated lumber under all conditions of exposure to rainfall. Conditions studied included up to eight days of drying, 13 consecutive days of rainfall and 18 days of alternating wet and dry periods.

Most lumber storage yards have their own drainage systems which discharge directly to fresh or marine waters. Acute lethal static bioassay tests (LT_{50}'s) using rainbow trout underyearling were performed on two pure stormwater samples discharging from such yards. The fish became excited upon introduction to the effluent, exhibited coughing and erratic swimming within 10 minutes and mortality in all fish occurred within 40 to 120 minutes. The acute lethal toxicity for salmonids of 32 to 130 ppb total chlorophenols was exceeded virtually 100% of the time at all the storage yards monitored.

RÉSUMÉ

Ce rapport documente la contamination d'écoulement d'eau pluviale avec des chlorophénols lessivés de la surface de bois traité en Colombie-Britannique. L'écoulement des eaux pluviales provenant des scieries et des terminaux d'exportation de bois était une source significative suspectée de chlorophénols dans les cours d'eau adjacents basé sur une étude d'Environnement Canada en 1978. Pendant 1986 et 1987, une étude de quatre mois sur le terrain fut entreprise à cinq scieries et deux terminaux d'exportation de bois. Les sites représentaient une manutention typique du bois et des méthodes de traitement incluant des bassins de trempage de même que des systèmes de vaporisation à basse et haute pression. L'écoulement du lessivage dégouttant directement du bois et du site fut analysé pour le 2,3,4,6-tétrachlorophénol et pentachlorophénol utilisant une méthode de gaz chromatographique.

Il fut découvert que le lessivage du bois traité commencerait après une pluie continue de 1.0 à 1.5 mm. Le bois traité par trempage a lessivé jusqu'à 158 000 parties par milliard et a géneré des eaux d'ecoulement jusqu'à 6 600 parties par milliard en chlorophénols totaux. Le bois vaporisé à basse pression a lessivé jusqu'à 576 000 parties par milliard en chlorophénols totaux. Le bois vaporisé à haute pression a lessivé jusqu'à 9 800 parties par milliard et a généré un écoulement moyen du site jusqu' à 1 968 parties par milliard en chlorophénols totaux. Il fut découvert que les chlorophénols se lessivent du bois traité sous toutes les conditions d'exposition à la pluie. Les conditions étudiées comprennent jusqu' à huit jours sans précipitations, 13 jours consécutifs de pluie et 18 jours de périodes alternant entre sèches et mouillées.

Les dépôts d'entreposage de bois ont souvent leurs propres systèmes de drainage lesquels déversent directement dans les eaux fraîches ou marines. Des tests de bio-essai statique de toxicité aiguë létale (TL_{50}) utilisant des truites arc-en-ciel de moins d'un an furent conduits sur deux échantillons purs d'eaux d'écoulement provenant de tels dépôts. Les poissons devinrent excités à l'introduction de l'effluent, commencèrent à tousser et à nager erratiguement en moins de 10 minutes et tous les poissons furent morts entre 40 et 120 minutes. La toxicité létale aiguë pour les salmonidés de 32 à 130 parties par milliard en chlorophénols totaux fut dépassée pratiquement 100% du temps à tous les dépôts d'entreposage échantillonnés.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

EXECUTIVE SUMMARY

Introduction

Chlorophenol wood protection chemicals are a high priority for assessment and control in British Columbia because of their heavy usage, potential for release, high toxicity and persistance in the environment. Controlled laboratory studies of chlorophenols have established that acute toxicity (death within 96 hours) occurs at concentrations of 32 to 130 parts per billion (ppb) for juvenile salmon species (6). This is equivalent to 1 drop of pure chemical in 10 barrels (360 gallons) of water.

Background

Stormwater runoff from sawmills and lumber export terminals was suspected as a significant source of contamination based on findings in a 1978 Environment Canada study (4). In 1983 a joint government/industry report was developed to improve chemical handling, worker safety and environmental protection although the issue of protection from rainfall was left unresolved (6).

In late 1986 a field study was initiated by Environment Canada which measured the extent to which rainfall could be contaminated with chlorophenols leaching from treated lumber. The objectives of the study were to undertake a sampling program of stormwater monitoring and conduct chemical analysis to determine concentrations of 2,3,4,6-tetrachlorophenol (TTCP) and pentachlorophenol (PCP) in the runoff. Five sawmills and two lumber export terminals were chosen from 29 facilities in the lower Fraser Valley and they were monitored over a four month period from the end of October 1986 to the end of January 1987.

The sample sites were chosen to cover the full range of chemical application technology which included diptank treatment, low pressure spray (old techology) and high pressure spray (new technology). The effect of drying times were measured by monitoring lumber which was freshly treated and exposed directly to rainfall to lumber which had up to eight days of dry storage before exposure. The mills were located in areas where annual rainfall varied from 1094 mm (Vancouver Airport) to 1800 mm (Whonnock) and daily accumulation ranged from 3 mm to 60 mm.

Contaminated rainwater was collected in two types of samples; as leachate dripping from the lumber stacks before it reaches the paved yard surface, and as diluted yard runoff discharging to the storm sewer. The leachate was collected continuously in heat treated pyrex glass trays and transferred to amber glass bottles (to protect against ultraviolet light) while the yard runoff was collected directly as grab samples in amber glass bottles. All samples were stored at 4°C prior to analysis by a gas chromatography method.

At six of the sites, water quality parameters including total and suspended solids, total organic carbon, oil and grease, nitrogen, phosphorus and total metals were measured. During each sampling run, the temperature, dissolved oxygen content, pH and electrical conductivity of the runoff was continuously monitored. At two of the sites, static LT_{50} fish bioassays using rainbow trout were performed. The LT_{50} is the lethal toxicity time at which 50% of the test organisms die after continuous exposure to the undiluted effluent.

Dip Treated Lumber

Undiluted leachate from a stack of dip treated lumber was monitored for eight rainfall events over 13 days with a total precipitation of 239 mm (Figure 3). Samples were collected of leachate dripping from the exterior of the packages as well as percolating through the interior. Total chlorophenol concentrations reached 90 000 ppb on exterior drippings and 158 748 ppb on the interior drippings. After 12 days of continuous rainfall the concentrations were still above 8 000 ppb. Three drainage basins which stored dip treated lumber were monitored for one rain event and each site had already experienced from 7 mm to 23 mm of rainfall prior to the test. In these cases a significant proportion of the chemical may have already been washed off and the average total chlorophenol concentrations in yard runoff ranged from 258 ppb to 528 ppb with peaks as high as 6 624 ppb (Figures 4, 5, 6).

Low Pressure Sprayed Lumber

Lumber which was treated by low pressure spray systems (old spray technology) was monitored over various drying times ranging from zero to eight days after treatment. Lumber which had zero fixation time experienced direct washoff and total chlorophenol concentrations of up to 576 000 ppb were found in water dripping from the wood. Direct washoff would occur at the green chain sorting line where the lumber was pulled from the covered conveyor and piled in stacks outside the roofed area. In some cases there were no rain gutters so that roof runoff was directed onto the freshly treated wood in addition to direct rainfall. The yard runoff from such sites had average total chlorophenol concentrations of up to 27 542 ppb which were the highest of any situation monitored (Figure 8). The three mills where this type of runoff was observed were situated on the shores of the Fraser River and discharged their runoff directly to near shore surface zones.

Low pressure spray treated lumber which had up to eight days of drying after treatment had total chlorophenol concentrations of up to 15 910 ppb dripping from the wood. Yard runoff from the sites averaged up to 545 ppb total chlorophenols (Figure 13). These samples were taken from a yard which had 1/3 to 1/2 of the total lumber capacity in it and higher lumber loading would likely increase the concentrations in the runoff.

High Pressure Sprayed Lumber

High pressure spray systems (new spray technology) operate at over two atmospheres of pressure and produce lumber which is almost dry to the touch immediately after treatment. All the sites monitored contained lumber which was rough cut and unplaned which resulted in a much higher surface area per board than in any of the other situations. The average total chlorophenol concentration in water dripping from this type of wood was 9 829 ppb and storage yard runoff from these sites averaged up to 1 968 ppb (Figure 20).

Total Runoff and Loading Estimates

Whenever there was measurable rainfall at a treated lumber storage yard there were measurable chlorophenols in the runoff. Rainfall intensities and durations were a significant factor with higher intensities and longer durations increasing the quantities of chlorophenols leached. It was found that rainwater dripping from the wood after the end of a rain event would dry on the yard surface and then be washed in a concentrated form down the storm drain at the start of the next storm. The way the lumber is cut, strapped and stacked on the yard also affected the quantity of chemical leached, and it was found that leaching from the tops and sides of the packages occurs within 1.0 to 1.5 mm of continuous rainfall.

The annual total runoff generated at lumber storage yards on the lower Fraser River from Kanaka Creek to the mouth was estimated at 490 000 to 775 800 m^3/year with total chemical loading up to 916 kg/yr of pure chlorophenol. The annual runoff volume to Burrard Inlet was estimated at 511 000 to 850 000 m^3/yr which contains up to 523 kg/yr of pure chlorophenols. Runoff to Howe Sound at Squamish was estimated at 165 000 to 261 000 m^3/yr with up to 85 kg/yr of pure chemical.

Many of the treated lumber storage yards drainage systems are not cross connected with other systems and will discharge directly to the surface and near shore areas of rivers and marine waters. The lower Fraser River is affected by tidal action which will block these drains for up to 12 hours and cause rainwater to back up in the drainage systems and sometimes pool on the yard. The discharge of a pool of rainwater (contaminated with 1 200 ppb of chlorophenols) to the Fraser River during an ebb tide was simulated using a computer generated model (Figure 22). The simulation estimated that a plume at a concentration of 100 ppb (which is toxic to fish) could extend up to 12 m from shore and up to 60 m downstream. Elevated shoreline chlorophenol concentrations of 10.0 - 15.0 ppb in Fraser River water were measured approximately 200 m downstream of a large outfall after a storm event such as the one simulated (1).

Fish Bioassays

Acute lethal static bioassays (LT_{50}'s) were performed at the Environmental Protection Bioassay Laboratory by placing juvenile rainbow trout in tanks filled with pure stormwater effluent. The fish became excited upon introduction to the effluent, were exhibiting coughing responses within 5 minutes, followed by erratic swimming after 10 minutes. After 20 minutes they had lost equilibrium, exhibited irregular gill movement and were unresponsive to touch. The test is designed to last for up to 96 hours, however death of all the test specimens occured within 40 to 120 minutes. General water quality analysis performed on the bioassay samples and other samples indicate that the majority of the parameters were within acceptable levels. Aluminum, iron and silicon were elevated in one of the bioassay samples and may have had a minor contribution to its toxicity.

Rainfall occurs year round in the British Columbia coastal regions with 6-7 days of precipitation averaging 6 mm/day occuring during July which is the dryest month (Figure 23, 24). This is sufficent rainfall to produce the type of runoff discussed earlier. The direct affect such discharges have on resident, migratory fish, and other aquatic organisms has not been documented. Migratory juveniles such as salmon, steelhead trout and eulachons are most likely to be affected during the downstream migration in late February through June which occurs in most of the coastal rivers, especially the Fraser. Resident fish species are likely to receive a continuous input of chlorophenols. It is conceivable that fish kills of juveniles could occur in the aftermath of a significant storm event and that these kills would go undetected because the small fish are not highly visible and could be washed away or eaten by other fish and birds.

CONCLUSIONS

Based on the data collected and the observations made during the 1986/1987 study of storm water runoff from five saw mills and two lumber export terminals it can be concluded that:

1. The levels of chlorophenols in mill runoff is dependent upon the following parameters:

    1. Initial chemical formulation;
    2. Treatment application method;
    3. Lumber cut (rough vs planed);
    4. Lumber packaging and stacking;
    5. Lumber drying time;
    6. Rainfall intensity and duration;
    7. Amount of treated lumber on site;
    8. Normal vs abnormal operations (i.e. has the lumber been cut or treated properly); and
    9. General housekeeping practices.

2. Chlorophenols will leach from treated lumber under all conditions of exposure to rainfall. This includes up to eight days of drying, 13 consecutive days of rainfall and 18 days of alternating wet and dry periods. The highest concentrations were measured in rainwater dripping directly from the lumber packages before further dilution occurred on the paved storage yard. The wood exposed to rainfall for the first time, ranged from 8 816 ppb to 576 000 ppb. The average concentrations in surface runoff draining from the lumber storage yards was found to range from 180 to 27 500 ppb total chlorophenols. These concentrations were in the same order of magnitude as those found in simulated rainfall studies conducted by Forintek Canada Corporation.

3. Total annual loading of chlorophenols to the environment can be

estimated using the local average total precipitation, storage yard area and average concentration of chlorophenols in yard runoff for the specific lumber storage conditions.

4. Stormwater runoff from storage yards containing chlorophenate treated lumber can be acutely toxic to fish. Acute lethal static fish bioassays of pure stormwater runoff resulted in 100% mortality within 40 to 120 minutes.

5. The acute lethal toxicity (96 hr LC_{50}) range of 32 to 130 ppb for salmonids was exceeded virtually 100% of the time at all the storage yards monitored.

6. Storm water runoff from wood protection mills contains a complex mixture of contaminants. The concentrations of the majority of these contaminants lie within acceptable ranges and would not be expected to pose a threat to the receiving environment. Elevated concentrations of specific metals occurred infrequently and therefore do not constitute cause for concern. The chlorophenol component of the wood protection stormwater effluent is of primary concern.

7. The alkaline buffers used to maintain the chlorophenate in solution before application to lumber may buffer the acidic reaction at the lumber interface after application thereby inhibiting the fixation of the chlorophenols to the wood surface.

8. The leaching of chlorophenols may be reduced by alternate or additional forms of protection which include:

   - wrapping of treated lumber with water resistant papers or plastic;
   - total coverage of treated lumber;
   - use of kiln drying in place of chlorophenols;
   - coating with wax or polymer sealing films;
   - alternative chemicals with low leachability;
   - treatment of contaminated runoff;
   - combinations of the above.

1 INTRODUCTION

Chlorophenol wood protection chemicals are a high priority for assessment and control in British Columbia because of their toxicity, large quantities used and potential for environmental releases. Stormwater runoff from saw mills and lumber export terminals was suspected as a significant source of contamination based on findings recorded in a 1978 Environment Canada study of chlorophenol contamination in receiving water adjacent to mill sites.

In 1984, a joint Environment Canada/B.C. Ministry of the Environment/B.C. Forest Industry report entitled "Chlorophenate Wood Protection, Recommendations for Design and Operation", (or "Code of Practice") was developed to improve chemical handling techniques, worker safety and environmental protection.

A recommendation for covered final storage of chlorophenol treated lumber was not included in the Code due to insufficient data available at that time. An interim recommendation of 1/2 hour covered drip time plus two hours of covered fixation time was included in the Code until leaching data was available.

The Code was distributed to the B.C. forest industry mills in 1984 and a one year period was adopted for voluntary implementation of the technical recommendations. The mills were monitored for compliance with the code recommendations by using a mill survey questionaire. The 1984 compliance assessment survey report (7) estimated that "most mills had installed containment and recycle systems in mix rooms, on spray units and in dip tank drip areas. Most chemical storage areas were also contained and covered. However, many dip tanks and lumber drip areas were uncovered and few mills provided covered final storage for their treated lumber.

In 1984 Environment Canada commissioned Forintek Canada Corp to perform a laboratory leaching study on chlorophenate treated lumber (5). The study found that the treated lumber stacks have an absorptive capacity and leaching from a lumber package did not occur before 20 minutes (for freshly dipped) to 3 hours (for sprayed lumber) after a simulated rainfall of 50 - 80 mm/day began. This was 7 to 10 times the average rainfall intensity expected during the study period.

A field study by Environment Canada was initiated in late 1986 to determine the degree of chlorophenol leaching from treated wood and contamination of stormwater runoff.

1.1 Objectives and Criteria

The objectives of the "stormwater leaching study" were:

1. To undertake a sampling program to determine chlorophenol concentrations in storm water at 10 sawmills/export terminals using sodium tetra/pentachlorophenate.
2. To conduct chemical analysis on the water samples to determine concentrations of 2,3,4,6-tetrachlorophenol (TTCP) and pentachlorophenol (PCP).

Locations for the storm water study were selected according to the following criteria:

1. Environmental sensitivity of mill location;
2. Release problems associated with the site;
3. Deficiency of containment technology on the site;
4. Past problems associated with the site;
5. Treatment technology (to cover the full range of oldest to newest including dip tanks, low pressure spray and high pressure spray systems) and
6. The forms of packaging were to include; rough cut loose packages and; planed, strapped and end sealed packages.

1.2 Number of Mills in the Region

The 1986 Environment Canada, Compliance Assessment Report on Wood Protection (anti-sapstain) Facilities in British Columbia identified 100 wood protection locations (7). Seventy-seven plants (sawmills and export terminals) reported the use of chlorophenols.

Based on the criteria in the code-of-practice and information in the assessment report, 31 wood protection sites were identified in the lower Fraser River, Burrard Inlet and Howe Sound area. Of these, 15 were surveyed to meet the criteria for the stormwater study. Ten sites were selected for the study and five lumber mills and two export terminals were eventually monitored (Figure 1). The monitoring occurred over a four month period from the end of October 1986 to the end of January 1987.

1.3 Technology of Chemical Application

There are three variations of chlorophenate application technology used in the forest industry, dip treatment, low pressure, and high pressure spray application. (For detailed descriptions see reference #6.)

1.3.1 Dip Tanks.

Dip treatment involves a batch system where a package of lumber is either carried into a tank filled with treatment solution by a lumber straddle carrier or lowered into a tank by a hydraulic fork lift system. In-line dipping during lumber production is achieved by using rollers to depress lumber into a chemical solution tank on a production sorting chain.

In all cases the lumber is saturated and wet to the touch after processing and is usually allowed to drip on a pad to remove excess solution. Drip times ranged from ½ hour to 24 hours for the study mills.

1.3.2 Low Pressure and High Pressure Spray Systems.

Spray systems provide continuous in-line treatment of individual pieces of rough and planed lumber in the production mill. The lumber is passed through the spray box longitudinally or transversly as rough cut in the sawmill or dimensioned lumber in the planer mill. Low pressure sprayed lumber is generally found in older mills and many of the boxes are custom made by sawmill millwrights. The spray has a large droplet size and the lumber feels wet to the touch after exiting the spray box.

High pressure spray boxes are used in longitudinal or transverse systems. The nozzles have very small orifices (several thousandths of an inch) and produce a very fine mist. Lumber exiting the box does not feel wet to touch after exiting the spray box.

1.4 Treated Lumber Storage

The covered storage of treated lumber ranged from zero to 24 hours

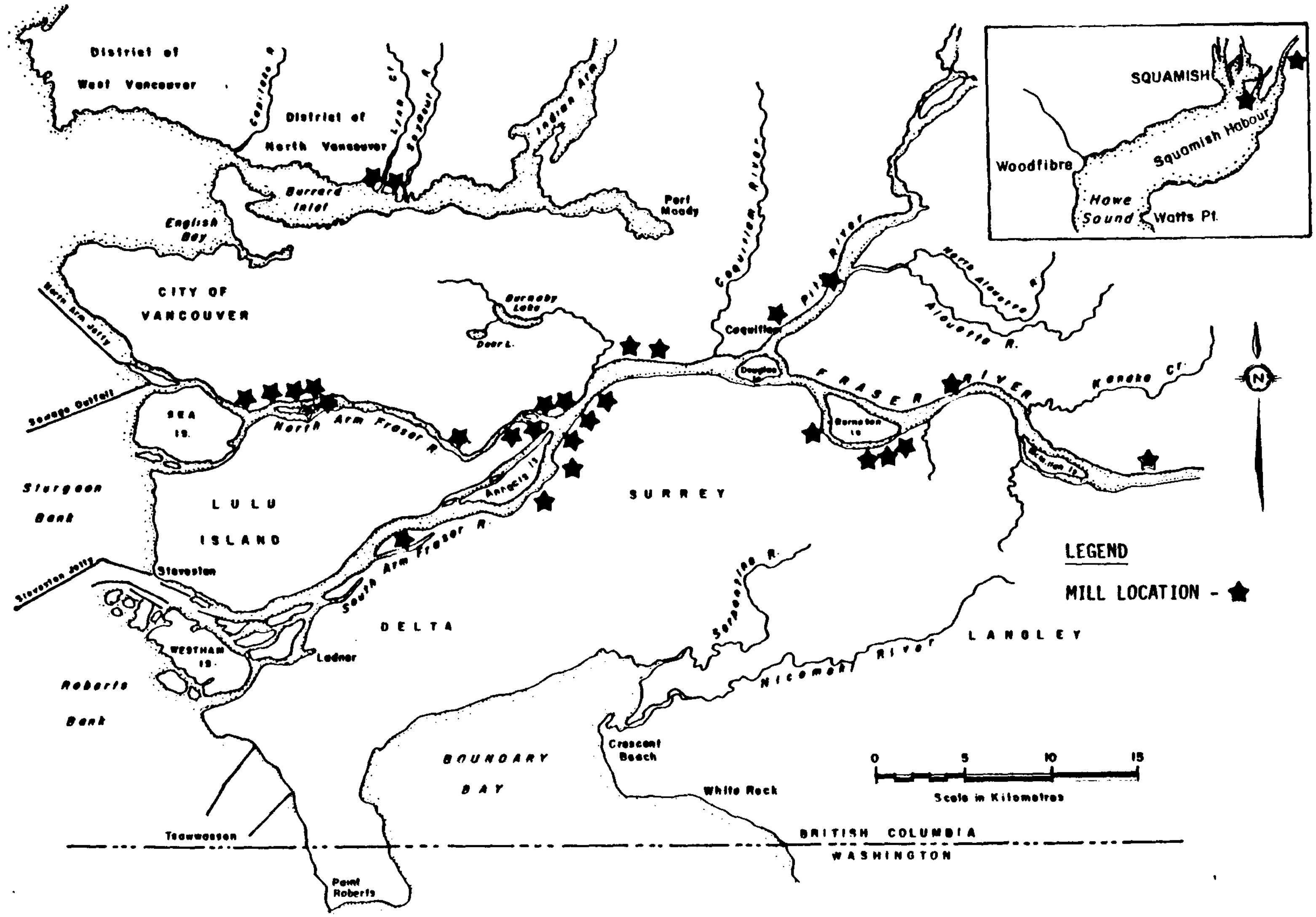


FIGURE I LOCATION OF SAWMILLS AND LUMBER EXPORT TERMINALS IN THE LOWER MAINLAND USING CHLOROPHENATE ANTI-SAPSTAIN CHEMICALS and in most cases was ½ to 2 hours long. In many cases rough cut lumber is treated, piled as unstrapped packages 1.0 m high x 1.1 m wide and stacked three packages high. The lumber is then stored on the yard for up to three months depending on the grade and market after which it is moved to the planer mill for dimensioning. A second treatment is applied after planing and the lumber is cut to length, packaged by tightly wrapping with two to three metal straps and end sealed with a colored paint. These packages are then moved to a storage yard and stacked three to seven packages high to await shipment. The second storage time may also be up to three months or more depending on the grade and market conditions.

The lumber is then shipped to export terminals or United States destinations by rail, truck, barge or ship and may experience a waiting period of several months to one year on the terminal yards. Lumber storage at the terminal was generally four to seven packages high.

1.5 Total Annual Precipitation: 30 Year Average Values

Precipitation is monitored by the Atmospheric Environment Service of Environment Canada at numerous stations in the province. For most stations the precipitation is recorded in hourly intervals and total accumulations are reported in daily, monthly and annual totals. In general the average station has statistical data based on 30 years of observations. Total precipitation is highly variable over the province and even in relatively small geographical regions within the same city. Proximity to water bodies and land elevations are predominant factors. Annual 50th percentile precipitation values in the study area ranged from 1 094 mm at Vancouver International Airport to 2 222 mm at Squamish. Table 1 lists the statistical records for the major stations in the study areas as well as other major centers in B.C.

1.5.1 Rainfall Frequency and Intensity. Table 2 lists rainfall frequencies, accumulations and storm intensity probabilities for the two extreme ranges within the study area. These numbers are based on 30 year averages and they indicate that six to seven days of measurable rainfall over 5-7 mm per event can be experienced during the dryest month of July

TABLE 1 **TOTAL ANNUAL PRECIPITATION IN BRITISH COLUMBIA: 30 YEAR VALUES (mm) (22)**

SITE	STUDY AREA						
	VANCOUVER AIRPORT	BURNABY EAST	NEW WESTMINSTER	WHONNOCK 269 ST.	NORTH VAN. 2ND NARROWS	SQUAMISH	PORT ALBERNI
PERCENTILE							
95% <	1 360	-	1 846	-	2 223	-	2 401
75% <	1 173	-	1 603	2 003	2 022	2 505	2 074
50% <	1 094	1 425	1 501	1 923	1 778	2 222	1 881
25% <	998	-	1 291	1 670	1 657	2 064	1 517
5% <	798	-	1 096	-	1 339	-	1 155
MEAN	1 113	1 455	1 577	1 835	1 826	2 269	1 891
S.D.	157	-	230	204	243	244	318

SITE	VICTORIA AIRPORT	NANAIMO DEPARTURE BAY	PORT HARDY	PRINCE RUPERT	PRINCE GEORGE	FORT NELSON	KAMLOOPS	PRINCETON	HOPE
PERCENTILE									
95%<	1 081	1 149	2 313	3 089	769	616	356	510	2 376
75%<	988	1 000	1 921	2 643	649	498	295	392	1 900
50%<	868	926	1 727	2 391	534	430	255	362	1 662
25%<	768	838	1 562	2 195	441	381	216	288	1 527
5%<	596	679	1 389	1 845	371	317	178	225	1 100
MEAN	873	945	1 783	2 432	-	452	251	345	1 716
S.D.	134	152	271	245	-	85	58	70	347

- = No Value
*S.D. = Standard Deviation

Note: "95%<", means that 95% of the annual totals will be less than the given value indicating that contaminated runoff is a year round problem.

Storm intensity probabilities indicate total rainfall accumulation of 44.2 mm to 78.7 mm/day are possible. These events have caused flooding problems at the treatment sites and storage yards, as well as creating large quantities of runoff.

TABLE 2 STORM WATER CRITERIA: RAINFALL FREQUENCY AND INTENSITY

MONTH	MEASURABLE RAINFALL (days/month)	AVERAGE RAINFALL (mm/day)	MONTHLY AVERAGE RAINFALL (mm/month)
Vancouver Airport			
September	10.0	6.71	67.1
October	15.0	7.6	114.0
November	18.0	8.3	150.1
December	21.0	8.7	182.4
January	20.0	7.7	153.8
February	16.0	7.2	114.7
March	16.0	6.3	101.0
April	13.0	4.6	59.6
May	10.0	5.2	51.6
June	10.0	4.5	45.2
July	6.0	5.3	32.0
August	8.0	5.1	41.1
ANNUAL TOTAL	163.0		1 112.0

CONTINUED...

TABLE 2 **(Continued)**

MONTH	MEASURABLE RAINFALL (days/month)	AVERAGE RAINFALL (mm/day)	MONTHLY AVERAGE RAINFALL (mm/month)
Squamish			
September	12.0	10.6	127.0
October	15.0	20.1	301.3
November	18.0	17.5	314.4
December	21.0	16.6	347.8
January	19.0	16.5	313.2
February	16.0	14.6	234.3
March	15.0	12.6	188.9
April	13.0	11.5	149.1
May	11.0	7.1	77.2
June	10.0	6.9	68.5
July	7.0	7.5	52.3
August	8.0	9.1	73.0
ANNUAL TOTAL	165.0		2 247.0

STORM INTENSITY PROBABILITIES
Vancouver Airport
1 day cumulative rainfall of 44.2 mm every 2 years
2 days cumulative rainfall of 60.6 mm every 2 years
3 days cumulative rainfall of 70.1 mm every 2 years
Squamish
1 day cumulative rainfall of 78.7 mm every 2 years
2 days cumulative rainfall of 116.4 mm every 2 years
3 days cumulative rainfall of 152.5 mm every 2 years

2 SAMPLING PROCEDURES

Drainage basin markings on lumber storage yards were often obsolete due to the settling of the pavement after several years of use. The sample sites were surveyed using a level and transit to establish true elevation, basin size and lumber content.

Initial plans to use automatic samplers were abandoned due to the combination of the risk of cross contamination, difficulty of secure storage in an active production area and lack of power supplies. All chlorophenol and water quality samples were collected as manual grabs.

2.1 Sampling of Undiluted Leachate for Chlorophenols

Leachate dripping from treated lumber was collected in heat treated, pesticide analysis grade, pyrex glass trays prior to further dilution on the mill yard. The trays were inserted between the spaces used to separate the lumber stacks. The samples were collected as a continuous composite of which a 1 L aliquot was taken whenever there was sufficient volume.

2.2 Yard Runoff Flow Measurement

Sandbags wrapped in polyethylene bags were used to form a dam around the manhole and direct all flow to one location (Figure 2). During most storm events the water would migrate in a particular low channel in the basin to the manhole and only during short periods of high intensity rainfall did runoff flood the sand bags.

A calibrated bucket was used to monitor flow whereby time to fill a standard 15 L volume was measured using a stop watch. Since all flow was directed to one area the total flow could be collected. A minimum of three determinations of the flow rate were used to calculate each recorded measurement (Figure 2).

2.3 Sampling of Yard Runoff for Chlorophenols

All samples were collected in 1.0 litre amber glass pesticide analysis grade bottles with foil lined lids (Figure 2). The samples were collected manually by moving the bottles back and forth across the runoff flow until the desired volume was collected. Sampling frequency was adjusted to reflect significant changes in site activity and storm intensity. In general, when a rapid change in activity or storm intensity occurred sampling frequency was increased. At the start of a storm event an initial 1.0 L grab was taken of the runoff followed by one hour of 15 minute composites. The 15 minute composites were made up of 2x7.5 minute grabs of 500 mls each. Depending on the progression of the storm intensity and site activity the 15 minute composites were extended to ½ hour composites of 2x15 minutes 500 ml grabs. (This was the sampling regime used most often). The ½ hour composites would then be extended to one hour composites made of 4-15 minute grabs of 250 mls. The longest composite time was four hours made up of 4-1 hour grabs of 250 ml volumes.

After sampling, the bottles were stored in coolers and delivered to the laboratory within 12 to 20 hours for storage and analysis. All samples were kept at 4^{o}C after collection.

2.3.1 Analysis of Yard Runoff for Chlorophenols. Chlorinated phenols were determined by using an extraction procedure followed by derivatization and then quantification by gas chromatography using an electron capture detector (Appendix I, Appendix II). An internal quality control program by the contract laboratory (Appendix II) and an external quality control program by the West Vancouver Laboratory Services - Environmental Protection (EP Lab) was carried out using blanks, spiked samples and split duplicates of field samples (Appendix III).

2.4 Sampling of Yard Runoff for Other Water Quality Parameters

Storm water effluent samples were collected for water quality analyses from six of the seven mills monitored. No samples were collected from Mill #3.

As with the sample collection for chlorophenol analysis, sampling for other water quality parameters began at "first flush" with 7.5 minute intervals combined as 15 minute composites for the first three hours. Thereafter, the storm water effluent was sampled at 15 minute intervals combined as hourly composites. Some variation in sampling frequency occurred as a result of storm characteristics.

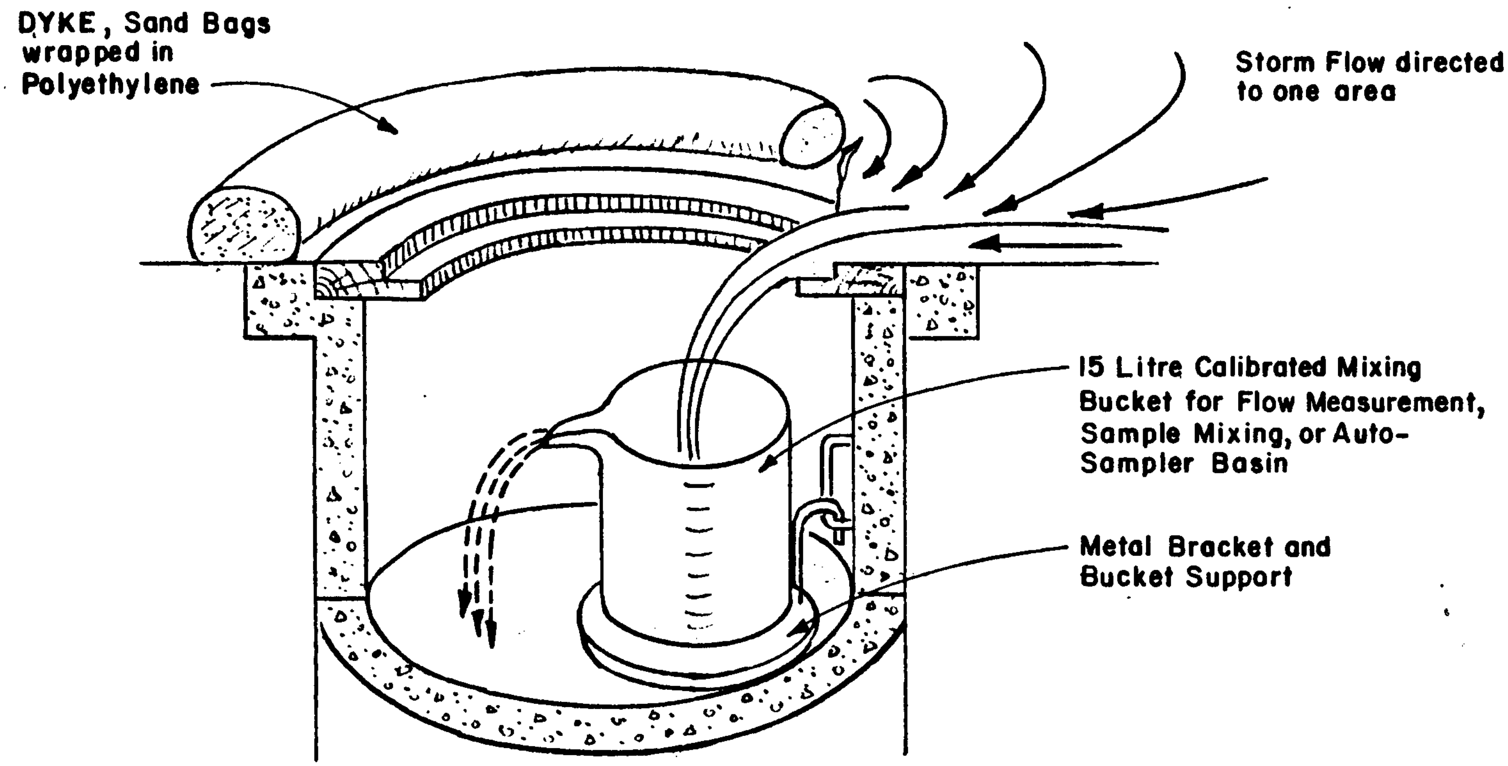


FIGURE 2 DIAGRAM OF MANHOLE SAMPLING APPARATUS

Samples collected for total and suspended solids, total organic carbon, oil and grease, nitrogen (as NO_2, NO_3 and NH_3), phosphorous and metals were collected, preserved and stored for analysis in accordance with the methodology outlined in the Environment Canada Laboratory Manual (20). Laboratory analyses were performed either by CanTest Laboratories Limited or the EP Laboratory.

2.5 Sampling of Yard Runoff for Fish Bioassays

Two acute lethal static fish bioassay tests (LT_{50}*) were performed using undiluted yard runoff collected at mills #4 and #6. Grab samples were collected in one litre, amber glass bottles each time a runoff sample was collected for chlorophenol analysis. The bioassay grabs were composited in two 12.5 L heat treated glass jars. The composite samples were stored in the dark at 4°C and the bioassays were performed within 36 hours of sample collection.

2.6 Physical Water Quality Measurements

Water temperature, dissolved oxygen, pH and conductivity measurements were made in the field using a Hydrolab Surveyor II *in situ* water quality analyzer with field data logger (Model 5100-A). Visual observations of dirt, turbidity, color, oil films and flow were also recorded in the following format.

*LT_{50} is the Lethal Toxicity time at which 50% of the test organisms die after continuous exposure to the undiluted effluent.

Water Quality and Flow Measurements

Note the presence of oil films, dirt, turbidity, color, flow, pH, conductivity, temperature, dissolved oxygen. Maximum interval of 1 hour.

Start Time ________________

	Flow Time to Fill 15 l seconds	Flow l/s	pH	Conductivity	Temperature °C	Dissolved Oxygen mg/l
0.00 hr						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						

Comments ____

2.7 Recording Weather Conditions and Total Precipitation

Storm conditions and total precipitation were recorded in the following format.

Weather Conditions

Duration of rainfall conditions, i.e. specify the intensity at a maximum one hour interval corresponding to sampling times: i.e. fog, drizzle, steady rain, down pour and cumulative rain gauge reading in mm.

	Intensity	mm		Intensity	mm
0 hr			13 hr		
1 hr			14 hr		
2 hr			15 hr		
3 hr			16 hr		
4 hr			17 hr		
5 hr			18 hr		
6 hr			19 hr		
7 hr			20 hr		
8 hr			21 hr		
9 hr			22 hr		
10 hr			23 hr		
11 hr			24 hr		
12 hr					

Comments ____

2.8 Recording Site Activity

The following observations were recorded at all sites at all storm events.

Industrial Activity: Mill ______________________

Date ______________________

- Type of Lumber produced

  rough ☐ , planed ☐ , packaged ☐ , end sealed ☐ , other ______________

- Treatment Method: Brand of Chlorophenate ______________

  sprayed high pressure ☐, sprayed low pressure ☐, drive-in dip ☐, chain dipped ☐

  hydraulic dip ☐, cross chain spray? or dip? ☐, longitudinal spray ☐

- Drip Time ______________________
- Covered Storage Time ______________________
- Volume of Wood in the Storage Basin ______________ m^3
- Lumber dimensions: length ______________ m
- height ______________ m

  width ______________ m
- Lumber Package dimensions: length ______________ m

  height ______________ m

  width ______________ m
- Height of Lumber Stacks or Number of Packages per Stack ______________
- Drainage Basin Area __________ m x __________ m (or sketch on back page)
- Comments (Identify all sources of chlorophenates which may discharge to the catch basin .

  ____

  ____

  ____

3 DIP TREATED LUMBER

Hydraulically dipped lumber was monitored under a variety of conditions including:

- Leachate dripping directly from planed lumber before further dilution by rainfall combined with drying times after treatment varying from zero to 24 hours.
- Runoff from the mill yard containing wood which was rough cut, unstrapped and had greater than 24 hours drying time after treatment.
- Runoff from mill yards containing wood which was planed, strapped and end sealed and had greater than 24 hours drying time.

3.1 Dipped Lumber (Planed), Undiluted Leachate, Mill #2, November 13-20, 1986

Undiluted leachate from a specific lumber stack was monitored for eight rainfall events over 13 days with a total precipitation of 239 mm (Figure 3A). Samples were taken of leachate running off the exterior of the lumber package as well as percolating through the interior (Figure 3).

Exterior leachate ranged from 698 ppb to 90 000 ppb with an average value of 50 288 ppb total chlorophenols. The low values occurred before the lumber stacks became saturated. Interior leachate ranged from 5 854 to 158 748 ppb averaging 54 000 ppb total chlorophenols (Figure 3B).

The packages were freshly dipped and stored in a drainage area for 24 hours prior to the test. A fresh bundle of lumber was added to the test stack on November 19. Figure 3B shows the trends in leaching over time.

The total exterior concentrations peak first as a result of the wetting of exterior surfaces. These concentrations show a rapid decline with time as the quantity of easily leachable chemical decreases.

The total interior concentrations peak several days later as time is required for the lumber package to saturate. The interior concentrations are much higher which may be attributed to several factors including liquids entrained between the tightly packed lumber surfaces and the longer surface contact time as the water percolates through the stack. These concentrations are several orders of magnitude greater than the LC_{50} for salmonids.

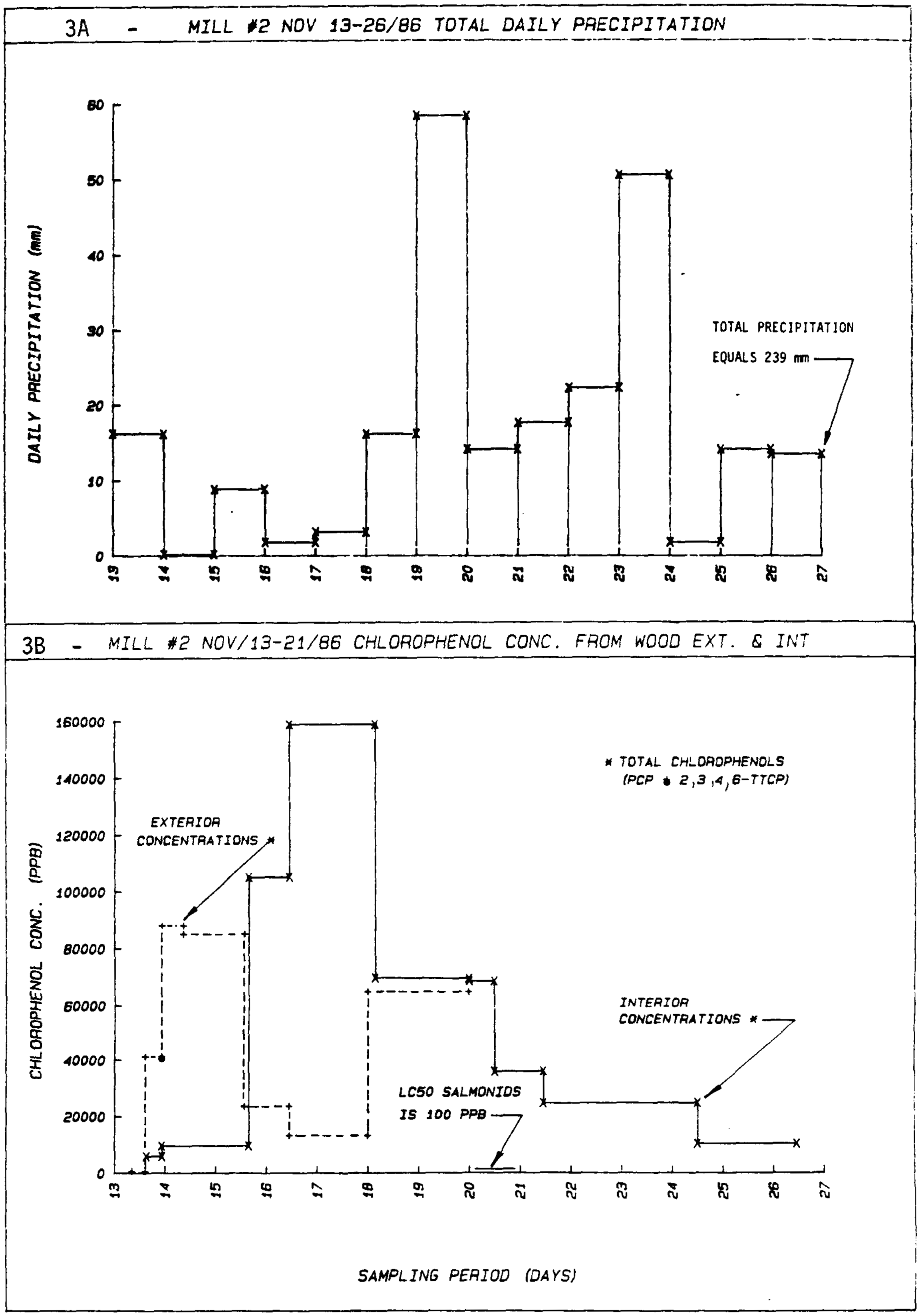


FIGURE 3 MILL #2, NOVEMBER 13 - 26, 1986 MONITORING OF UNDILUTED LEACHATE FROM DIPPED LUMBER.

TABLE 3 **AVERAGE CONCENTRATIONS OF CHLOROPHENATES LEACHING DIRECTLY FROM TREATED LUMBER BEFORE DILUTION ON THE MILL YARD**

LUMBER TREATMENT	INTERIOR DRIP (PPB)				EXTERIOR DRIP (PPB)			
	n	$\bar{x}$ (TTCP)	$\bar{x}$ (PCP)	$\bar{x}$ (TOTAL)	n	$\bar{x}$ (TTCP)	$\bar{x}$ (PCP)	$\bar{x}$ (TOTAL)
Dipped Lumber, Leachate	10	20 123	35 854	55 977	17	9 800	22 502	32 302
Low Pressure Spray (Washoff)				ND	3	96 409	78 063	174 472
Low Pressure Spray, Leachate	2	4 843	3 973	8 816	6	3 210	36 697	39 907
High Pressure Spray, Leachate				ND	21	5 899	3 930	9 829

ND = No Data Collected

Table 3 indicates that the total concentration of chlorophenol averaged 55 977 ppb in interior package drippings and 32 302 ppb in exterior package drippings.

3.2 Dipped Lumber - Rough Cut, Unstrapped - Yard Runoff - Mill #4 - Drain 1 - December 20, 1986

The storage area for dipped lumber at mill #4 was co-monitored with the area used for spray treated lumber. During the monitoring period no lumber was added or removed from the site. There was no specific runoff collection basin and surface slopes were such that runoff could flow to the perimeter of the site. Primary drainage occurs at two locations and samples were taken at site TD1 (Figure 4).

3.2.1 Precipitation, Flow, Concentration and Loading. Precipitation was continuous, moderate to heavy throughout the test period with a total accumulation of 15.0 mm (Figure 4A).

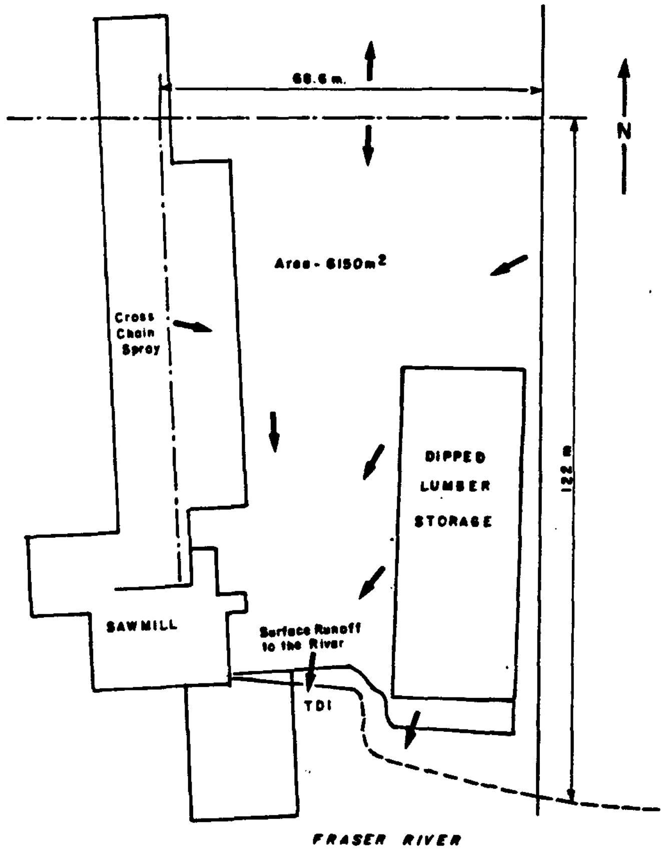
Flow rate was difficult to measure because the discharge was nonspecific. Some small barriers were set up to direct the major portion of the flow for measurement. Flow fluctuations did correlate directly with rainfall patterns (Figure 4A vs. 4B).

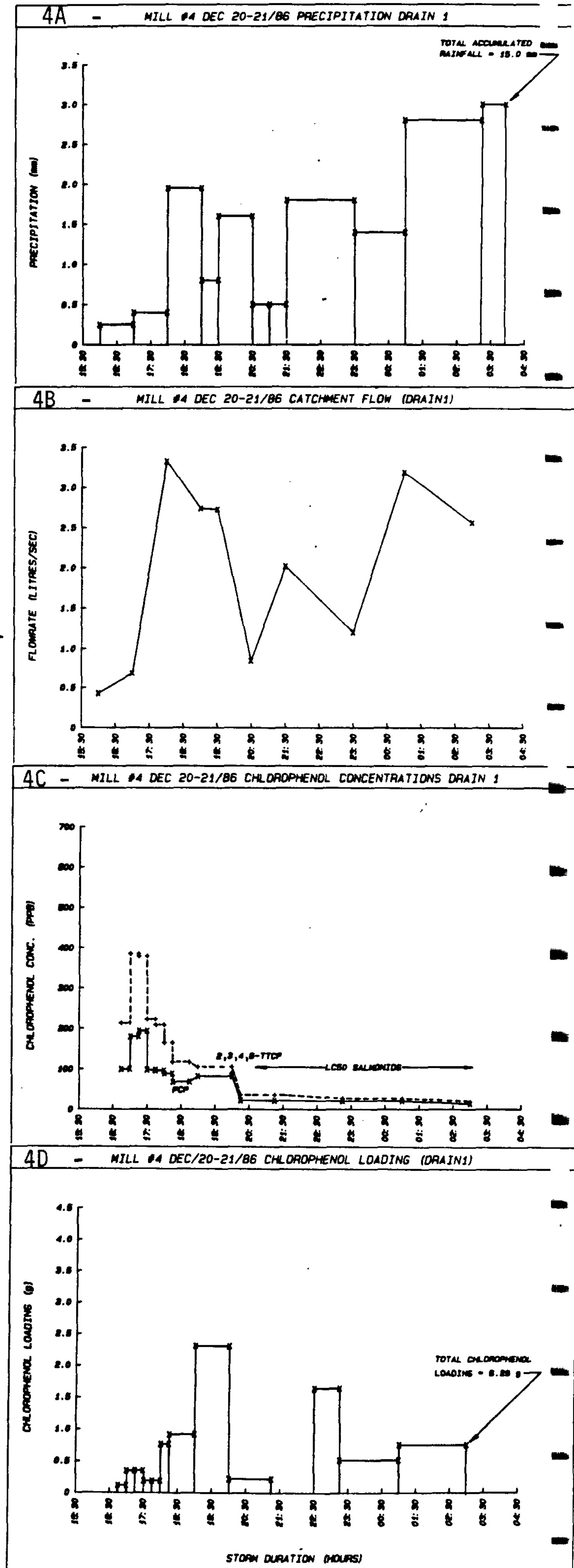
The lumber in the drainage basin had an undetermined mixture of storage times and had experienced an unspecified quantity of rainfall. No freshly dipped lumber had been added to the drainage basin for several days.

Chlorophenol concentrations were generally lower than expected, however the nonspecific flow pattern and previous rainfall may have been the major cause. Total concentrations averaged 1X-2X the LC_{50} for salmonids (Figure 4C). Loading was significant at 8.28 grams for the test period and is expected to be higher under conditions where freshly treated lumber is stored and all the runoff discharged to one location (Figure 4D).

3.3 Dipped Lumber (Planed, Strapped and End Sealed), Yard Runoff

The runoff from catchment basins containing lumber which had been planed, strapped, end sealed and then dip treated was monitored at two sites. Each site had greater than 24 hours of drying time before exposure to rainfall.





<u>LUMBER TREATMENT AND HANDLING VARIABLES</u>

1) <u>APPLICATION METHOD</u>		
	ROUGH CUT	HYDRAULIC DIP : 4850 ppm TETRA WITH DIATOX 1920 ppm PENTA
2) <u>LUMBER TYPE</u>		70% HEMLOCK/ 30% FIR
3) <u>PACKAGING</u>		
	LOOSE PACKAGES LUMBER DIMENSIONS	0.025 m x 0.102 m (1" x 4")
	PACKAGE DIMENSIONS	1.02 m x 1.02 m (40" x 40")
4) <u>FINAL TREATMENT DATE</u>		VARIOUS
5) <u>DRYING TIME</u>		SEVERAL HOURS TO DAYS, LUMBER IS TREATED BY HYDRAULIC DIPPING AND ALLOWED TO DRIP ABOVE THE TANK FOR ONE HOUR. THE LUMBER HAS BEEN OBSERVED TO BE STILL DRIPPING WHILE BEING TRANSPORTED TO THE YARD.
6) <u>SITE OBSERVATIONS</u>		
		DURING THE MONITORING PERIOD NO LUMBER WAS ADDED OR REMOVED FROM THE SITE. THERE IS NO SPECIFIC DRAINAGE PATTERN ON THE SITE AND RUNOFF DISCHARGES DIRECTLY TO THE SURFACE OF THE FRASER RIVER AT SEVERAL SITES. FOR THIS REASON. DILUTION FACTORS CAN NOT MATCH THE RAINFALL PATTERN.
7) <u>LUMBER LOADING</u>		20.4 BOARD FEET/SQUARE METER.
8) <u>TOTAL FLOW VOLUME</u>		92 250 l (20 319 gal)
9) <u>AVERAGE CONCENTRATIONS</u>		88 ppb PENTA-CHLOROPHENOL <u>171 ppb TETRA-CHLOROPHENOL</u> 258 ppb TOTAL

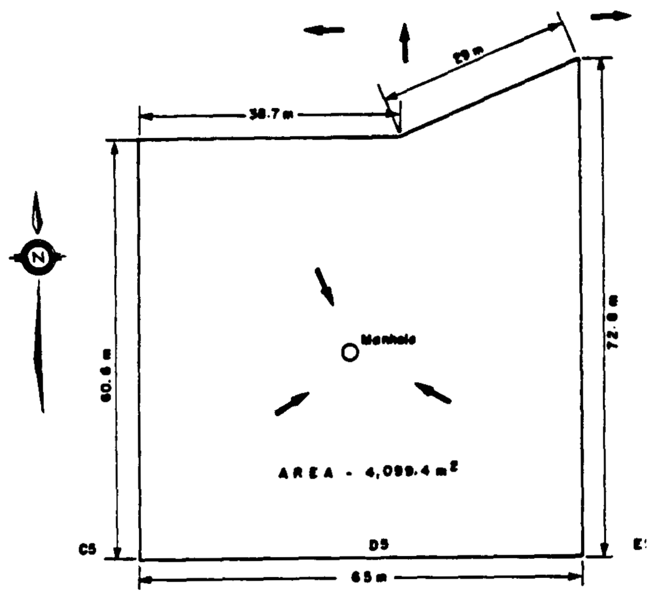
FIGURE 4 MILL #4, DECEMBER 20 - 21, 1986 STORM EVENT.

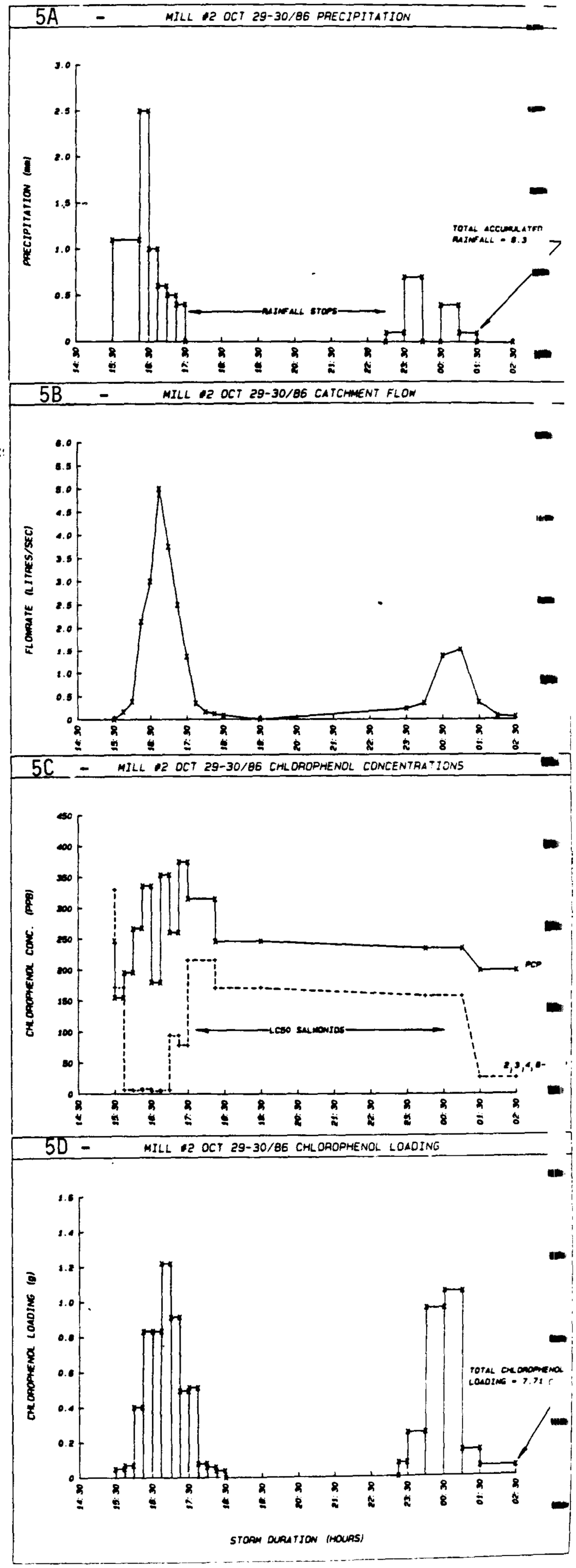
3.3.1 **Mill #2, October 29-30, 1986.** The lumber stored in the drainage basin had been subjected to 23 mm of rainfall 48 hours prior to the October 29 storm event (Figure 5).

3.3.1.1 **Precipitation, Flow, Concentrations and Loading.** Precipitation and flows co-related directly in that flows matched increases and decreases in rainfall with very little lag time (Figure 5A vs 5B). Cumulative precipitation for the test was 6.3 mm over 8 1/2 hours (Figure 5A). The lumber density in the drainage basin was 87.9 boardfeet/m^2 and had been stored under dry conditions for 12 days. This was followed by 23 mm of precipitation over a 48 hour period prior to the test.

The concentration of PCP was generally higher than TTCP which is unexpected due to the 2:1 TTCP/PCP ratio in the dip formulation (Figure 5C). The LC_{50} for salmonids was exceeded an average of 2.5X for PCP an 1.0X for TTCP. Total chlorophenol loading for the test was 7.7 g (Figure 5D).

3.3.2 **Mill #2, November 13, 1986.** This site was a different drainage basin than the site monitored on October 29, 1986. The lumber in this basin had been stored for four days and had already experienced 6.1 mm of rainfall within the previous 48 hours (Figure 6).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	NONE	
PLANED CUT	DIPPED IN WOODBRITE 24	3260 ppm TETRA 1540 ppm PENTA

2) LUMBER TYPE — HEMLOCK/BALSAM/FIR

3) PACKAGING

STRAPPED LUMBER		
LUMBER DIMENSIONS	0.05 m x 0.15 m	(2" x 6")
PACKAGE DIMENSIONS	0.61 m x 0.91 m	(2ft x 3ft)

4) FINAL TREATMENT DATE — OCTOBER 15, 1986

5) DRYING TIME — TWELVE DAYS

6) SITE OBSERVATIONS

- SUBJECTED TO 23 mm OF RAINFALL 48 HOURS PRIOR TO THE OCTOBER 29TH TEST.
- STEADY RAIN BEGAN AT 14:30
- OIL SLICK WAS VERY EVIDENT

7) LUMBER LOADING — 87.9 BOARDFEET/SQUARE METER

8) TOTAL FLOW VOLUME — 22 456 l (4946 gal)

9) AVERAGE CONCENTRATIONS — 259 ppb PENTA-CHLOROPHENOL; 98 ppb TETRA-CHLOROPHENOL

FIGURE 5 MILL #2, OCTOBER 29-30, 1986 STORM EVENT.

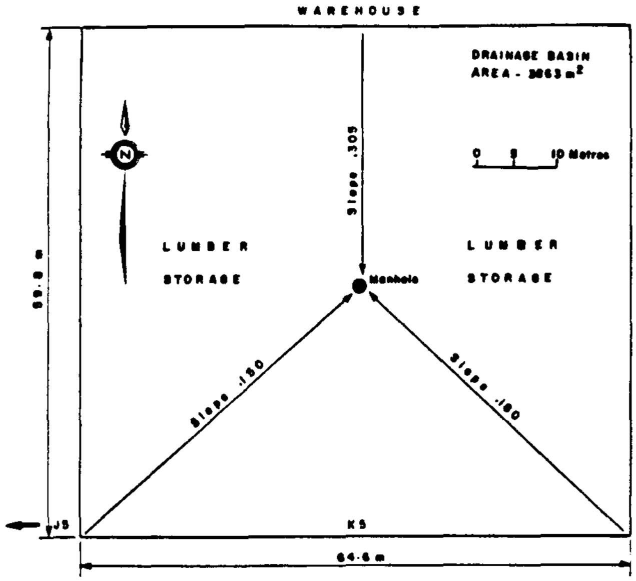
3.3.2.1 **Precipitation, Flow, Concentration and Loading.**

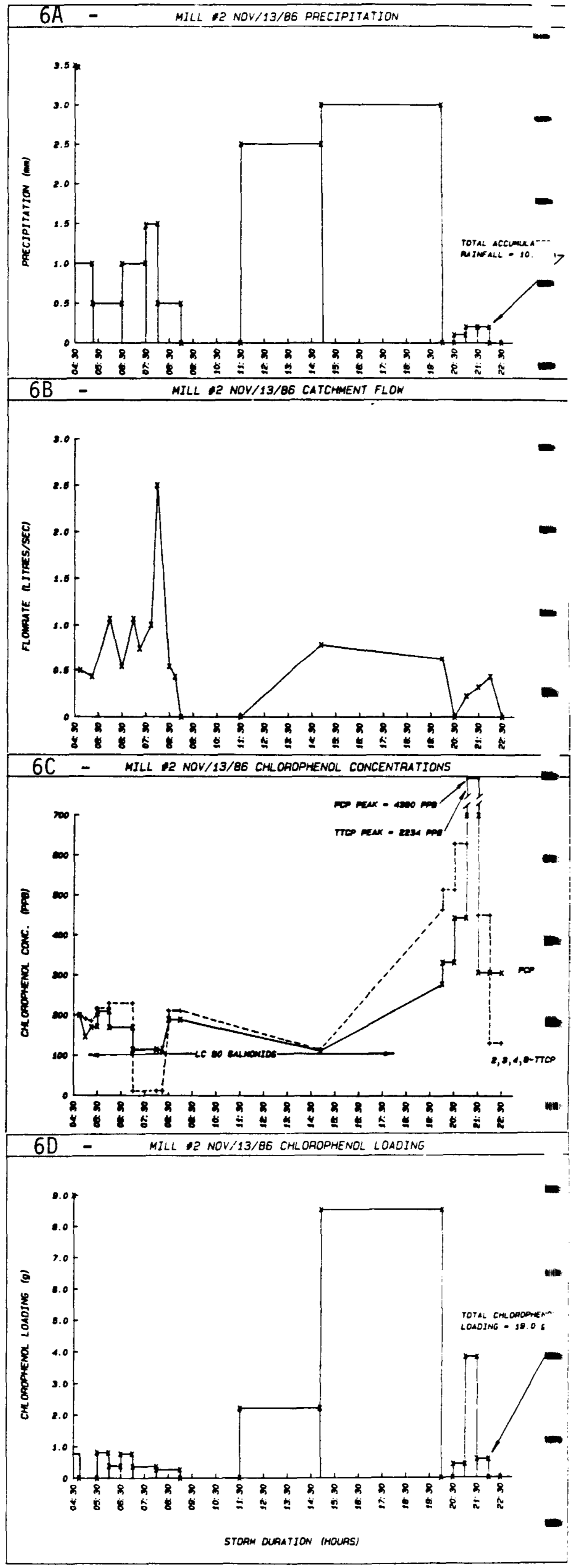
Precipitation and flows followed the same pattern of direct correlation observed elsewhere. Total accumulation was 10.5 mm over 18 hours (Figure 6A).

Lumber density in the drainage basin was 35 boardfeet/m^2 of which 32 boardfeet/m^2 was dipped, 3 boardfeet/m^2 was treated elsewhere. The lumber was subjected to 6.3 mm of rain within 48 hours of the test.

In this case TTCP concentrations averaged higher than PCP which correlates to the dip formulation. Average concentrations were 2.5X the LC_{50} for salmonids for both PCP and TTCP (Figure 6C).

A significant peak occurred at the end of the storm where TTCP was 22X and PCP was 44X the LC_{50}. This occurred when heavy rainfall ended abruptly and flow to the stormdrain was primarily undiluted leachate. Concentrations of 2 234 ppb TTCP and 4 390 ppb PCP were recorded. Total chlorophenol loading was 19.0 g (Figure 6D).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	NONE	
PLANED CUT	DIPPED IN WOODBRITE 24	3260 ppm TETRA 1540 ppm PENTA
	SPRAYED ELSEWHERE	FORMULATION NOT KNOWN

2) LUMBER TYPE — HEMLOCK/BALSAM/FIR

3) PACKAGING

STRAPPED LUMBER		
LUMBER DIMENSIONS	0.05 m x 0.15 m	(2" x 6")
PACKAGE DIMENSIONS	0.61 m x 0.91 m	(2ft x 3ft)

4) FINAL TREATMENT DATE — NOVEMBER 8, 1986

5) DRYING TIME — MOVED TO DRAINAGE BASIN ON NOVEMBER 9, 1986

6) SITE OBSERVATIONS

- SUBJECTED TO 6.1 mm OF RAINFALL 48 HOURS PRIOR TO THE NOVEMBER 13TH TEST.
- NOV. 10 – WHEN THE LUMBER WAS MOVED TO THE STORAGE AREA, SOME DRIPPING OF CHLOROPHENATES WAS OBSERVED. SOME WASHOFF OCCURED.
- NOV. 13 – STEADY RAIN THROUGHOUT THE AFTERNOON. NOTICIBLE DRIPPING FROM THE WOOD NEW LUMBER WAS ADDED TO THE DRAINAGE BASIN DURING THE DAY.

7) LUMBER LOADING — 32 BOARD FEET/ SQ. METER DIPPED; 3 BOARD FEET/ SQ. METER SPRAYED

8) TOTAL FLOW VOLUME — 40 561 l (8934 gal)

9) AVERAGE CONCENTRATIONS — 249 ppb PENTA-CHLOROPHENOL; 279 ppb TETRA-CHLOROPHENOL; 528 ppb TOTAL

FIGURE 6 MILL #2, NOVEMBER 13, 1986 STORM EVENT.

4 LOW PRESSURE SPRAYED LUMBER

Low pressure sprayed lumber was monitored under the following conditions:

- Leachate dripping directly from planed lumber before dilution on the mill yard with drying times from zero to greater than 8 days.
- Runoff from mill yards containing wood which was planed, strapped, end sealed and had from zero to 8 days drying time.

4.1 Low Pressure Sprayed Lumber (Zero to Eight Days Drying Time), Undiluted Leachate

Leachate from low pressure sprayed lumber with zero drying time is essentially direct washoff of chlorophenate solution from the treated lumber. This situation occurs where treated lumber is pulled from the sorting chains after treatment and stacked in piles outside the roofed area. In several cases the sorting chain roofs did not have gutters. Consequently lumber was washed with roof runoff in addition to direct impact by rainfall. The lumber piles are constantly "recharged" with chemicals by the addition of new boards. When the stacks are large enough a straddle type lumber carrier removes the wood to a storage area to await further processing such as planing or packaging. The average total chlorophenol concentration from three samples was 174 474 ppb which was the highest of the situations monitored (Table 3).

Six samples of undiluted leachate from lumber which was planed, strapped, end sealed and had from 24 hours to eight days of drying were analyzed. The average total chlorophenol concentration was 8 816 ppb for interior and 39 907 ppb for exterior package undiluted leachate (Table 3). The lower concentrations can be attributed to the longer drying times before exposure to rainfall.

4.2 Low Pressure Sprayed Lumber (Zero Drying Time) Yard Runoff

After the undiluted leachate drips from the freshly treated lumber packages to the paved yard surface it migrates to the storm drain. During this migration it becomes diluted by rainfall falling in the yard area not covered by lumber as well as by roof drains which may discharge to the yard.

Three such sites were monitored over two storm events per site and the following observations were made.

4.2.1 **Mill #3, November 13, 1986.** Monitoring was conducted at this site in a drainage basin which services 32 lumber loading bays of the planer mill sorting chain. Sixteen lumber loading bays are serviced by each drain (Figure 7). Data on this day reflects lumber that was treated twice (re-run) due to improper dimensioning on the first production run.

4.2.1.1 **Precipitation, Flow, Concentration and Loading.** Rainfall was steady and moderate and there was a direct co-relation of flow rate to rainfall intensity although a short lagtime was evident in flow rate response to changes in precipitation intensity. Total accumulation was 3.1 mm over six hours (Figure 7A).

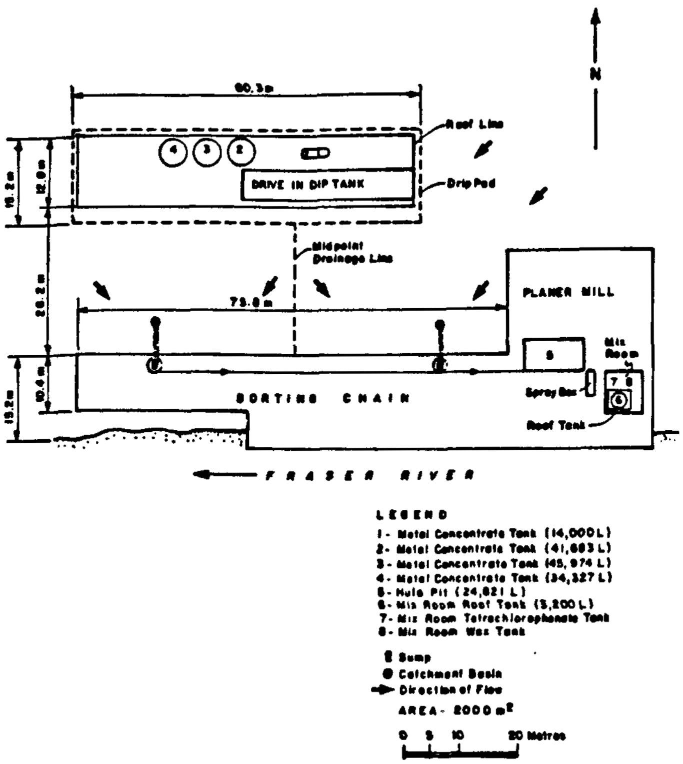
The drainage basin contained a constantly varying quantity of sprayed and dipped lumber. The concentration of TTCP always exceeded that of PCP and averaged 15 384 ppb and 7 771 ppb respectively. Total chlorophenates were never less than 13 000 ppb or 130X the LC_{50} for salmonids (Figure 7C).

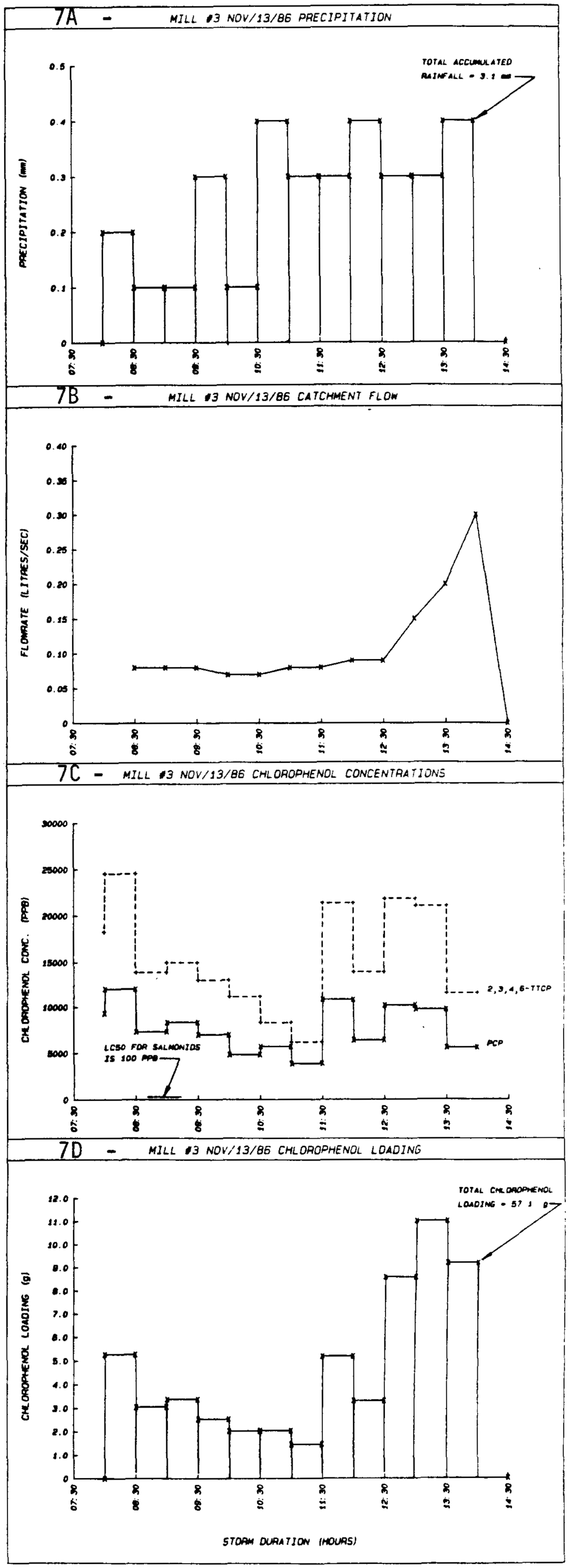
These values are extremely high and were plainly evident in the yellow staining of the runoff by the wax/chlorophenol emulsion. Total runoff for the entire basin was estimated at 8 553 L. This runoff was intended to be collected and recycled as makeup water, however, the collection system was not observed to be operating and it is expected that all flow was discharged directly to the nearshore area of the Fraser River. Total loading was calculated at 57.1 g total chlorophenols or 114 g for the entire basin (Figure 7D).

4.2.2 **Mill #3, November 18, 1986.** Monitoring was conducted at this site a second time during a normal operating run (Figure 8).

4.2.2.1 **Precipitation, Flow, Concentration and Loading.** Rainfall was sporadic ranging from 1.0 to 3.0 mm/hr with a total accumulation of 6.5 mm in 3.5 hours. There was direct correlation of flow rate to rainfall intensity with a short lagtime in the flow rate response (Figure 8A vs. Figure 8B).

On November 18 the average concentrations of TTCP and PCP exceeded the LC_{50} by 161X and 114X reaching 26 314 ppb TTCP and 24 977 ppb for PCP during the lowest flow conditions. A total flow of 21 796 L (4,800 gal) was estimated. The average total concentration was 27 542 ppb (Figure 8C).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	DIPPED IN DIATOX, 3803 ppm TETRA 941 ppm PENTA
PLANED CUT	LOW PRESSURE SPRAY, 7566 ppm TETRA SEABRITE 1390 ppm PENTA

2) LUMBER TYPE — HEMLOCK/BALSAM

3) PACKAGING

THE QUANTITIES OF LUMBER IN THE DRAINAGE AREA WAS VARIABLE AND CONTAINED BOTH DIPPED AND SPRAYED STACKS. A TOTAL OF 32 LOADING BAYS ON THE SPRAY LINE WERE OPERATING OF WHICH 16 WERE MONITORED FOR THIS TEST.

4) FINAL TREATMENT DATE — NOVEMBER 13, 1986

5) DRYING TIME — NONE. LUMBER WAS SUBJECT TO WASHOFF WHEN PULLED FROM THE GREEN CHAIN TO THE LOADING BAYS.

6) SITE OBSERVATIONS

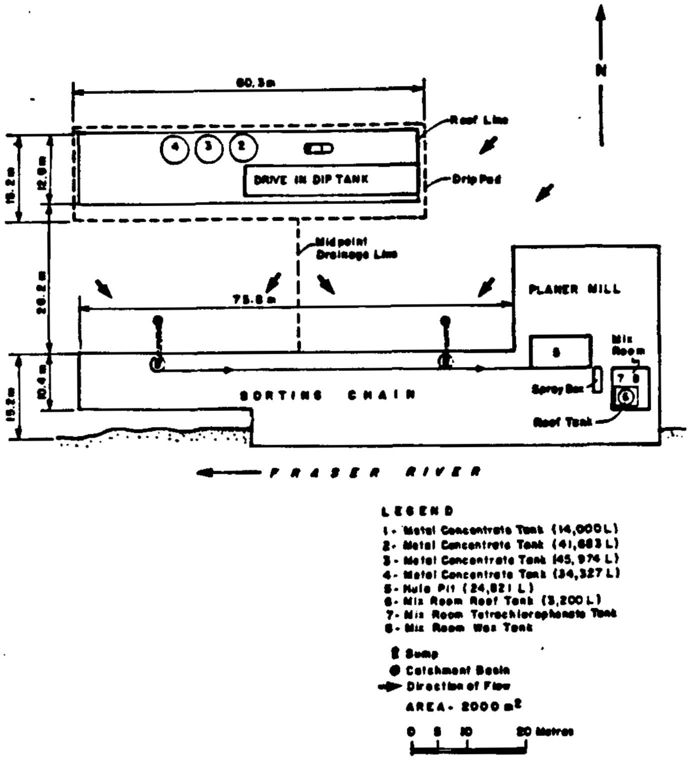
- SOME OF THE LUMBER WAS SUBJECTED TO 4.8 mm of RAINFALL 24 HOURS PRIOR TO THE NOVEMBER 13TH TEST.

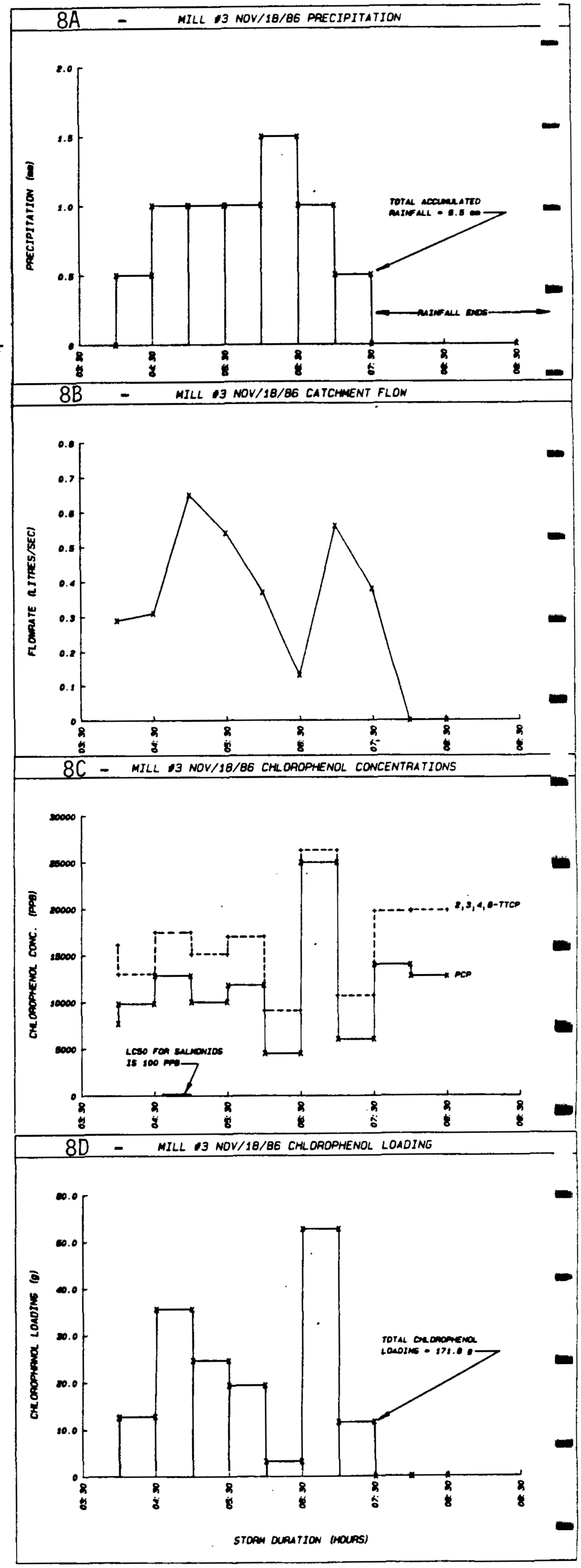
NOV. 13
- STEADY RAIN THROUGHOUT THE MONITORED PERIOD CONSIDERABLE RUNOFF FROM LUMBER IN LOADING BAYS.
- A DIMENSIONING ERROR MADE DURING THE NIGHT SHIFT REQUIRED THAT THE NOVEMBER 12TH PRODUCTION RUN BE REMANUFACTURED AND RETREATED ON NOVEMBER 13TH.

8) TOTAL FLOW VOLUME — 8553 l (1884 gal)

9) AVERAGE CONCENTRATIONS
7 774 ppb PENTA-CHLOROPHENOL
15 384 ppb TETRA-CHLOROPHENOL
23 158 ppb TOTAL

FIGURE 7 MILL #3, NOVEMBER 13, 1986 STORM EVENT.





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	DIPPED IN DIATOX, 3803 ppm TETRA 941 ppm PENTA
PLANED CUT	LOW PRESSURE SPRAY, 7566 ppm TETRA SEABRITE 1390 ppm PENTA

2) LUMBER TYPE — HEMLOCK/BALSAM

3) PACKAGING

THE QUANTITIES OF LUMBER IN THE LOADING BAYS WERE VARIABLE AND CONTAINED BOTH DIPPED AND SPRAYED STACKS. A TOTAL OF 16 LOADING BAYS ON THE SPRAY LINE WERE OPERATING.

4) FINAL TREATMENT DATE — NOVEMBER 18, 1986

5) DRYING TIME — NONE. LUMBER WAS SUBJECT TO WASHOFF WHEN PULLED FROM THE GREEN CHAIN TO THE LOADING BAYS.

6) SITE OBSERVATIONS

- SOME OF THE LUMBER WAS SUBJECTED TO RAINFALL 24 HOURS PRIOR TO THE NOVEMBER 18TH TEST.
- NOV. 13 - RAINFALL WAS SPORADIC, RANGING FROM LIGHT TO HEAVY.
- OBVIOUS RUNOFF FROM LUMBER IN THE LOADING BAYS
- THIS WAS A NORMAL PRODUCTION RUN

7) LUMBER LOADING — VARIABLE, LUMBER WAS REMOVED ON A CONTINUOUS BASIS AND NO ESTIMATE WAS MADE OF THE AVERAGE QUANTITY IN THE BASIN AT ANY GIVEN TIME.

8) TOTAL FLOW VOLUME — 21 796 l (4,800 gal)

9) AVERAGE CONCENTRATIONS — 11 459 ppb PENTA-CHLOROPHENOL
16 468 ppb TETRA-CHLOROPHENOL
27 542 ppb TOTAL

FIGURE 8 MILL #3, NOVEMBER 18, 1986 STORM EVENT.

The total chlorophenol loading for November 18 was 171.8 grams for 16 lumber bays (Figure 8D). It would be expected that the total chlorophenol loading would be greatest on the day that lumber was retreated (November 13) however this was not observed. The highest concentrations and loadings occurred on November 18 (Figure 8D) and may be explained by the storm characteristics on the two days. Rainfall on November 18 was at times intense and occurred with gusting wind which cleared the drainage area of accumulated water. On November 13 however, rain was moderate and there were no winds. Consequently large pools of contaminated water remained in the drainage basin and may account for the lower value.

It must be noted that the data presented represents the release occurring at only one storm drain (½ drainage area). The total loadings must be multiplied by 2X to represent the entire drainage area.

The storm water recovery system is designed to discharge storm water directly to the Fraser River after collecting effluent for the first two hours of a storm event. This system was not operational during either test period.

4.2.3 **Mill #6, December 22, 1986.** Mill #6 uses a low pressure spray system for final treatment of planed lumber. The spray is a 6:1 formulation of water and Wood Sheath (Seabrite) at 18 916 ppm TTCP (Figure 9).

4.2.3.1 **Precipitation, Flow, Concentration and Loading.** Light but steady precipitation began at 08:00 to 10:30 after which it was light and intermittent. A total rainfall of 5.4 mm in 5.5 hours was recorded (Figure 9A). Flow rates responded directly to the rainfall pattern (Figure 9A vs. Figure 9B). Construction debris and wet soil was deposited nearby and runoff from this activity also entered the sewer.

The rainfall pattern was such that fresh washoff which was stained with the yellow wax emulsion did not appear to reach the drain until the 11:30-14:30 hour period. Total chlorophenol concentration averaged 195 ppb (Figure 9C). By this time flows had become negligible and most of the contamination would remain on the paved yard until the next rainfall. The light loading of 1.38 g corresponds to the low concentration and flow conditions (Figure 9D).

4.2.4 Mill #6, January 23, 1987

4.2.4.1 Precipitation, Flow, Concentration and Loading.

Precipitation began at 06:00 and was relatively high for a brief period. This was followed by a three hour period of light rainfall after which the storm developed and a total of 3.0 mm fell in the ten hour period. Flows were generally responsive to changes in rainfall (Figure 10A vs. Figure 10B).

Chlorophenol concentrations were high, ranging from 150-850 ppb for PCP and 400-2 200 ppb for TTCP. Concentrations were very responsive to dilution by flows. Rainfall was light to moderate. Past operations at this mill discharged concentrated washings from the spray box to the ground directly below the mill. This has been rectified. A sump pump located approximately 39 m hydraulically downhill from the spray box collects and discharges groundwater directly to the storm drain during periods when flooding is caused by high tide or rain. This pump discharged at 14:18 hours and contained 2 160 ppb TTCP and 633 ppb PCP. Ground water contamination is indicated at this site.

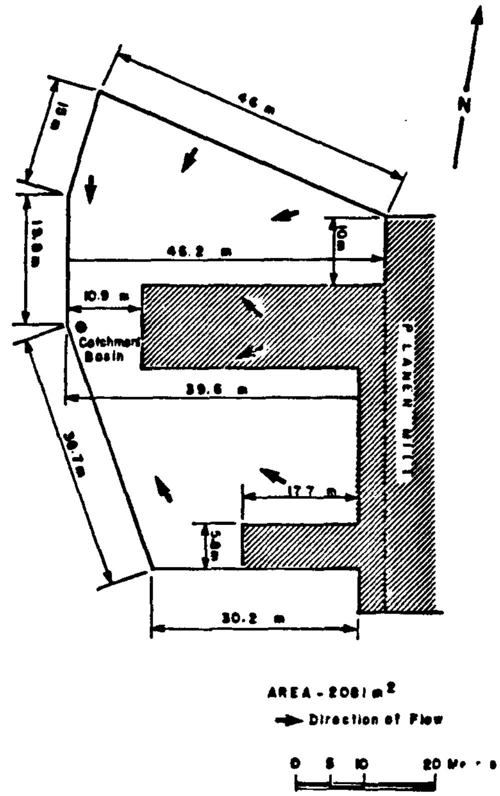
4.2.5 Mill #5, January 27, 1987.

Mill #5 does not treat rough cut lumber. A low pressure spray with a wax emulsion is used to treat planed lumber. The spray formulation is a pure (technical grade) pentachlorophenate solution called CHAPCO-C1 mixed as a ratio of 12:1 water to PCP concentrate. The application spray concentration is 20 833 ppm. Water samples were collected of leachate dripping directly from the lumber and of runoff from the planer mill loading bays. Flow and loading calculations are based on ½ the drainage basin area at the planer mill (Figure 11).

4.2.5.1 Precipitation, Flow, Concentration and Loading.

Precipitation was very light with only 1.1 mm in 6.5 hours (Figure 11A). Flow reached a maximum of 0.3 L/s and was very responsive to rainfall. Flow was continuous throughout the test though it was less than 0.1 L/s for 67% of the time (Figure 11B).

The concentration of PCP in the runoff averaged 5 000 ppb



LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	LOW PRESSURE SPRAY TETRA SAPSTAIN	: UNKNOWN ppm
PLANED CUT	WOOD SHEATH (SEA BRITE)	: 18,916 ppm

2) LUMBER TYPE — HEMLOCK/FIR

3) PACKAGING

LOOSE PACKAGES — LUMBER IS PULLED FROM THE SORTING CHAINS AND DIRECTLY EXPOSED TO RAINFALL.

QUANTITY OF LUMBER IN THE DRAINAGE BASIN. — VARIABLE

4) FINAL TREATMENT DATE — DECEMBER 22, 1986

5) DRYING TIME — ZERO

6) SITE OBSERVATIONS

- THE MILL STARTED RUNNING AT 07:00, LOADING BAYS WERE 1/2 FULL WHEN THE SHIFT STARTED.
- RAINFALL BEGAN AT 08:00
- RISING TIDE BEGAN TO FLOOD STORM DRAIN AT 10:50.
- AT 11:23 - 11:26, FLOODING BEGINS UNDER THE MILL AND THE SUMP PUMP BEGINS PUMPING FROM THE STAND PIPE AND DISCHARGES TO THE STORM SEWER.

7) LUMBER LOADING — VARIABLE.

8) TOTAL FLOW VOLUME — 11 237 L (2,475 gal)

9) AVERAGE CONCENTRATIONS — 65 ppb PENTA-CHLOROPHENOL, 130 ppb TETRA-CHLOROPHENOL, 195 ppb TOTAL

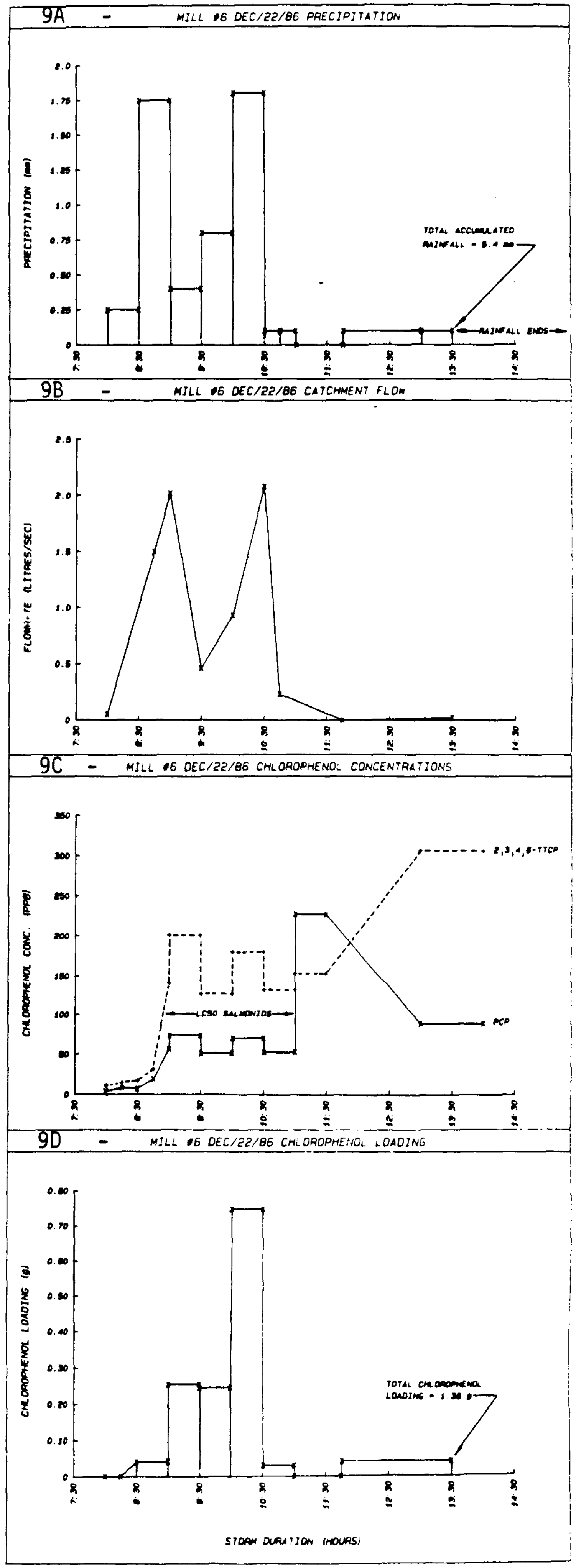
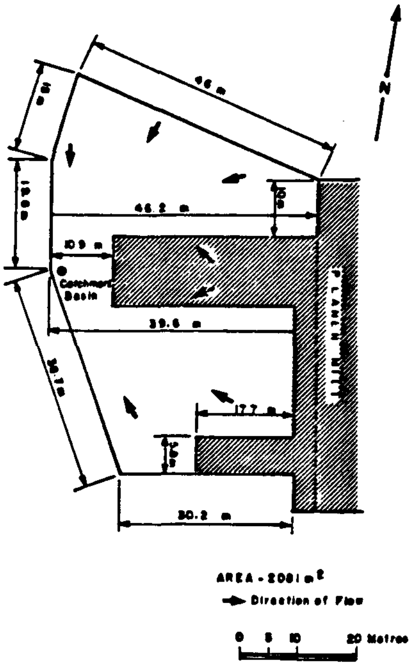
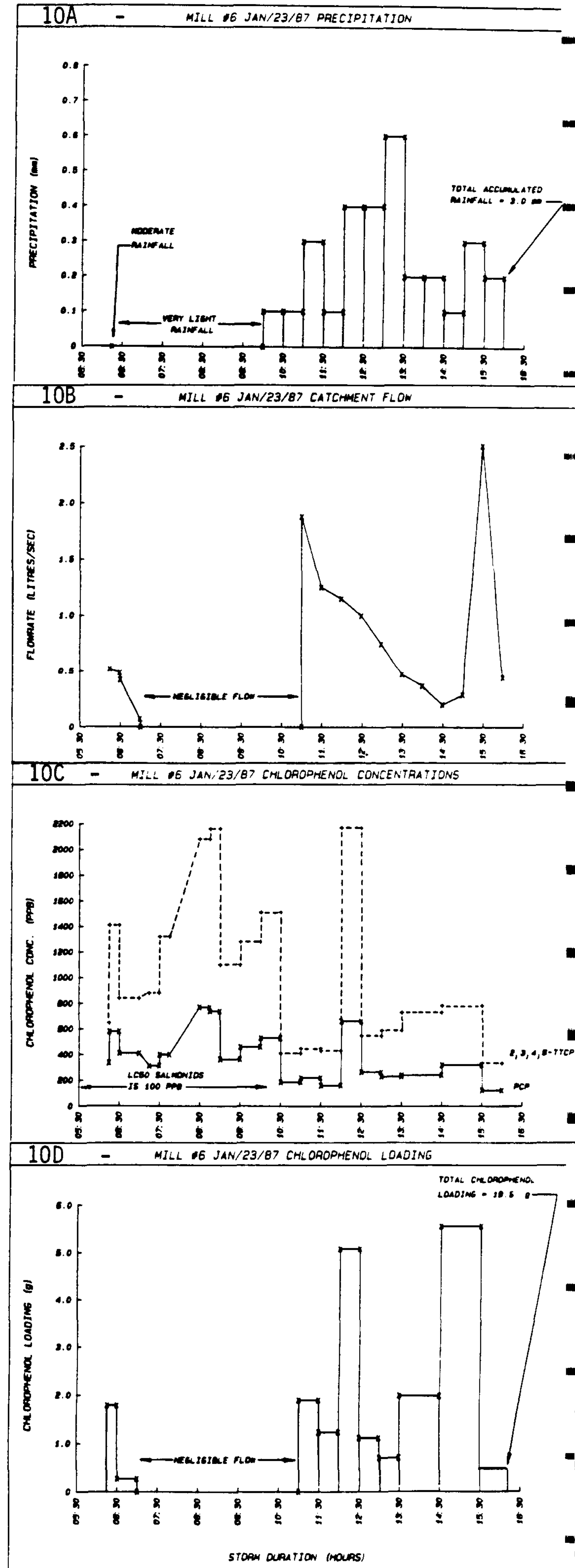


FIGURE 9 MILL #6, DECEMBER 22, 1986 STORM EVENT.





LUMBER TREATMENT AND HANDLING VARIABLES

1) **APPLICATION METHOD**

ROUGH CUT	LOW PRESSURE SPRAY TETRA SAPSTAIN	: UNKNOWN ppm
PLANED CUT	WOOD SHEATH (SEA BRITE)	: 18,916 ppm

2) **LUMBER TYPE** — HEMLOCK/FIR

3) **PACKAGING**

LOOSE PACKAGES	LUMBER IS PULLED FROM THE SORTING CHAINS AND DIRECTLY EXPOSED TO RAINFALL.
QUANTITY OF LUMBER IN THE DRAINAGE BASIN.	VARIABLE

4) **FINAL TREATMENT DATE** — JANUARY 23, 1987

5) **DRYING TIME** — ZERO

6) **SITE OBSERVATIONS**

- THE MILL STARTED RUNNING AT 07:00. LOADING BAYS WERE 1/2 FULL WHEN THE SHIFT STARTED.
- AT 14:18 A SUMP PUMP FROM A STAND PIPE WHICH DRAINS GROUND WATER FROM BELOW THE MILL BEGAN PUMPING DIRECTLY TO THE STORM DRAIN.

7) **LUMBER LOADING** — VARIABLE.

8) **TOTAL FLOW VOLUMES** — 6 243 L (1375 gal)

9) **AVERAGE CONCENTRATIONS**
384 ppb PENTA-CHLOROPHENOLS
1 035 ppb TETRA-CHLOROPHENOLS
1 419 ppb TOTAL

FIGURE 10 MILL #6, JANUARY 23, 1987 STORM EVENT.

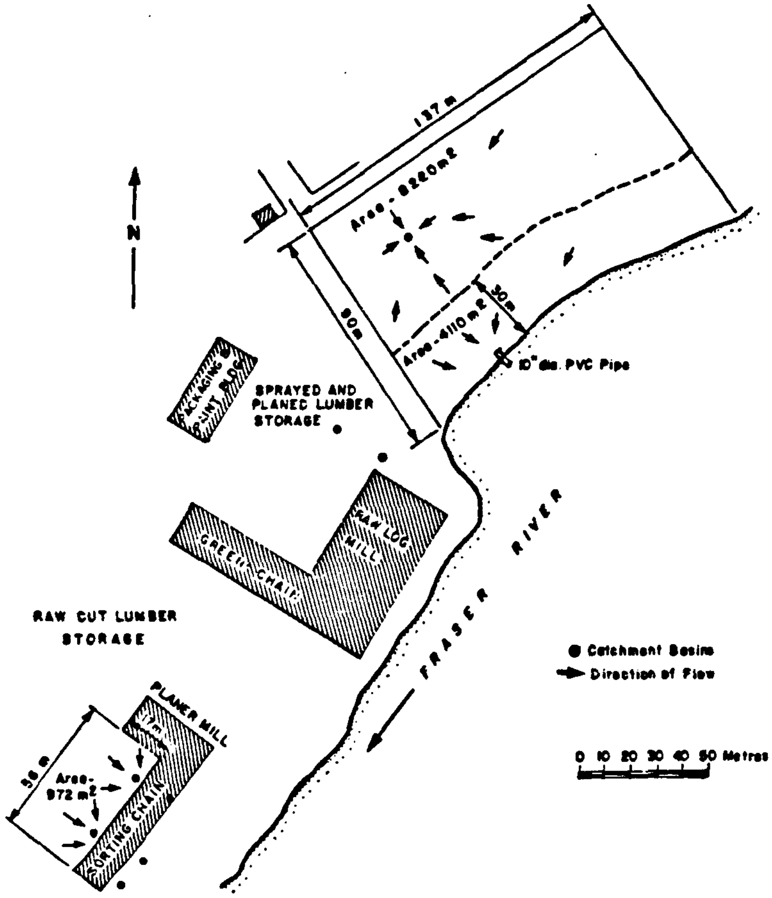
(Figure 11C) and total loading was 7.51 grams which is very high for such a low rainfall (Figure 11D). This effluent is believed to discharge directly to the Fraser River although the exact location of the outfall has not been located. Total volume discharged was calculated at 1 069 L.

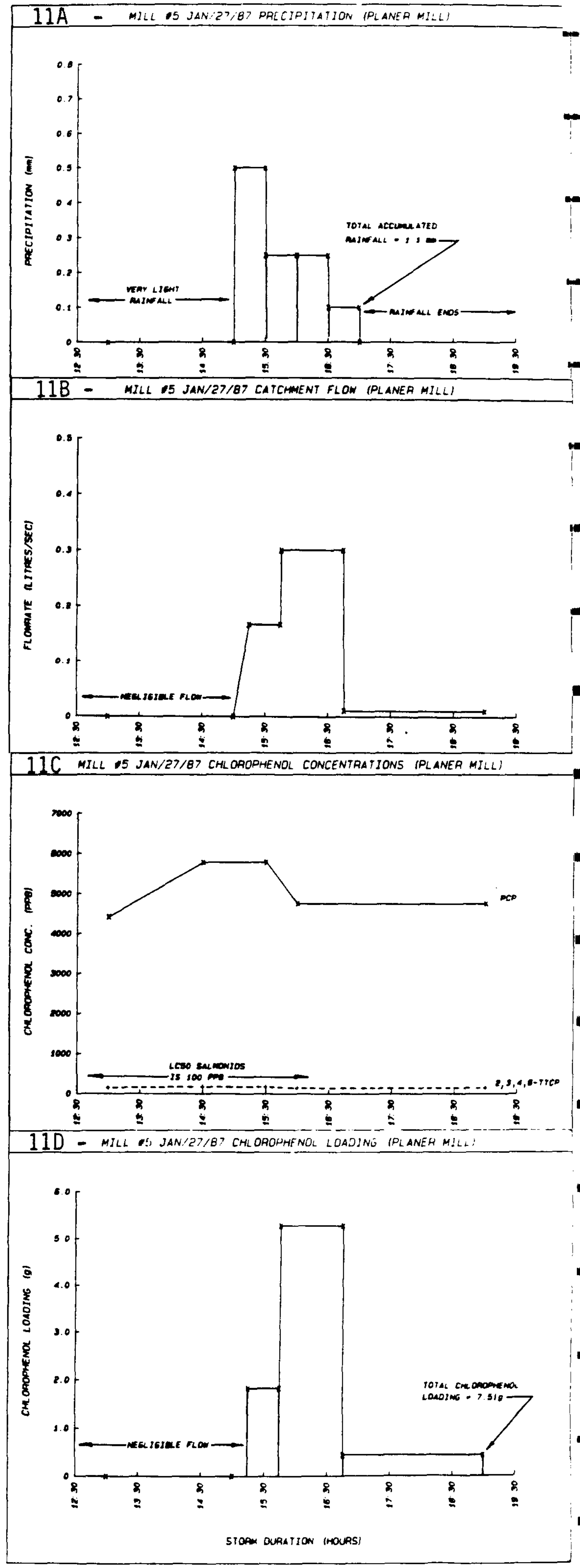
4.2.6 Mill #5, January 29, 1987. A second rainfall event was monitored at this site which uses CHAPCO-Cl sodium pentachlorophenate low pressure spray on planed lumber (Figure 12).

4.2.6.1 Precipitation, Flow, Concentration and Loading. Precipitation was light and continuous over the five hour storm event with a total rainfall of 3.2 mm. Flow was responsive to the rainfall pattern (Figure 12A vs. Figure 12B).

The concentrations in the effluent average 11 160 ppb total chlorophenols which is typical of the high values measured at other mills in which low pressure sprayed lumber is directly exposed to rainfall (Figure 12C).

Total loading was 7.42 grams which is believed to discharge directly to the Fraser River (Figure 12D).

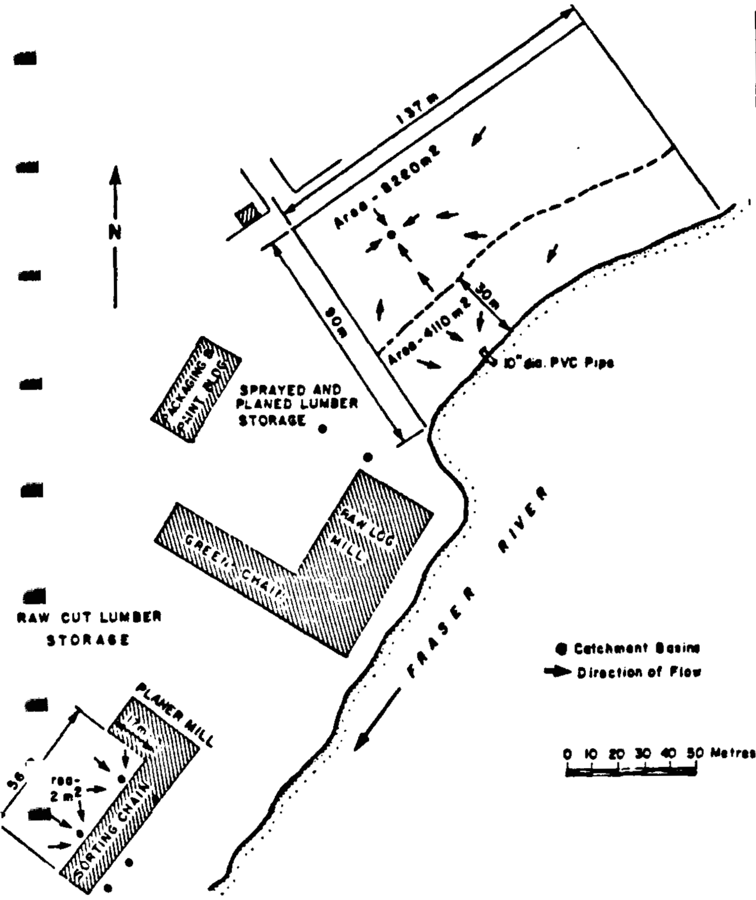


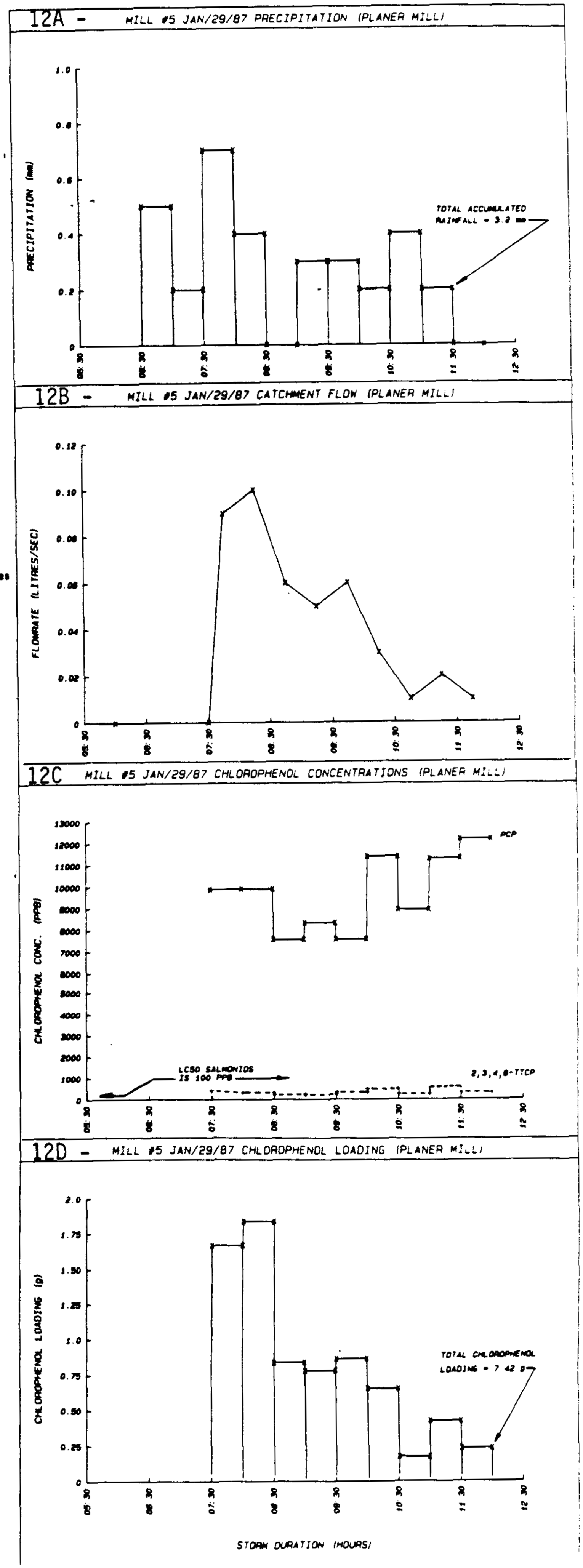


LUMBER TREATMENT AND HANDLING VARIABLES

1)	APPLICATION METHOD	
	ROUGH CUT	NO TREATMENT
	PLANED CUT	CHAPMAN C-1 : 20 833 ppm PCP (20-30%, AVG=25%)
2)	LUMBER TYPE	HEMLOCK/FIR
3)	PACKAGING	
	LOOSE PACKAGES	LUMBER IS PULLED FROM THE SORTING CHAINS AND DIRECTLY EXPOSED TO RAINFALL.
	QUANTITY OF LUMBER IN THE DRAINAGE BASIN.	VARIABLE
4)	FINAL TREATMENT DATE	JANUARY 27, 1987
5)	DRYING TIME	ZERO
6)	SITE OBSERVATIONS	- THE PLANER MILL SHIFT RAN FROM 07:30-15:30 and 16:00 to 00:30. - AT 14:30 PRODUCTION STOPPED FOR BLADE SHARPENING IN THE PLANER MILL.
7)	LUMBER LOADING	VARIABLE.
8)	TOTAL FLOW VOLUMES	1 069 L (235 gal)
9)	AVERAGE CONCENTRATIONS	4 983 ppb PENTA-CHLOROPHENOL 160 ppb TETRA-CHLOROPHENOL 5 143 ppb TOTAL

FIGURE 11 MILL #5, JANUARY 27, 1987 STORM EVENT.





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	NO TREATMENT
PLANED CUT	CHAPMAN C-1 : 20 833 ppm PCP (20-30%, AVG=25%)

2) LUMBER TYPE — HEMLOCK/FIR

3) PACKAGING

LOOSE PACKAGES	LUMBER IS PULLED FROM THE SORTING CHAINS AND DIRECTLY EXPOSED TO RAINFALL.
QUANTITY OF LUMBER IN THE DRAINAGE BASIN.	VARIABLE

4) FINAL TREATMENT DATE — JANUARY 29, 1987

5) DRYING TIME — ZERO

6) SITE OBSERVATIONS

- THE PLANER MILL SHIFT RAN FROM 07:30-15:30 and 16:00 to 00:30.
- LUNCH BREAK OCCURED AT 11:00 DURING WHICH NO FRESH LUMBER WAS ADDED TO DRAINAGE BASIN.

7) LUMBER LOADING — VARIABLE.

8) TOTAL FLOW VOLUME — 3 110 L (685 gal)

9) AVERAGE CONCENTRATIONS — 9550 ppb PENTA-CHLOROPHENOLS
610 ppb TETRA-CHLOROPHENOLS

11 160 ppb TOTAL

FIGURE 12 MILL #5, JANUARY 29, 1987 STORM EVENT.

4.3 Low Pressure Sprayed Lumber (Long Dry Times) Yard Runoff

This section deals with yard runoff from low pressure sprayed lumber which has had drying periods of 24 hours or more prior to exposure to rainfall. All lumber was planed, strapped and end sealed.

4.3.1 Mill #1 - October 25, 1986. Low pressure sprayed lumber was monitored over two rainfall events and the following discussion refers to Figure 13.

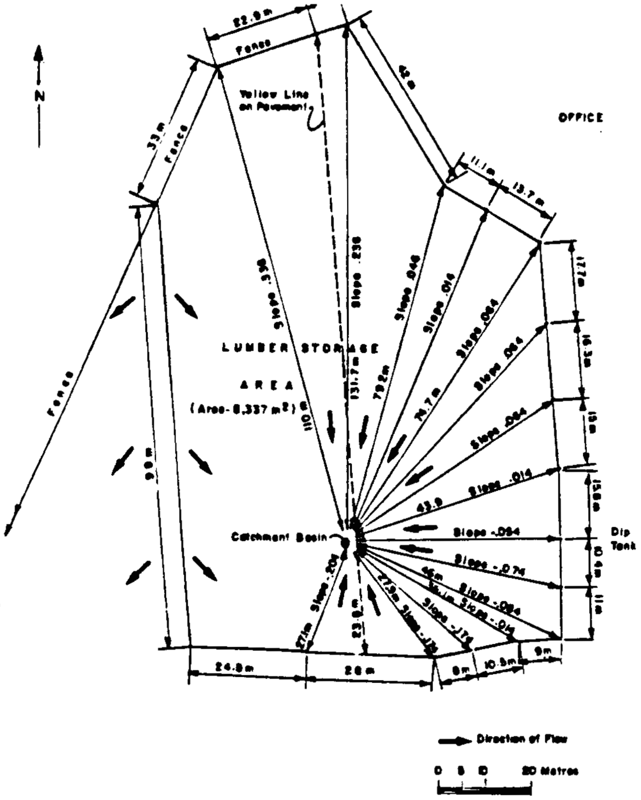
4.3.1.1 Precipitation, Flow, Concentration and Loading. Precipitation and flow correlated directly and the large size of the drainage basin and quantity of lumber stored in it maintained measureable runoff for 3 hours after the end of the storm event. Total precipitation was 3.0 mm over 6 hours (Figure 13A).

The rough lumber was treated by drive-in dip and then planed and retreated by low pressure spray of a wax/chlorophenate emulsion prior to end sealing, strapping and delivery to the terminal. The lumber density in the drainage basin was 197 boardfeet/m^2 and had been stored in dry conditions for eight days.

The concentration of TTCP was generally higher than PCP which is expected due to formulations used in treating the rough and planed product. TTCP averaged 3.3X and PCP averaged 2X the LC_{50} (Figure 13C). A significant proportion of the total chlorophenol loading of 11.61 g occurred in the last two hours of flow (Figure 13C vs. Figure 13D). This flow consists of undiluted leachate. The drainage basin is capable of holding 2 to 3 times the lumber volume and this would conceivably increase concentrations and loadings proportionately.

4.3.2 Mill #1, October 26, 1986. The same drainage basin was monitored over a second rainfall event. The following discussion refers to Figure 14.

4.3.2.1 Precipitation, Flow, Concentration and Loading. Precipitation and flows correlate directly with a heavy rainfall of 21.0 mm over 7 hours (Figure 14A vs. Figure 14B).



LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	DIPPED IN DIATOX, 3803 ppm TETRA 941 ppm PENTA
PLANED CUT	LOW PRESSURE SPRAY, 7566 ppm TETRA SEABRITE 1390 ppm PENTA

2) LUMBER TYPE — HEMLOCK/BALSAM

3) PACKAGING

STRAPPED LUMBER		
LUMBER DIMENSIONS	0.075m x 0.20m	(3" x 8")
PACKAGE DIMENSIONS	0.61 m x 0.91m	(2ft x 3ft)

4) FINAL TREATMENT DATE — OCTOBER 17, 1986

5) DRYING TIME — EIGHT DAYS

6) SITE OBSERVATIONS

- 15 HOURS SINCE LAST RAINFALL
- CONCENTRATIONS OF CHLOROPHENATES LEACHING FROM THE WOOD. (PPb)

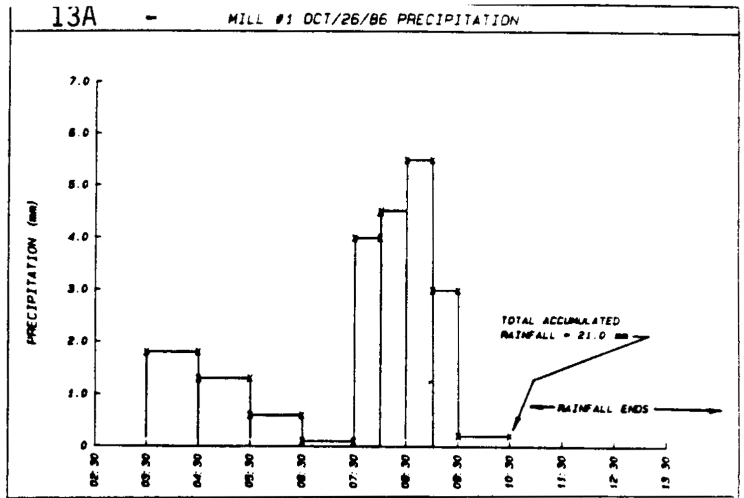
SITE	2,3,4,6-TTCP	PCP
LUMBER PACKAGE EXTERIOR DRIP		
08:00 - 08:30	4 287	4 310
08:31 - 10:30	5 785	6 013
LUMBER PACKAGE INTERIOR DRIP		
08:30 - 09:45	8 858	7 052

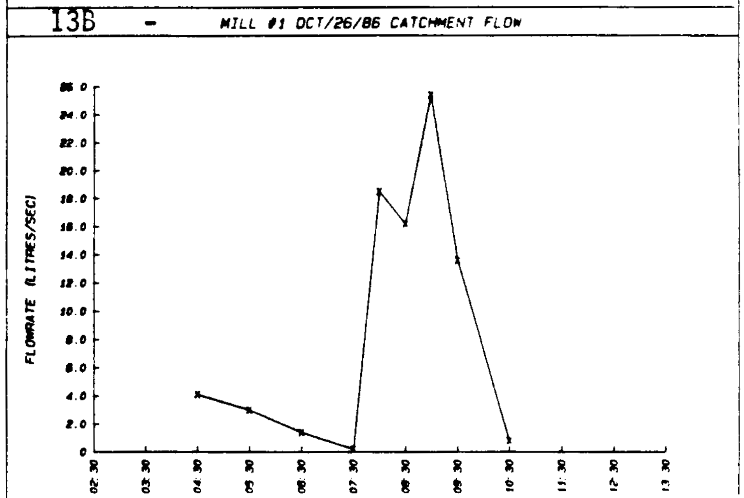
7) LUMBER LOADING — 197 BOARD FEET/SQUARE METER
NOTE THAT THIS BASIN WAS LESS THAN 1/2 FULL.

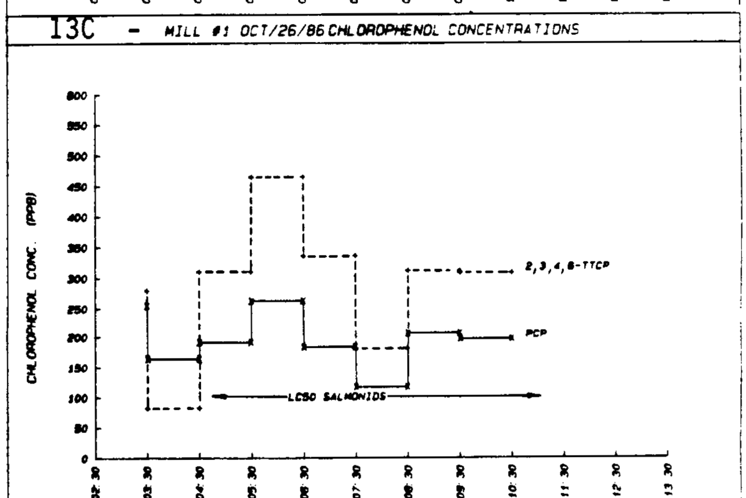
8) TOTAL FLOW VOLUME — 175 077 L (38 563 gal)

9) AVERAGE CONCENTRATIONS — 197 ppb PENTA-CHLOROPHENOLS
284 ppb TETRA-CHLOROPHENOLS

481 ppb TOTAL







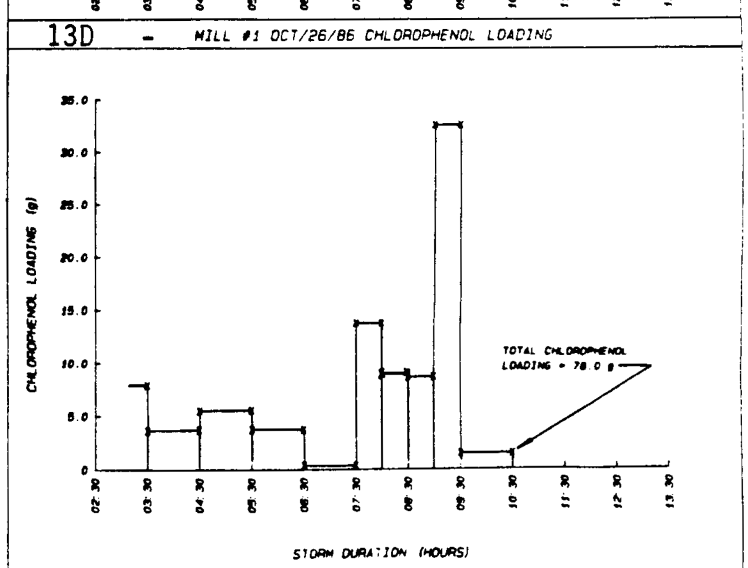
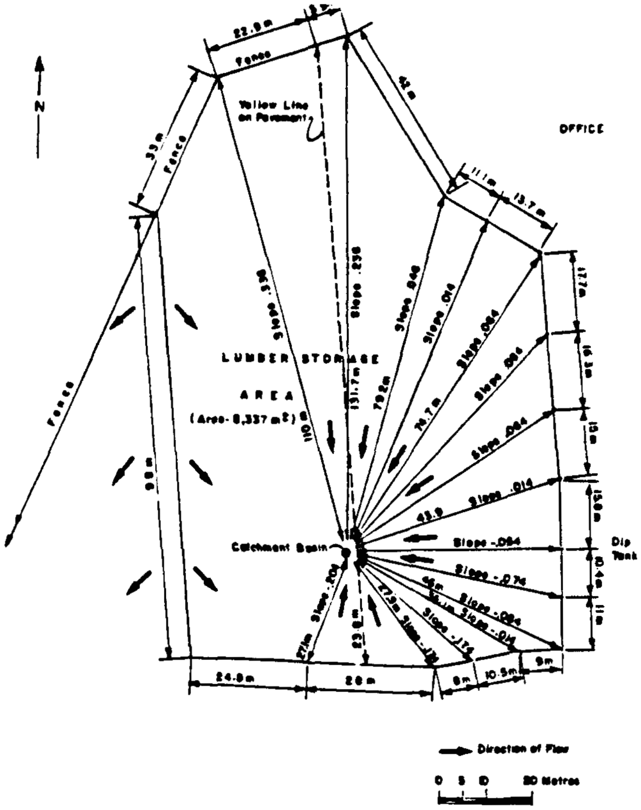


FIGURE 13 MILL #1, OCTOBER 25, 1986 STORM EVENT.



LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	DIPPED IN DIATOX, 3803 ppm TETRA 941 ppm PENTA
PLANED CUT	LOW PRESSURE SPRAY, 7566 ppm TETRA SEABRITE 1390 ppm PENTA

2) LUMBER TYPE — HEMLOCK/BALSAM

3) PACKAGING

STRAPPED LUMBER		
LUMBER DIMENSIONS	0.075m x 0.20m	(3" x 8")
PACKAGE DIMENSIONS	0.61 m x 0.91m	(2ft x 3ft)

4) FINAL TREATMENT DATE — OCTOBER 17, 1986

5) DRYING TIME — EIGHT DAYS

6) SITE OBSERVATIONS

- 15 HOURS SINCE LAST RAINFALL
- CONCENTRATIONS OF CHLOROPHENATES LEACHING FROM THE WOOD. (PPb)

SITE	2,3,4,6-TTCP	PCP
LUMBER PACKAGE EXTERIOR DRIP		
08:00 - 08:30	4 287	4 310
08:31 - 10:30	5 785	6 013
LUMBER PACKAGE INTERIOR DRIP		
08:30 - 09:45	8 858	7 052

7) LUMBER LOADING — 197 BOARD FEET/SQUARE METER
NOTE THAT THIS BASIN WAS LESS THAN 1/2 FULL.

8) TOTAL FLOW VOLUME — 175 077 L (38 563 gal)

9) AVERAGE CONCENTRATIONS —
197 ppb PENTA-CHLOROPHENOLS
284 ppb TETRA-CHLOROPHENOLS

481 ppb TOTAL

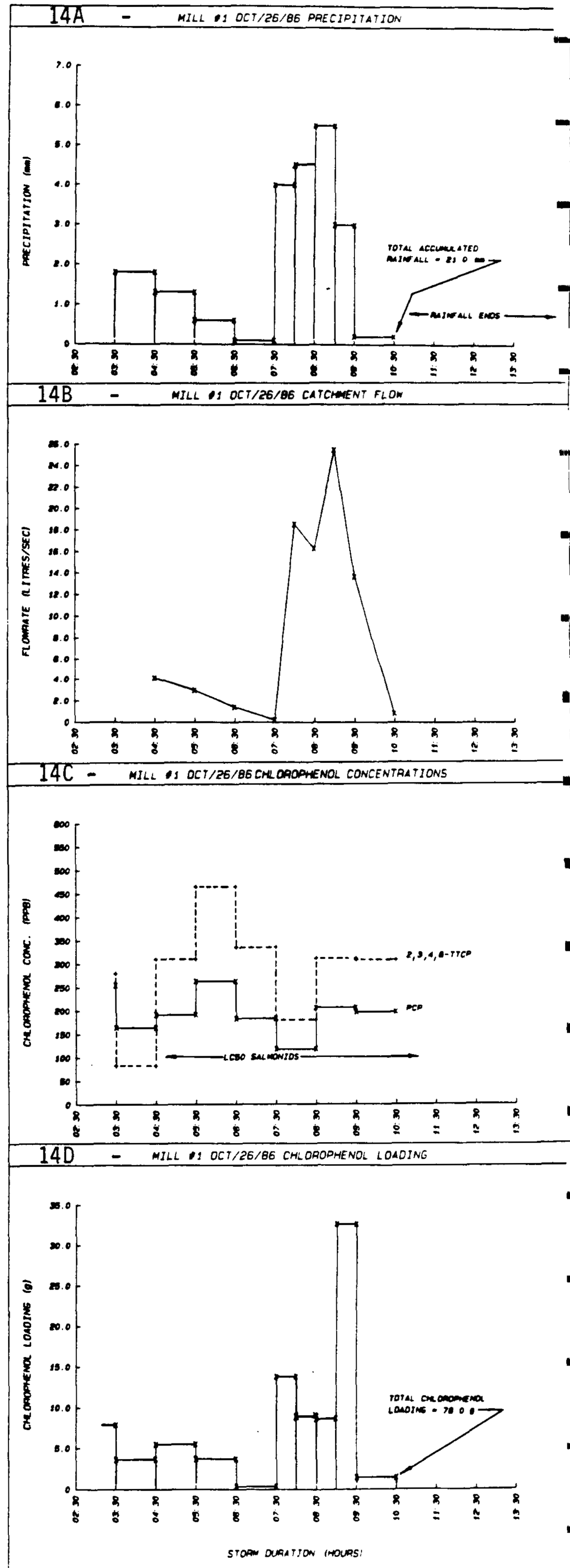


FIGURE 14 MILL #1, OCTOBER 26, 1986 STORM EVENT.

The lumber density was 197 board feet/m^2 and had been subjected to 3.0 mm of rainfall in the previous 24 hours. The high rainfall of the October 26 event did not decrease the average chlorophenol concentration significantly as PCP was 1.75X and TTCP was 3X the LC_{50} (Figure 14C). Total rainfall was 7X the previous day while total loading was 6.7X at 78.0 g total chlorophenols (Figure 14D).

4.3.3 **Mill #4, November 19-20, 1986.** Mill #4 uses a high pressure spray system to treat the rough cut product. A second low pressure spray system at 280 KPa is used for spraying planed product. The spray formulation uses a 30:1 formulation of DIATOX which is 6 466 ppm TTCP and 1 600 ppm PCP (Figure 15).

4.3.3.1 **Precipitation, Flow, Concentration and Loading.** A total precipitation of 44.6 mm in 18.5 hours qualifies this as a 2-4 year storm in which such a rainfall intensity occurs only once in every two to four years (Figure 15A). The precipitation and flow profile show a general direct correlation with the exception that flow far exceeds that which can be calculated based on rainfall and drainage basin area (Figure 15B). The flooding of the entire mill area resulted in obvious spill-over from other basins to the basin being monitored.

Chlorophenol concentrations show two anomolies to the regular pattern observed in most cases: concentration will normally decrease with increase in flows; concentrations decrease with decrease in lumber loading to the drainage basin.

During this storm event the lumber density decreased from 156 boardfeet/m^2 to 75 boardfeet/m^2 over the 12 hours from noon to midnight as lumber was being shipped for export. The storm reached its peak during the period of 19:00 to 22:30 hours at which time the greatest quantity of lumber was removed from the site. The yard workers' break occurred from 20:30-21:30 hours. Just prior to leaving on the break the yard workers observed that the tent shelter (for the technical crew monitoring the storm drain) was about to be blown over by the high winds. To prevent this occurrence several stacks of lumber were deposited by the workers adjacent to the shelter located next to the drain. The wind intensity increased and collapsed the shelter at approximately 21:00 hours. The lumber was removed at the end of the break and placed in the normal storage area well away from the drain at 21:30 hours. The lumber placed by the drain immediately contaminated the runoff raising the concentration 2-4X at the same time the rainfall intensity and runoff reached its peak value (Figure 15C). When the lumber was removed the concentrations quickly returned to normal dilution levels. After the major rainfall peak ended the concentrations rose as dilution over the entire yard decreased. Factors which caused the concentrations to rise after the major rainfall event were (1) the lower volume of lumber left in the basin was freshly exposed when the upper bundles were removed for shipping; (2) the packages left were thoroughly soaked by the high intensity rainfall so that large volumes of concentrated interior and exterior drippings began to leach to the drainage basin.

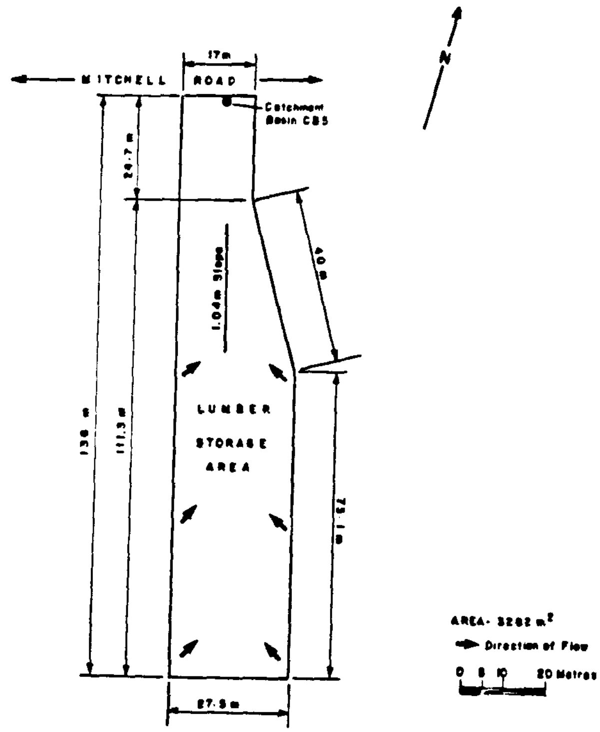
The concentration of PCP and TTCP averaged 2X and 4X the LC_{50} over the entire period of the storm. The total loading of the storm was 140.8 grams of chlorophenols (Figure 15D).

The total volume of contaminated runoff produced in this drainage basin (excluding the quantity due to flooding) is estimated at 146 cubic meters (32 087 gal). The total volume produced on the entire mill storage yard (21,071 m^2) would be 939 m^3 (205,808 gal).

This storm was preceded by an 18 mm/day storm and followed by three days at 14.8, 13.2 and 29 mm for a total 6 day yard volume of 2 566 448 L (564,054 gal) all of which would require storage and/or treatment.

4.3.4 **Mill #5, November 13, 1986.** Planed lumber treated under low pressure spray with a formulation of 20 833 ppm PCP is packaged, strapped, end sealed and stored in a storage yard adjacent to the Fraser River. The time since final treatment was one day to three months with an average storage time of 2 weeks or less. The lumber was exposed to a maximum of 15 mm of rain prior to the test (Figure 16).

4.3.4.1 **Precipitation, Flow,Concentration and Loading.** Precipitation was continuous, light to moderate with a total accumulation of 3.3 mm over 6



LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	827 KPA HIGH PRESSURE SPRAY WITH DIATOX	: 7760 ppm TETRA 1920 ppm PENTA
PLANED CUT	280 KPA LOW PRESSURE SPRAY WITH DIATOX	: 6466 ppm TETRA 1600 ppm PENTA

2) LUMBER TYPE — 70% HEMLOCK/ 30% FIR

3) PACKAGING

LOOSE PACKAGES LUMBER DIMENSIONS	0.05 m x 0.10 m	(2" x 4")
	0.05 m x 0.15 m	(2" x 6")
	0.05 m x 0.20 m	(2" x 8")
	0.05 m x 0.25 m	(2" x 10")
	0.05 m x 0.30 m	(2" x 12")
PACKAGE DIMENSIONS	0.61 m x 0.91 m	(24" x 36")

4) FINAL TREATMENT DATE — VARIOUS

5) DRYING TIME — ZERO TO SEVERAL DAYS, FRESH LUMBER WAS CONTINUALLY BEING ADDED AND REMOVED. THE LUMBER GENERALLY HAS A VARIABLE PERIOD OF AT LEAST SEVERAL HOURS PRIOR TO END SEALING AND STRAPPING.

6) SITE OBSERVATIONS

- DURING THE MONITORING PERIOD A LARGE SHIP MENT OF LUMBER WAS REMOVED FROM THE SITE REDUCING LUMBER DENSITY FROM 46.7 TO 22.9 BOARD METERS/SQ. M. DURING THIS PERIOD THE QUANTITY OF FRESH SURFACE AREA EXPOSED TO THE RAINFALL WOULD HAVE DOUBLED.
- DURING THE PERIOD OF 20:00 - 21:00 SEVERAL STACKS OF LUMBER WERE PLACED ADJACENT TO THE SEWER PROVIDING SHELTER FROM THE HIGH WINDS AND RESULTING IN CONTAMINATION AT THE MONITORING SITE.

7) LUMBER LOADING

AT THE START OF SAMPLING. — 156 BOARD FEET/SQUARE METER.

AT THE END OF SAMPLING. — 75 BOARD FEET/SQUARE METER.

8) TOTAL FLOW VOLUME — 146 377 L (32 241 gal)

9) AVERAGE CONCENTRATIONS — 131 ppb PENTA-CHLOROPHENOLS
211 ppb TETRA-CHLOROPHENOLS
342 ppb TOTAL

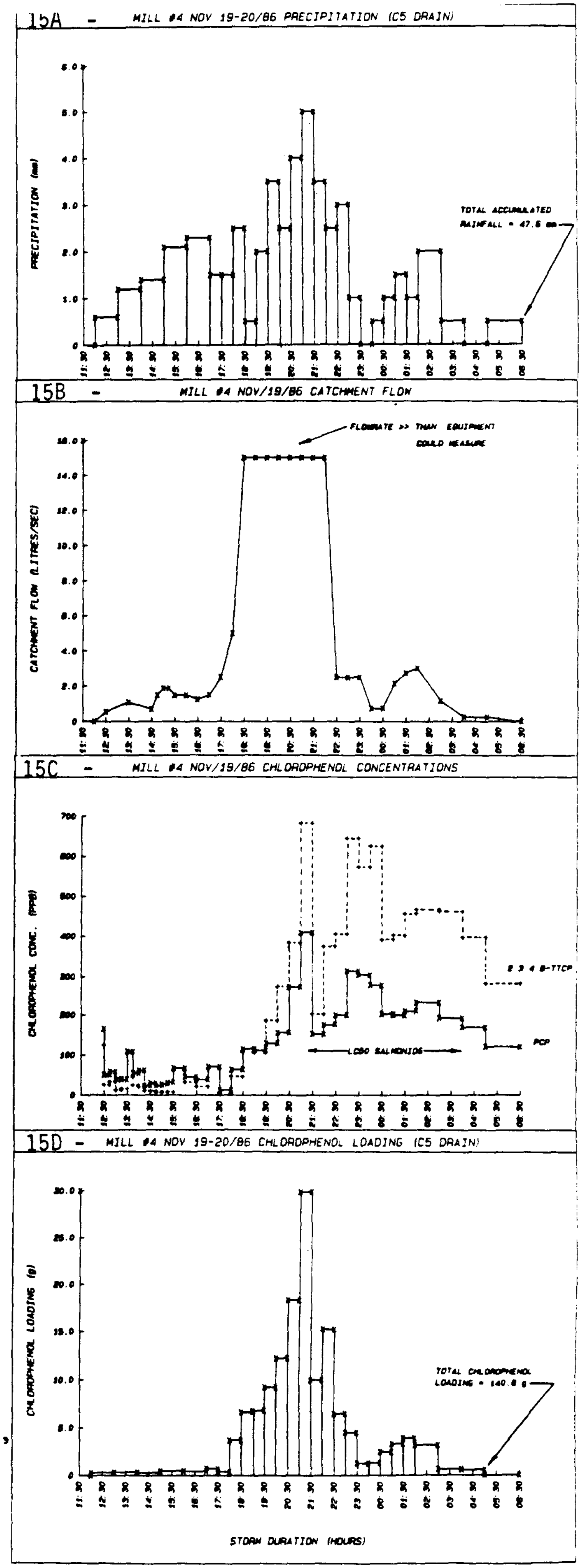
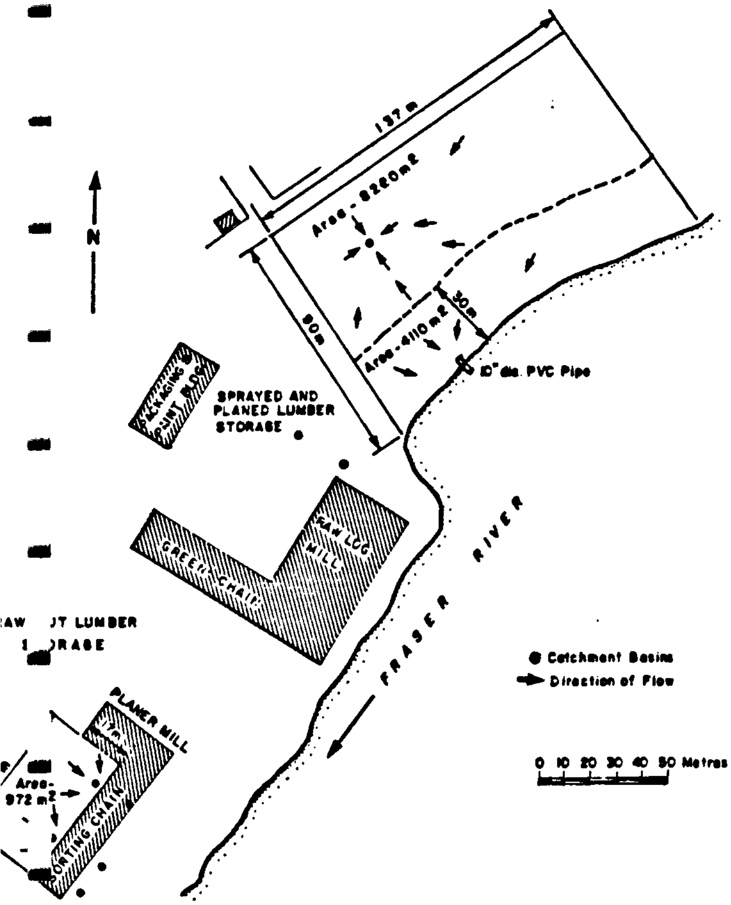
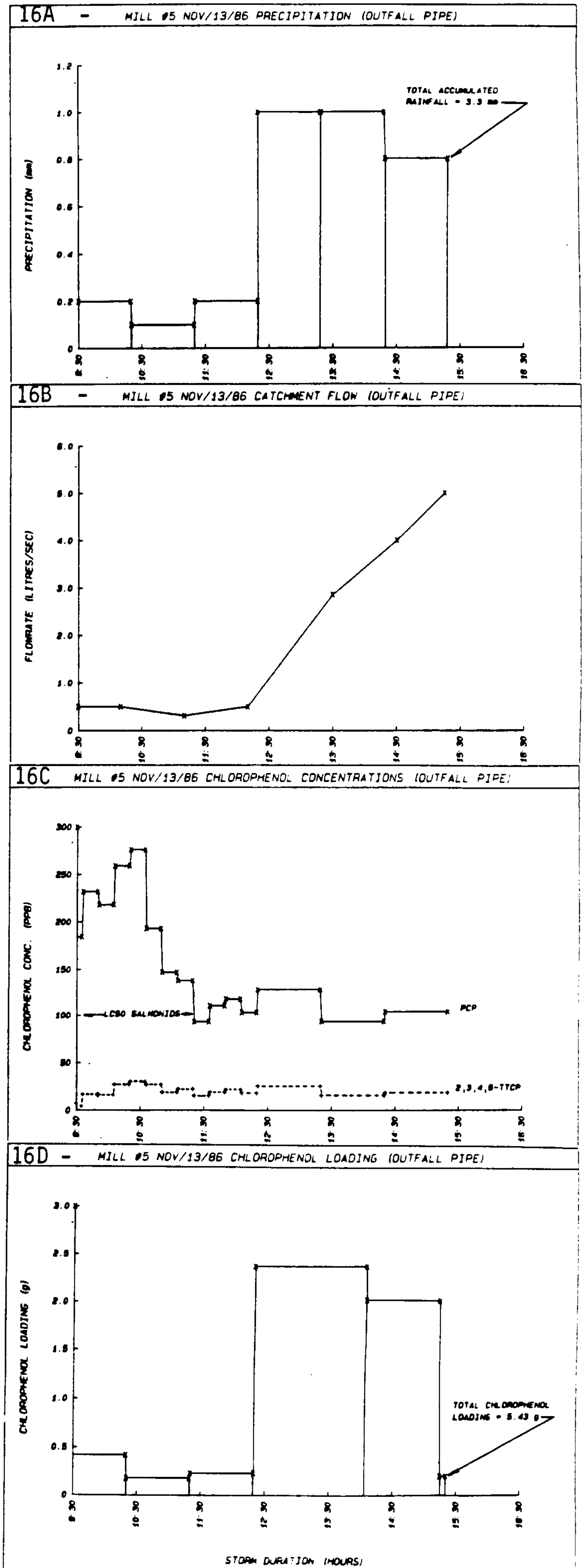


FIGURE 15 MILL #4, NOVEMBER 19 - 20, 1986 STORM EVENT.

hours (Figure 16A). Flow was collected from a paved drainage basin of 8 220 m^2 and discharged directly to the Fraser River with no further dilution. The monitoring was discontinued six hours into the storm event at which time the flow was greater than 5.0 L/s (Figure 16B).

Concentration varied inversely with flow rate averaging 150 ppb PCP over the entire event (Figure 16C). Total chlorophenol loading was 5.43 g (Figure 16D). The lumber loading was estimated at 40 boardmeters per square meter. Total runoff for the storm event over the entire yard is estimated at 27 126 L (5,974 gal).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD		
	ROUGH CUT	NO TREATMENT
	PLANED CUT	CHAPMAN C-1 : 20 833 ppm PCP (20-30%, AVG=25%)
2) LUMBER TYPE		HEMLOCK/FIR
3) PACKAGING		LUMBER IS STRAPPED AND END SEALED FOR SHIPMENT
4) FINAL TREATMENT DATE		VARIABLE - ONE DAY TO THREE MONTHS MAJORITY IS ONE DAY TO TWO WEEKS
5) DRYING TIME		VARIABLE
6) SITE OBSERVATIONS		LUMBER GRADED #2 OR BETTER REMAINS ON THE YARD FOR A MAXIMUM OF 2 WEEKS LUMBER GRADED #3 OR LOWER REMAINS ON THE YARD UP TO THREE MONTHS.
7) LUMBER LOADING		144 BOARD FEET/SQUARE METER
8) TOTAL FLOW VOLUMES		27 126 L (5,974 gal.)
9) AVERAGE CONCENTRATIONS		160 ppb PENTA-CHLOROPHENOL 20 ppb TETRA-CHLOROPHENOL 180 ppb TOTAL

FIGURE 16 MILL #5, NOVEMBER 13, 1986 STORM EVENT.

5 HIGH PRESSURE SPRAYED LUMBER

Spray systems which operate at over two atmospheres (200 Kpa) pressures are considered high pressure systems in this study. High pressure sprayed lumber was monitored under a variety of conditions including:

- Leachate dripping directly from rough cut lumber before further dilution by rainfall. Drying times prior to exposure varied from zero to several days.
- Runoff from mill yards containing wood which was rough cut where drying time prior to exposure varied from zero to 18 days.

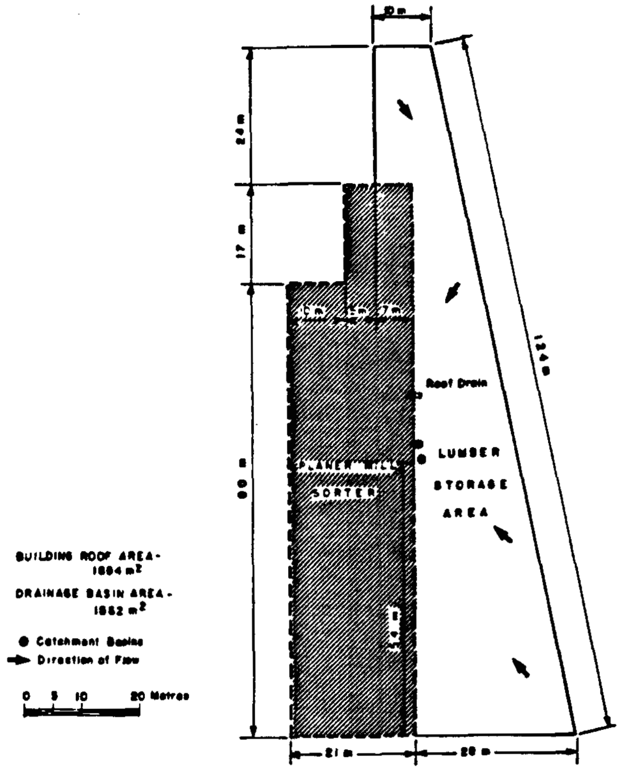
All lumber packages were unstrapped and of varying lengths.

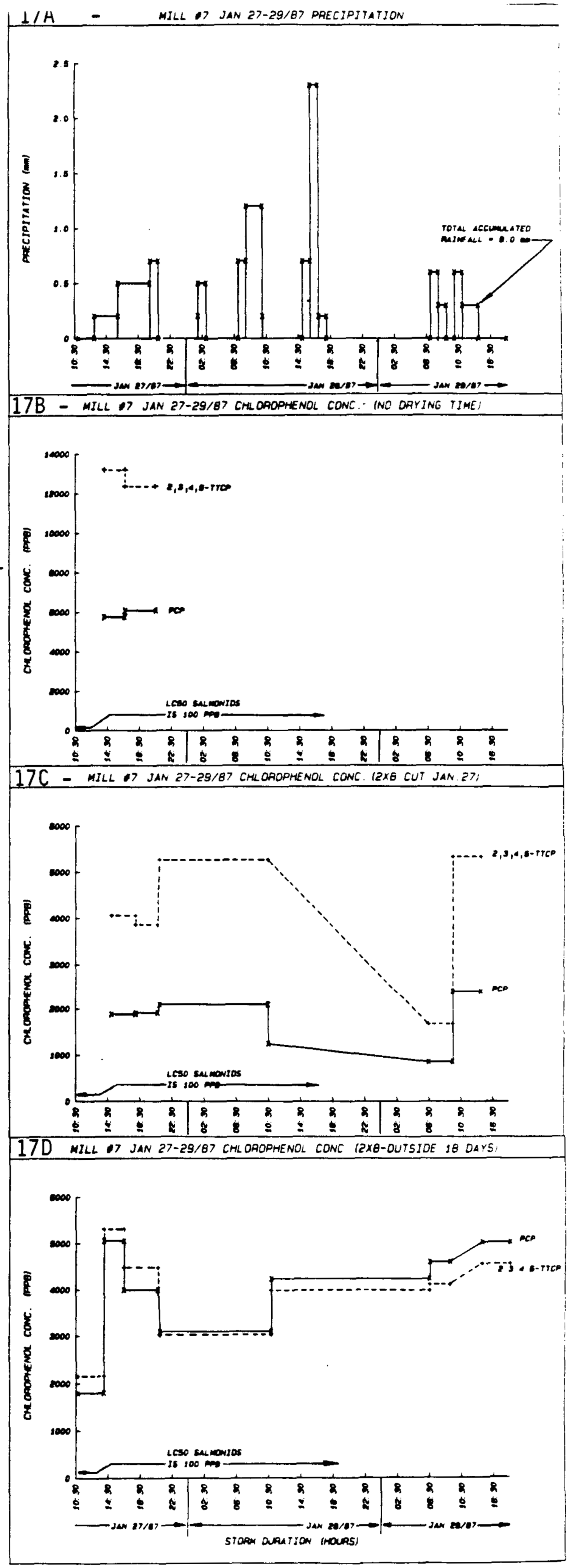
5.1 High Pressure Sprayed Lumber - Undiluted Leachate

A total of 21 samples of undiluted leachate from high pressure sprayed lumber were analyzed for chlorophenols. (Table 3). The average concentrations of 5 899 ppb TTCP and 3 930 ppb PCP, were generated from rough cut lumber with drying times varying from zero to 18 days.

5.1.1 **Mill #7, January 27-29/1987 (Zero Drying Time).** The undiluted leachate dripping from high pressure treated lumber was monitored over a three day period after three different storage times. The rainfall events were the same for all three situations. In general the rainfall consisted of short rainfall events for a total of three day accumulation of 9.0 mm (Figure 17A). Flow rate from the yard and runoff concentrations were not measured.

Leachate from high pressure sprayed lumber with zero drying time is essentially direct washoff of chlorophenate solution from the treated wood. This situation occurred at the timber line where large roughcut timbers (0.15m X 0.15m) were spray treated and discharge via conveyor directly to the exterior sorting yard. Leachate dripping from 2 layers of these timbers had concentrations of 14 000 ppb TTCP and 6 000 ppb PCP. These values were approximately 3X the concentration in leachate from the 24hrs to 18 day old timbers (Figure 17B).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT — 2068 KPA
HIGH PRESSURE SPRAY : 17636 ppm TETRA
WITH DIATOX 4363 ppm PENTA

2) LUMBER TYPE — HEMLOCK/FIR

3) PACKAGING

LOOSE PACKAGES
LUMBER DIMENSIONS — 0.05 m x 0.20 m (2" x 8")

PACKAGE DIMENSIONS — 1.01 m x 1.21 m (40" x 48")

4) FINAL TREATMENT DATE — JANUARY 27,1987

5) DRYING TIME — THE LUMBER MAY EXPERIENCE SEVERAL HOURS OF COVERED STORAGE BEFORE A CONVEYOR SYSTEM MOVES IT OUT ONTO THE YARD.

6) SITE OBSERVATIONS

THE LUMBER IN EACH PACKAGE IS SQUARED ON ONE END AND UP TO 1.1 M DIFFERING LENGTHS ON THE OTHER. THIS EXPOSES A MUCH LARGER SURFACE AREA TO RAINFALL.

7) LUMBER LOADING — WAS NOT RECORDED AS ONLY LEACHING CONCENTRATIONS WERE BEING MEASURED.

8) TOTAL FLOW VOLUME — 16 758 L (3,691 gal) FROM JAN 29-JAN 29/87

FIGURE 17 MILL #7, JANUARY 27 - 29, 1987 STORM EVENT.

5.1.2 Mill #7 January 27-29, 1987 (24-72 hours Drying Time).

Chlorophenol concentrations in stormwater leached from a stack of two packages of lumber which was freshly treated on January 27 was monitored over a three day period to January 29/87 (Figure 17C). There was a gradual increase in clorophenol concentration in the runoff from 12:00 hours January 27 to 18:30 hours January 28. This appears to correlate with the intermittant cycle of rain and dry periods. The concentration in leachate was lowest after the longest dry period from 18:30 hours January 28 to 07:00 hours January 29. Leachate concentrations quickly rose after the lumber became saturated. Concentrations averaged 2 000 ppb for PCP and 4 000 ppb for TTCP from water which leached through two stacks of lumber.

5.1.3 Mill #7 January 27-29, 1987 (18 Days After Treatment).

Leachate from a stack (four packages) of treated 2"X8" rough cut lumber was also monitored for chlorophenols from January 27 to January 29/87 (Figure 17D). This lumber had received a total of 71.7 mm of rainfall from its production date of January 9 to midnight January 26. In this case leachate was collected from the bottom of a stack of four lumber packages.

The concentrations of PCP and TTCP closely paralleled each other and averaged 4 000 ppb each which is similar to the previous case in which only two packages were monitored. As double the quantity of lumber was monitored in this case it appears half the readily leachable chlorophenate had been removed during the nine days on which rainfall was experienced in the 18 day storage period. The nine precipitation free days consisted of two groups of four and five days in which no rainfall occurred and total fixation to the lumber was not achieved in either of these periods.

5.2 High Pressure Sprayed Lumber - Yard Runoff

The yard runoff from two lumber mills storing high pressure sprayed, rough cut lumber was monitored over five storm events. The observations are summarized as follows.

5.2.1 Mill #4 - Center Drain, November 20, 1986. Mill #4 uses one of the most modern high pressure spray systems on the market. The system operates at 827 KPa and uses back flushing to maintain clean nozzles (Figure 18). The lumber in the drainage basin was rough cut which provides a very high surface area due to the surface texture and uneven board length. The lumber packages were unstrapped which allows easier percolation of the rainfall through the interior of the stack.

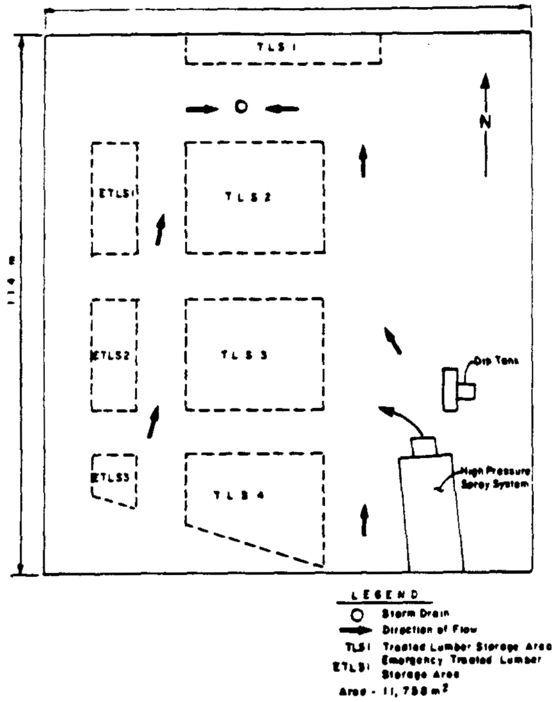
5.2.1.1 Precipitation, Flow, Concentration and Loading. Precipitation was moderate to high averaging 1.2 mm/hr for a total accumulation of 7.0 mm (Figure 18A). Flow rate was responsive to the rainfall pattern peaking at 6 L/s with at total volume 82 306 L (18,089 gal), (Figure 18B).

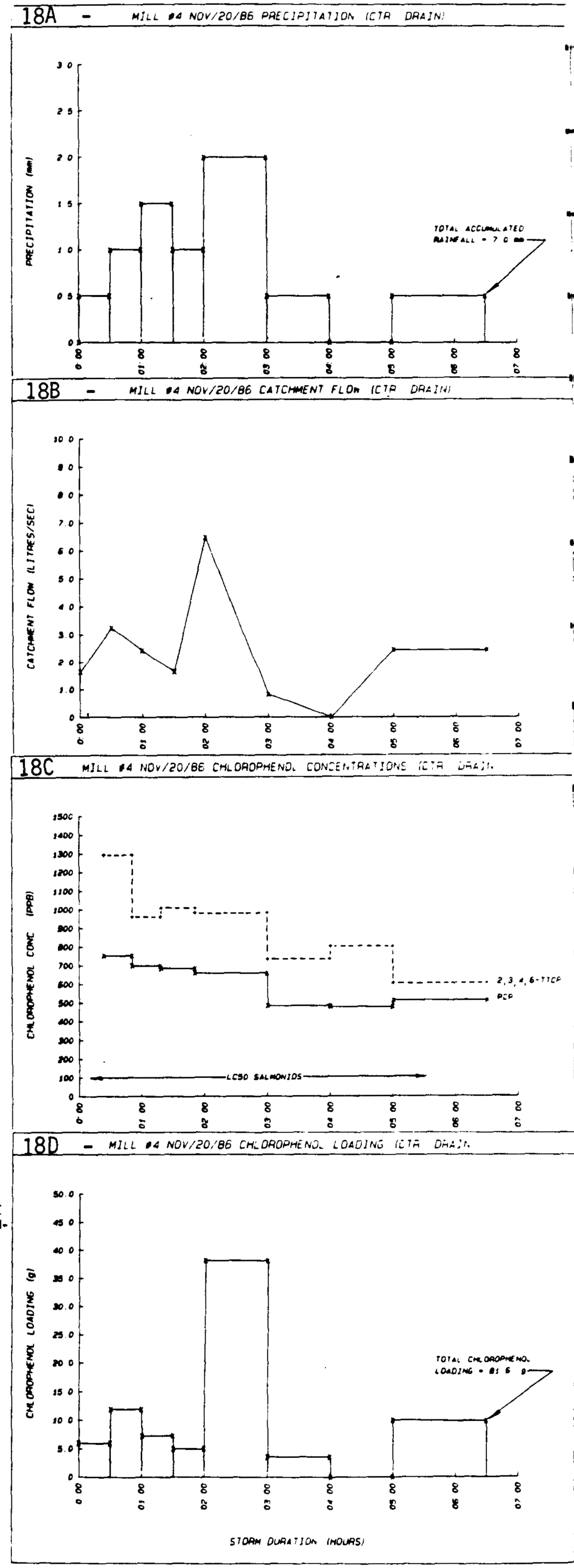
The concentration of PCP averaged 609 ppb PCP, 911 ppb TTCP or 6X and 9X the LC_{50} for salmonids. The total chlorophenol concentration was never less than 1 116 ppb or 11X the LC_{50} (Figure 18C). Total loading was 81.6 g (Figure 18D).

5.2.2 Mill #4 - Center Drain, November 25, 1986. The catchment basin servicing the high pressure sprayed rough cut lumber was monitored for chlorophenols and a bioassay (see Section 8.2) was also conducted on an equal volume composite of the runoff (Figure 19).

5.2.2.1 Precipitation, Flow, Concentration and Loading. Precipitation was continuous over a five hour period with a total accumulation of 3.7 mm (Figure 19A). Flow rate was responsive to the precipitation with little lag times or continuation of flow after the end of the rainfall period (Figure 19A vs. Figure 19B).

The concentrations of PCP averaged 305 ppb and TTCP averaged 742 ppb (Figure 19C). These high concentrations are likely caused by the large surface area of the rough cut lumber which provides greater exposure to rainfall. Loading was significant at 36.9 g for the storm event (Figure 19D).





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	827 KPA HIGH PRESSURE SPRAY WITH DIATOX	 : 7760 ppm TETRA 1920 ppm PENTA

2) LUMBER TYPE — 70% HEMLOCK/ 30% FIR

3) PACKAGING

LOOSE PACKAGES LUMBER DIMENSIONS	0.05 m x 0.10 m	(2" x 4")
	0.05 m x 0.15 m	(2" x 6")
	0.05 m x 0.20 m	(2" x 8")
	0.05 m x 0.25 m	(2" x 10")
	0.05 m x 0.30 m	(2" x 12")
PACKAGE DIMENSIONS	1.01 m x 1.21 m	(40" x 48")

4) FINAL TREATMENT DATE — VARIOUS

5) DRYING TIME — ZERO TO SEVERAL DAYS, FRESH LUMBER WAS CONTINUALLY BEING ADDED AND REMOVED. THE LUMBER GENERALLY HAS A VARIABLE PERIOD OF DRYING TIME IN COVERED SORTING BINS.

6) SITE OBSERVATIONS

- THE LUMBER IN EACH PACKAGE IS SQUARED ON ONE END AND UP TO 1.1 M DIFFERING LENGTHS ON THE OTHER. THIS EXPOSES A MUCH LARGER SURFACE AREA TO RAINFALL.
- TO OBTAIN PROPER COVERAGE THE HIGH PRESSURE SPRAY FORMULATION REQUIRES TWICE THE CONCENTRATION AS OTHER APPLICATION METHODS.

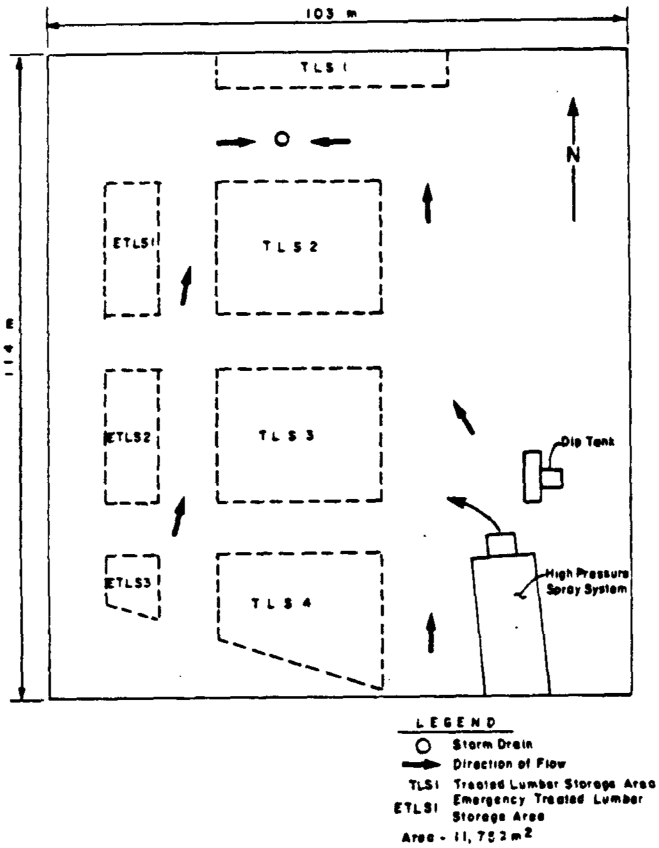
7) LUMBER LOADING — 73 BOARD FEET/SQUARE METER.

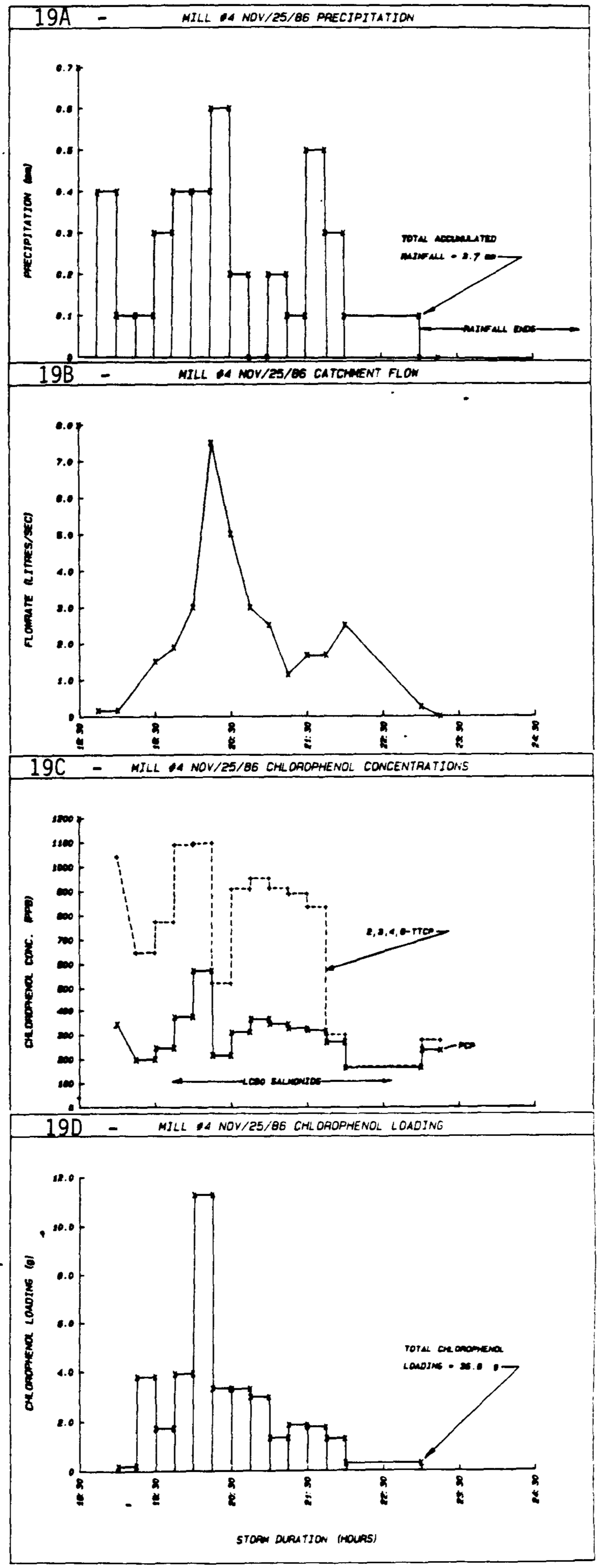
8) TOTAL FLOW VOLUME — 82 306 L (18129 gal)

9) AVERAGE CONCENTRATIONS — 609 ppb PENTA-CHLOROPHENOL
911 ppb TETRA-CHLOROPHENOL

1 520 ppb TOTAL

FIGURE 18 MILL #4, NOVEMBER 20, 1986 STORM EVENT.





LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	827 KPA HIGH PRESSURE SPRAY WITH DIATOX	: 7760 ppm TETRA 1920 ppm PENTA

2) LUMBER TYPE — 70% HEMLOCK/ 30% FIR

3) PACKAGING

LOOSE PACKAGES LUMBER DIMENSIONS	0.05 m x 0.10 m	(2" x 4")
	0.05 m x 0.15 m	(2" x 6")
	0.05 m x 0.20 m	(2" x 8")
	0.05 m x 0.25 m	(2" x 10")
	0.05 m x 0.30 m	(2" x 12")
PACKAGE DIMENSIONS	1.01 m x 1.21 m	(40" x 48")

4) FINAL TREATMENT DATE — VARIOUS

5) DRYING TIME — ZERO TO SEVERAL DAYS, FRESH LUMBER WAS CONTINUALLY BEING ADDED AND REMOVED. THE LUMBER GENERALLY HAS A VARIABLE PERIOD OF DRYING TIME IN COVERED SORTING BINS.

6) SITE OBSERVATIONS

- THE LUMBER IN EACH PACKAGE IS SQUARED ON ONE END AND UP TO 1.1 M DIFFERING LENGTHS ON THE OTHER. THIS EXPOSES A MUCH LARGER SURFACE AREA TO RAINFALL.
- TO OBTAIN PROPER COVERAGE THE HIGH PRESSURE SPRAY FORMULATION REQUIRES TWICE THE CONCENTRATION AS OTHER APPLICATION METHODS.

7) LUMBER LOADING — 73 BOARD FEET/SQUARE METER.

8) TOTAL FLOW VOLUME — 39 017 L (8594 gal)

9) AVERAGE CONCENTRATIONS — 305 ppb PENTA-CHLOROPHENOL
742 ppb TETRA-CHLOROPHENOL

1 047 ppb TOTAL

FIGURE 19 MILL #4, NOVEMBER 25, 1986 STORM EVENT.

5.2.3 **Mill #4, Center Drain, December 20-21, 1986.** The catchment basin servicing the high pressure sprayed lumber was monitored during a rainfall approximately 1.8X the average intensity and 2.6X the duration of the November 25 storm (Figure 20).

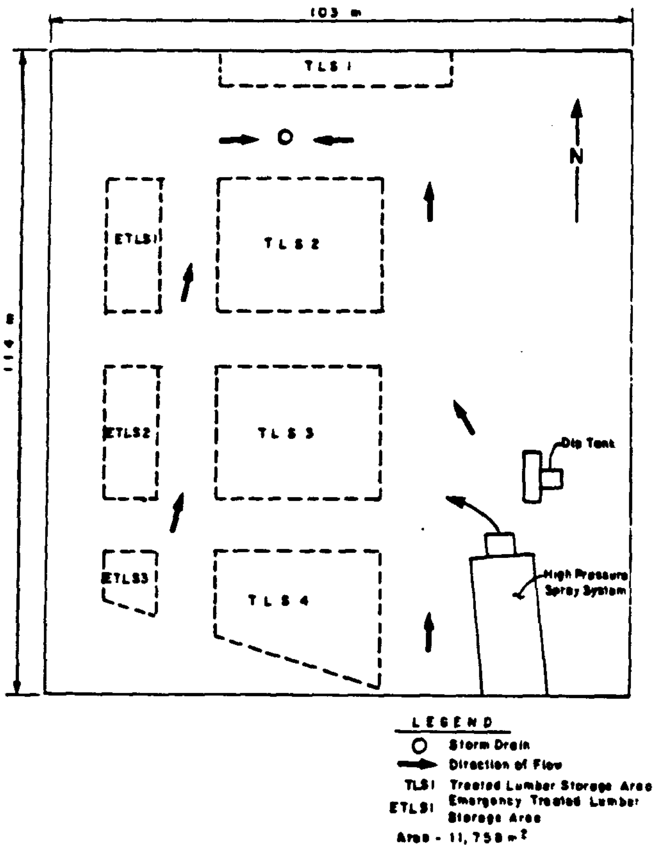
5.2.3.1 **Precipitation, Flow, Conductivity, Concentration, and Loading.** Precipitation was continuous and of moderate to heavy intensity over the 12 hour period with a total accumulation of 15.0 mm (Figure 20A). Flows were very responsive and correlated directly to rainfall intensities (Figure 20A vs. Figure 20B).

The total chlorophenate concentrations averaged 1 968 ppb and were never lower than 10X the LC_{50} for salmonids (Figure 20C). This high concentration combined with high flow resulted in a very high loading of 140.8 g over the monitoring period (Figure 20D).

5.2.4 **Mill #7, January 23, 1987.** Mill #7 uses a modern high pressure spray system which operates at 2 068 KPa. Back flushing spray nozzles were not installed in this system. The drainage basin monitored is used for storing large dimension timbers immediately after treatment is applied (Figure 21).

5.2.4.1 **Precipitation, Flow, Concentration and Loading.** Precipitation was light and steady over the monitoring period with total accumulation of 2.8 mm over six hours (Figure 21A). Flow rate did not correlate as well to precipitation as in many other locations and there were no apparent reason why the peak at 15:30 occurred (Figure 21B).

The lumber had been in the drainage basin for an extended period of time and received at least 7.8 mm of rainfall prior to the test. The mill was switching from cedar production to white wood so that new timbers began to be added to the drainage basin at approximately 10:30 hours. These timbers were distributed one at a time around the basin being sorted according to length. Most of the runoff was therefore generated from aged timbers. The concentration averaged 1 000 ppb for PCP and trace quantities of TTCP (Figure 21C). Total loading was 1.94 g which corresponds to the light rainfall and low flow rates (Figure 21D). This effluent discharges directly to the Fraser River.



LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD

ROUGH CUT	827 KPA HIGH PRESSURE SPRAY WITH DIATOX	: 7760 ppm TETRA 1920 ppm PENTA

) LUMBER TYPE — 70% HEMLOCK/ 30% FIR

) PACKAGING

LOOSE PACKAGES		
LUMBER DIMENSIONS	0.05 m x 0.10 m	(2" x 4")
	0.05 m x 0.15 m	(2" x 6")
	0.05 m x 0.20 m	(2" x 8")
	0.05 m x 0.25 m	(2" x 10")
	0.05 m x 0.30 m	(2" x 12")
PACKAGE DIMENSIONS	1.01 m x 1.21 m	(40" x 48")

) FINAL TREATMENT DATE — VARIOUS

5) DRYING TIME — ZERO TO SEVERAL DAYS, FRESH LUMBER WAS CONTINUALLY BEING ADDED AND REMOVED. THE LUMBER GENERALLY HAS A VARIABLE PERIOD OF DRYING TIME IN COVERED SORTING BINS.

SITE OBSERVATIONS

- THE LUMBER IN EACH PACKAGE IS SQUARED ON ONE END AND UP TO 1.1 M DIFFERING LENGTHS ON THE OTHER. THIS EXPOSES A MUCH LARGER SURFACE AREA TO RAINFALL.
- TO OBTAIN PROPER COVERAGE THE HIGH PRESSURE SPRAY FORMULATION REQUIRES TWICE THE CONCENTRATION AS OTHER APPLICATION METHODS.

LUMBER LOADING — 73 BOARD FEET/SQUARE METER OR SLIGHTLY HIGHER AS AN ACTUAL COUNT WAS NOT MADE.

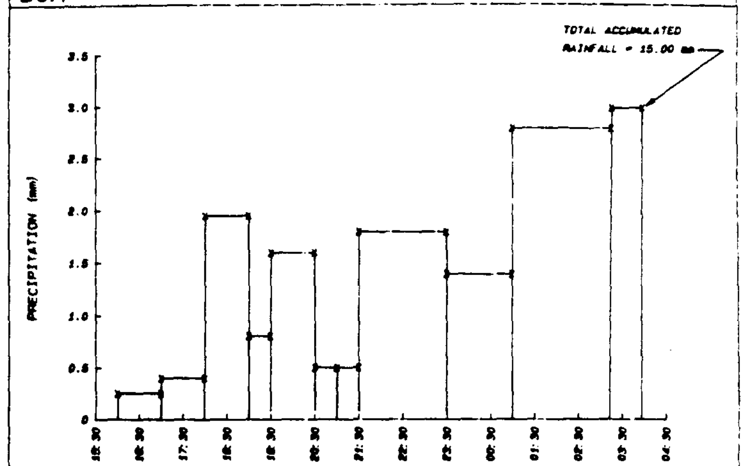
8) TOTAL FLOW VOLUME — 169 482 (37 330 gal)

9 AVERAGE CONCENTRATIONS — 740 ppb PENTA-CHLOROPHENOL
1 228 ppb TETRA-CHLOROPHENOL

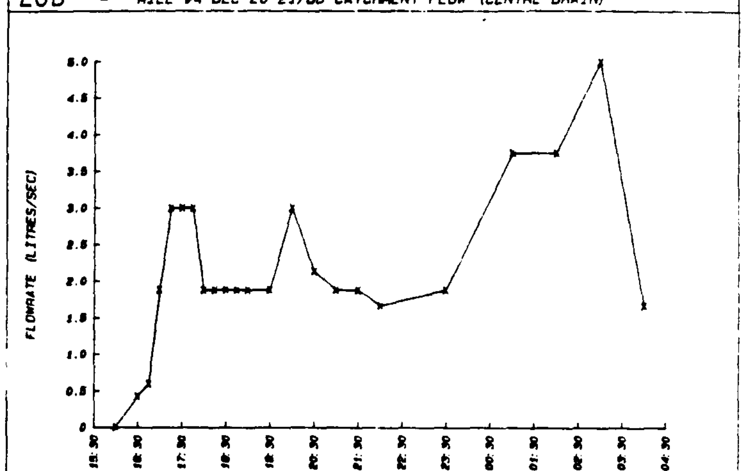
1 968 ppb TOTAL

IGURE 20 MILL #4, DECEMBER 20 - 21, 1987 STORM EVENT.

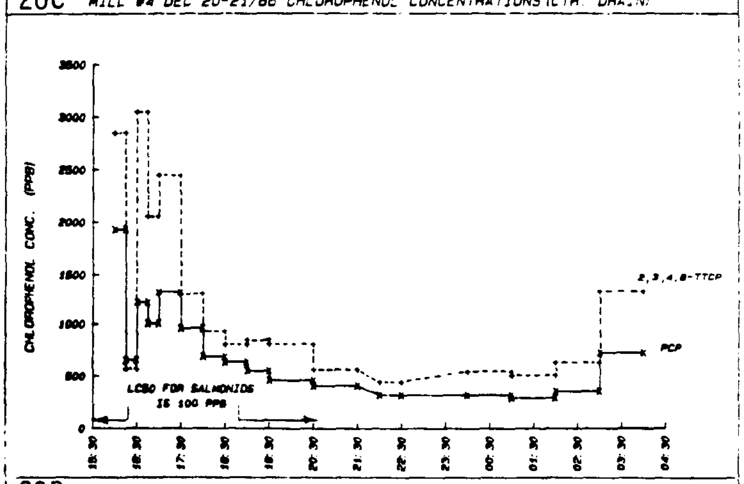
20A - MILL #4 DEC 20-21/86 PRECIPITATION (CENTRE DRAIN)



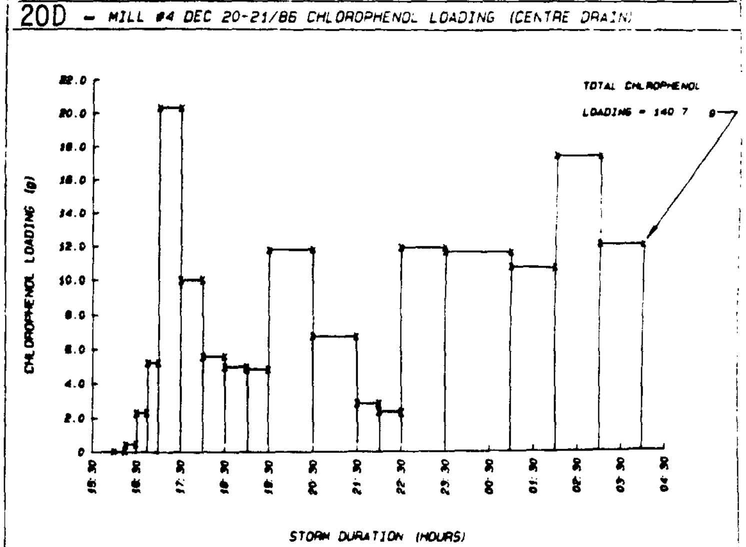
20B - MILL #4 DEC 20-21/86 CATCHMENT FLOW (CENTRE DRAIN)

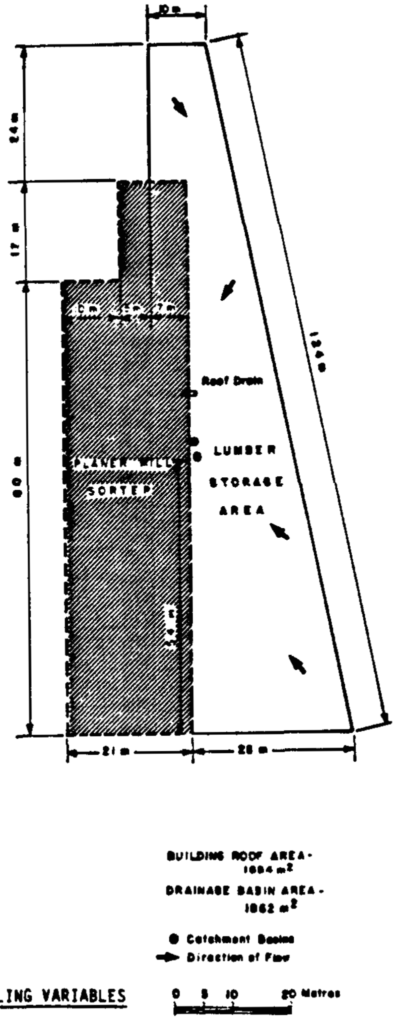


20C MILL #4 DEC 20-21/86 CHLOROPHENOL CONCENTRATIONS (CTR. DRAIN)



20D - MILL #4 DEC 20-21/86 CHLOROPHENOL LOADING (CENTRE DRAIN)

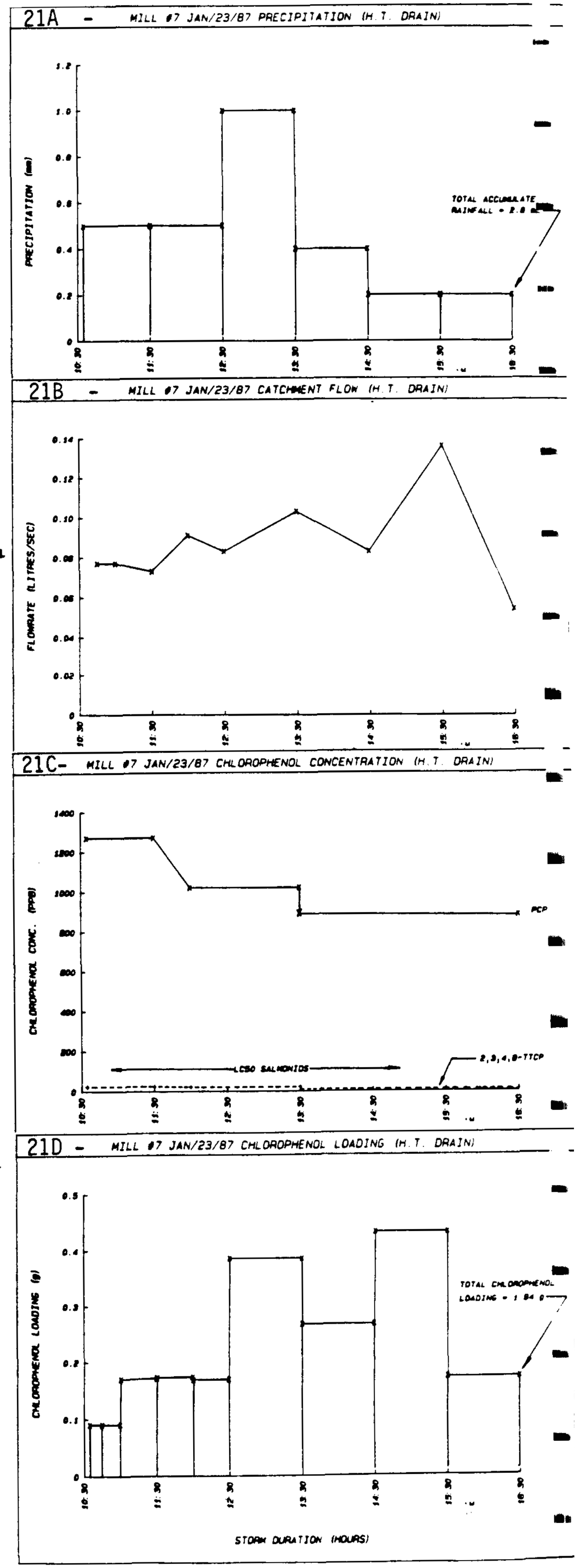




LUMBER TREATMENT AND HANDLING VARIABLES

1) APPLICATION METHOD	
ROUGH CUT	2068 KPA HIGH PRESSURE SPRAY : 17 636 ppm TETRA WITH DIATOX 4 262 ppm PENTA
2) LUMBER TYPE	HEMLOCK/FIR
3) PACKAGING	
LOOSE PACKAGES LUMBER DIMENSIONS	0.15 m x 0.15 m (6" x 6")
PACKAGE DIMENSIONS	VARIOUS
PACKAGE LENGTH	2.0 m - 8.0 m (6.5 FT. - 26 FT)
QUANTITY	5 234 BOARD METERS (18,319 BOARD FEET)
4) FINAL TREATMENT DATE	JANUARY 23, 1987
5) DRYING TIME	THE CURRENT STOCK OF LUMBER HAD BEEN IN THE DRAINAGE BASIN FOR SEVERAL DAYS TO WEEKS AND HAD BEEN EXPOSED TO 7.4 mm of RAIN. NEW LUMBER IS EXPOSED TO RAINFALL IMMEDIATLY AFTER TREATMENT.
6) SITE OBSERVATIONS	
	MINOR DRIPPING WAS CONTINUOUS BY 12:00.
7) LUMBER LOADING	23.5 BOARD FEET/SQUARE METER
8) TOTAL FLOW VOLUME	5 244 L (1,148 gal)
9) AVERAGE CONCENTRATIONS	1 056 ppb PENTA-CHLOROPHENATES 17 ppb TETRA-CHLOROPHENATES
	1 073 ppb TOTAL

FIGURE 21 MILL #7, JANUARY 23, 1987 STORM EVENT.



6 TOTAL RUNOFF AND CHLOROPHENOL LOADING ESTIMATES

Total runoff and chlorophenol loading estimates must incorporate a number of factors including, rainfall duration, intensity and frequency, lumber treatment method, surface and packaging characteristics, storage times and handling characteristics.

6.1 Observations and Assumptions Regarding Loading Estimates

Total loading and runoff calculations were based on the following observations which became apparent during the monitoring study.

1. A measurable rainfall will result in a measurable chlorophenol runoff.

   This is due to the fact that there is no such thing as an uncontaminated storage yard (i.e. the very first rainfall runoff on a brand new storage yard is considered uncontaminated runoff). Leaching from the exposed surfaces of the lumber stacks which are not leveled will begin within 1-2 mm of rainfall. When the runoff reaches the paved surface of the storage yard the yard will become contaminated. Leachate dripping from the lumber after the storm has ended will be highly contaminated with chlorophenols. This leachate will dry leaving a film of CP's on the yard. Upon the start of the next (even minor) storm event the runoff will immediately be highly contaminated from residual CP's on the yard. In most cases this becomes diluted until the event has progressed to the point where new leachate from the lumber is added to the yard runoff.

2. There is a constant (static) mix of treated lumber on the mill yard.

   The mill storage yard can be considered a fixed space which has a mass of lumber entering and leaving resulting in a relatively constant volume averaged over a given period of time. Lumber on the yard will be of various ages in exposure however the results show that chlorophenols continue to leach even after multiple rainfall exposures. The leach rate from a stack will decrease with time, however, a given stack of lumber will be removed from the yard and be replaced with a new stack. This will reinforce the supply of leachable material. Averaged over time a constant concentration of CP's over the yard can be expected.

3. Rainfall intensities and durations are significant factors in the short term.

It was apparent that increases in rainfall intensity and duration were a significant factor in increasing the quantities leached. This was especially evident when the lumber stacks became thoroughly soaked on the inner surfaces of the packages. Short duration, high intensity events will increase total loading although average concentrations will not necessarily be significantly higher due to the dilution effect of the high volumes of runoff.

4. Rainfall intensities and durations are not significant factors over the longer term.

Chlorophenols leached from lumber during a high intensity event and remaining on the yard after the end of the event will be washed away by a low intensity event following. The initial low concentration/high volume event can be followed by a high concentration/low volume event therefore an averaged concentration generated per millimeter of rainfall can be assumed.

5. Concentration in runoff is significantly affected by surface texture and packaging of the lumber.

It was found that the surface area of rough cut lumber is increased by the varying lengths of boards which are loosely packed (i.e. unstrapped) which agrees with findings by Cserjesi et. al. (5). A reduction in leachable surface area occurs when the boards are planed to a smoother surface, cut to the same length and tightly strapped. Average runoff concentrations should be calculated separately for these lumber types.

6. Total annual loading should be calculated using the appropriate average total precipitation and the storage yard area for the specific lumber type.

Runoff from the tops and sides of lumber packages occurs within 1.0-1.5 mm of continuous rainfall. The packages will absorb a portion of all rainfall striking it, however, after the exterior surface has been saturated the water absorbed by the packages will be negligible when compared to the total volume falling on the yard. It was found that the actual flow measured was approximately equivalent to rates calculated from rainfall accumulation. Therefore, the annual average rainfall monitored by the federal Atmospheric Environment Service should be used for calculation of total loading. Average runoff concentrations for the specific drainage basin should be used (Table 4). The loadings for each drainage basin type should be aggregated for a total mill loading.

7. Immediate washoff loading should be calculated separately.

Immediate washoff occurs at mills which treat the lumber and expose it to rainfall in an unroofed and uncontained catchment basin. These concentrations are found to be extremely high. The annual exposure should consider the number of rainfall days and the number of operational days per year as the washoff situation exists largely when the planer mills are operating.

6.2 Average Total Chlorophenol Concentrations in Storm Water Runoff From Various Lumber Treatment Scenarios

Total chlorophenol concentrations in drainage basin runoff was affected by various factors and was divided into five basic groups. The mean chlorophenol concentrations listed in Table 4 were generated from data collected at the study mills. These values can be used to estimate loadings for other regions that use similar technology.

TABLE 4 AVERAGE TOTAL CHLOROPHENOL CONCENTRATIONS IN STORM WATER RUNOFF BASED ON TREATMENT METHOD AND LUMBER CHARACTERISTICS

TREATMENT METHOD AND LUMBER CHARACTERISTICS	TOTAL CHLOROPHENOL CONCENTRATIONS PARTS PER BILLION (ug/l)			
	n	- S.D.	$\bar{x}$	+ S.D.
Dipped Lumber, Rough Cut, Drip Time Greater Than 24 Hours*	1	-	258	-
Dipped Lumber, Planed, Strapped and End Sealed, Greater Than 24 Hours Storage	3	322	443	564
Low Pressure Sprayed Lumber, Unstrapped, No Drying Time	6	2 069	13 562	25 055
Low Pressure Sprayed Lumber, Planed, Strapped, End Sealed, Greater Than 24 Hours Storage	3	328	456	559
High Pressure Sprayed Lumber, Rough Cut Unstrapped	4	967	1,402	1,837

n = number of samples, $\bar{x}$ = arithmetic mean, S.D. = Standard deviation

6.2.1 Dipped Lumber - Rough Cut, Drip Time Greater Than 24 Hours.

At the site used for monitoring dipped rough cut lumber it was difficult to determine the time period lumber was stored in the basin or the drainage patterns for the yard. The runoff discharged at several locations and a composite of all these discharges was impossible to collect. In the basin which was monitored the value of 258 ppb is suspected to be a low value, and a poor representation of the average concentration over the entire yard.

6.2.2 Dipped Lumber - Planed, Strapped and End Sealed, Greater Than 24 Hours Storage.

Similar difficulties mentioned in 6.2.1 were experienced at this site in addition to repeated theft of sampling equipment. The average total chlorophenol concentration in storm water runoff for the two storm events monitored was 443 $\pm$ 121 ppb and is also considered low. It was found that a significant proportion of the lumber had been in the basin over several storm events and that less than 40% was freshly treated lumber.

6.2.3 **Low Pressure Sprayed Lumber - Unstrapped, Varying Lengths, Zero Drying Time.** Lumber which is sprayed by a low pressure spray system and immediately exposed to rainfall yields significant washoff with an average concentration of 13 562 ± 11 493 ppb. The areas where this occurs is small relative to the mill yard size accounting for less than 2% of the total storage area in the lower Fraser River Watershed, however it accounts for up to 20% of the total loading of chlorophenols. These areas are generally found at the sorting chains of rough cut or planer mills.

6.2.4 **Low Pressure Sprayed Lumber - Planed, Strapped, End Sealed, Greater Than 24 Hours Dry Storage Time.** Of the total number of chlorophenols process units in operation, 68% are low pressure spray systems (7). In general the lumber treated by this method will have some period of covered storage. For lumber which had 24 hours to 8 days of dry storage time the yard runoff was found to average 456 ± 103 ppb total chlorophenols.

6.2.5 **High Pressure Sprayed Lumber - Rough Cut, Unstrapped.** Of the total number of chlorophenol process units in operation 4% are high pressure spray systems. The number of new systems coming into operation will increase as mills modernize. The high pressure systems within the study group of mills were used to treat rough cut lumber only. There is no data on high pressure sprayed planed lumber. The rough cut boards are stacked with varying lengths on one end and are unstrapped. The rough texture of the lumber provides greater surface contact with the water and the loose packaging allows easier interior wetting of the lumber package. The average concentration of total chlorophenols at such sites was found to be 1 402 ± 435 ppb.

6.3 Annual Total Runoff and Chlorophenol Loading to the Study Areas

Total runoff and chlorophenol loading was estimated for the three regions, Fraser River, Burrard Inlet and Howe Sound based on rainfall and lumber production criteria unique to each area. In general there are 25 to 27 mills capable of treating lumber in the Lower Fraser watershed, two in Burrard Inlet and two in Howe Sound at Squamish. Not all mills continually process treated lumber. Certain mills will exclusively cut cedar for portions of the year or for a whole year depending on market demand and thus the storage area used for such treated lumber will be reduced. The loading estimates for the Fraser River were based on the following:

- Where the actual storage yard area was not known an average total yard area of 22 370 m^2 was assumed (based on yard sizes from mills surveyed);
- Where a storage area of 22 370 m^2 was assumed this was multiplied by a factor of ½ to a value of 11 185 m^2 to account for partial usage of other wood species or new usage;
- The sum of the storage areas in each basin which was used for low pressure sprayed lumber was multiplied by a factor of 1.1 to account for lumber in transit or stored at other locations including retail lumber yards. The 1.1 factor was added as a result of finding treated lumber at retail lumber yards and the movement of lumber to export terminals and rail yards for shipment;
- The total runoff volumes were calculated in three annual total precipitation percentile values of 5%<, 50%< and 95%<.

The term "5%<" means that 5% of the annual total precipitation values will be less than the given value. The 50%< is essentially the mean total precipitation value for the region.

The total loading values are calculated using the following formula:

Low Year = (x - S.D.) x [5%<]
Average Year = (x) x [50%<]
High Year = (x + S.D.) x [95%<]

Where x = The arithmetic mean of the total chlorophenol concentration for the lumber type listed in Table 4.

Where S.D. = The standard deviation of the concentration assuming a normal distribution for the sample. (This was verified using the students T test at a 95% probability confidence limit.)

[95%<] = Annual flow rate accounting for the sum total of the drainage basin sizes for types listed in Table 4 and annual rainfall data listed in Table 1.

6.3.1 Annual Runoff and Chlorophenol Loading to the Lower Fraser River.

The lower Fraser River from Kanaka Creek to the mouth at Georgia Strait was divided into three areas as listed in Table 5. This was to account for the 50%< rainfall value which varied from 1 094 mm at Vancouver Airport to 1 923 mm at Whonnock. The runoff volumes generated were from 489 092 m^3/yr to 775 794 m^3/yr for a total chlorophenol loading of 226 kg/yr to 916 kg/yr.

6.3.2 Annual Runoff and Chlorophenol Loading to Burrard Inlet.

The two export terminals at Burrard Inlet near Second Narrows are located in a high rainfall area. Export terminals have a mix of wrapped, low pressure sprayed, high pressure sprayed and dipped lumber distributed throughout the terminal. Virtually all the lumber is planed, strapped and end sealed. Total runoff value for Burrard Inlet will range from 511 257 m^3 to 848 786 m^3 with a total chlorophenol loading of 205 to 523 kg per year. These yards are adjacent to marine waters and contain their own drainage systems. Further dilution will not occur before discharge to the receiving environment.

6.3.3 Annual Runoff and Chlorophenol Loading to Howe Sound at Squamish.

Runoff to Howe Sound at Squamish is generated from one lumber mill and export terminal which discharges directly to estuarine waters. The runoff volume will range from 164 749 m^3/yr to 260 895 m^3/yr. Rainfall is very high in this area at 2 222 mm/yr and the runoff volume will range from 164 749 m^2/yr. Total chlorophenol loading is estimated at 85 kg/yr.

TABLE 5 ANNUAL STORM WATER RUNOFF VOLUMES AND TOTAL CHLOROPHENOL LOADINGS

AREA	ANNUAL RUNOFF VOLUME (m^3/yr)			ANNUAL CHLOROPHENOL LOADING (kg/yr)		
	5%<	50%<	95%<	5%<	50%<	95%<
FRASER RIVER AT:						
- Whonnock/Pitt Meadows	146 487	198 796	215 336	62	158	252
- Surrey/New Westminster	177 856	243 578	299 563	72	148	240
- Burnaby/Vancouver/Richmond	164 749	215 388	260 895	92	193	320
Total: Fraser River	489 092	657 762	775 794	226	499	916
Burrard Inlet	511 257	678 875	848 786	205	346	523
Squamish	157 867	194 878	244 519	85	140	223

5%< = 5% of the annual totals will be less than the given value
50%< = 50% of the annual totals will be less than the given value
95%< = 95% of the annual totals will be less than the given value

6.4 Simulation of Discharge Plumes of Contaminated Storm Water

The discharge plume profile of a typical storm runoff from a lumber yard containing high pressure sprayed rough lumber, dipped rough lumber and low pressure sprayed lumber was simulated using the Motz-Benedict (MOBEN) Model for effluent discharge to a river (3) (Figure 22).

This model is applicable to simulation of a surface plume free from the shore and river bottom and is valid for low ambient currents where the buoyant discharge is low as defined by the jet Richardson number. (Where jet velocity should be greater or equal to twice the ambient river velocity.)

This model assumes that the jet is two dimensional, that the flow regime is completely turbulent and that tracer (chemical) concentration change other than by mixing is negligible.

6.4.1 Assumptions Made Regarding Storm Runoff.

The flow characteristics of the storm runoff were assumed under the following worst case conditions on the lower Fraser River which is strongly affected by tides.

- A storm of 7.0 mm intensity over six hours begins just after the tide gates are closed by a flood tide. The flood covers the gate for six hours backing up all runoff water.
- Flow from the tide gate will begin when the air lock is broken by the falling river level on ebb tide.
- Initial flow is very high (0.34 m^3/s) and of short duration. River velocity is low at 0.10 m/s.
- Second stage flow is one half initial flow at 0.17 m^3/s and river velocity is still 0.10 m/s.
- Third stage flow is 40% of first stage flow at 0.14 m^3/s and river velocity is increasinng to 0.15 m/s.
- The runoff concentration for all stages of flow is 1 200 ppb total chlorophenol which was typical of flow found at an actual site.
- The flow of the plume into the river is plotted for three concentration contours (isocons) of 50 ppb, 100 ppb and 200 ppb total chlorophenol (Figure 22).

6.4.2 **Runoff Simulations #1, #2, #3.** The initial high flow velocity of the outfall and low flow velocity of the river allows the plume to push up to 26 m into the river for the 200 ppb isocon, 42 m for the 100 ppb isocon and 56 m for the 50 ppb isocon.

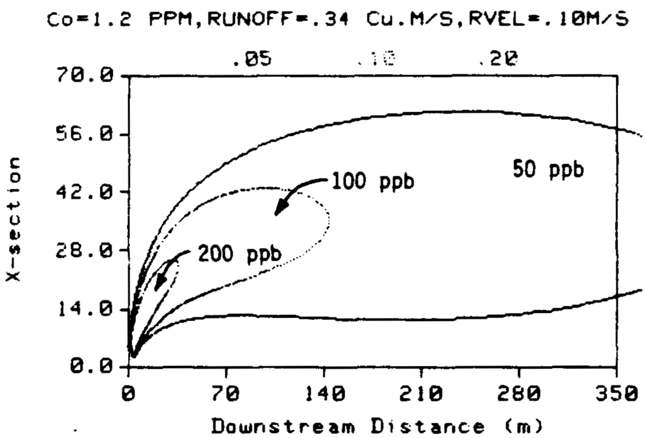
The simulation assumes that the stated flow rate of the outfall and the flow rate of the river remains constant which in the case of the lower Fraser will not apply. The storm water volume is usually a finite quantity with a decreasing head. The river flow velocity is constantly fluctuating due to tidal influence and is increasing on an ebb tide.

The second simulation reflects the decreasing head on the storm water flow by lowering the flow rate to 50% at 0.17 m^3/s. The 200 ppb isocon extends 14 m from shore, the 100 ppb-24 m and 50 ppb-31 m.

The third simulation reduces runoff to 40% of original flow and increases river velocity. In this case the 200 ppb isocon is 7 m from shore, the 100 ppb is 12 m and the 50 ppb is 15 m.

An actual field study of such a discharge has not been performed, however, the simulation was made based on realistic data observed during the monitoring program. Other plumes observed discharging from peat bogs which are highly colored suggest that the actual plume will be a combination of the early stages of simulations #1 and #2 and a major portion of simulation #3. It is significant to note that the downstream distance at which chlorophenol concentrations at or above the LC_{50} of 100 ppb could be observed approaches 60 m. The plume also hugs the shoreline (simulation #3) which is likely to have the most significant affect on juvenile fish (and other aquatic organisms).

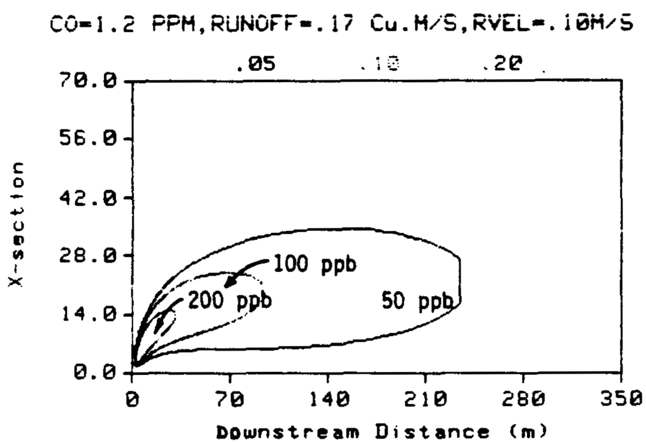
Elevated shoreline chlorophenol concentrations of 10.0-15.0 ppb in river water were measured approximately 200 m downstream of a large outfall after a storm event such as the one simulated. (1) The results of this simulation indicate that storm water discharges may produce potentially toxic affects in nearshore receiving waters.



Benedict Model
HP BASIC version, Environment Canada

Co=1.2PPM,RUNOFF=.34 Cu.M/S,RVEL=.10M/S

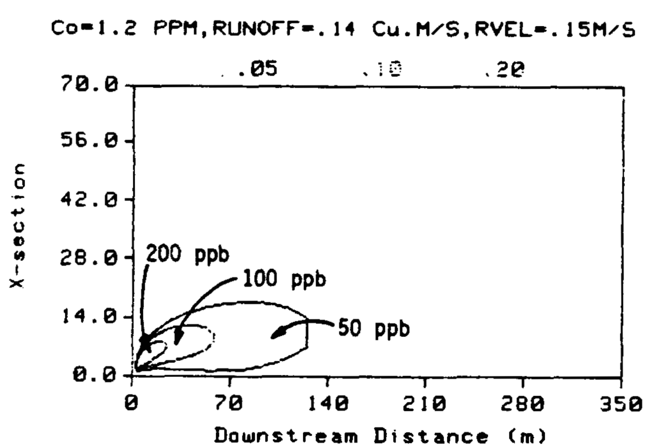
Discharge Angle	=	90.0	Degrees
Discharge Excess Concentration	=	1.2	mg/L
Volumetric Discharge Rate	=	.340	Cu m/sec
Discharge Width	=	.67	Meters
Discharge Depth	=	.67	Meters
Ambient Velocity	=	.10	Meters/sec
Ambient Concentration	=	0.00	mg/L
Concentration Cut-off Factor	=	.04	Delta-C/Delta-CO
Drag Coefficient	=	2.605	
Entrainment Coefficient	=	.228	
Convective Heat Transfer Factor	=	1	



Motz-Benedict Model
HP BASIC version, Environment Canada

CO=1.2 PPM,RUNOFF=.17 Cu.M/S,RVEL=.10M/S

Discharge Angle	=	90.0	Degrees
Discharge Excess Concentration	=	1.2	mg/L
Volumetric Discharge Rate	=	.170	Cu m/sec
Discharge Width	=	.67	Meters
Discharge Depth	=	.67	Meters
Ambient Velocity	=	.10	Meters/sec
Ambient Concentration	=	0.00	mg/L
Concentration Cut-off Factor	=	.04	Delta-C/Delta-CO
Drag Coefficient	=	.908	
Entrainment Coefficient	=	.302	
Convective Heat Transfer Factor	=	1	



Motz-Benedict Model
HP BASIC version, Environment Canada

Co=1.2 PPM,RUNOFF=.14 Cu.M/S,RVEL=.15M/S

Discharge Angle	=	90.0	Degrees
Discharge Excess Concentration	=	1.2	mg/L
Volumetric Discharge Rate	=	.140	Cu m/sec
Discharge Width	=	.67	Meters
Discharge Depth	=	.67	Meters
Ambient Velocity	=	.15	Meters/sec
Ambient Concentration	=	1.20	mg/L
Concentration Cut-off Factor	=	.04	Delta-C/Delta-CO
Drag Coefficient	=	.365	
Entrainment Coefficient	=	.390	
Convective Heat Transfer Factor	=	1	

FIGURE 22 COMPUTER SIMULATION OF STORMWATER DISCHARGE PLUME TO TIDAL INFLUENCED RIVER FLOW.

7 FISH BIOASSAYS OF PURE STORMWATER EFFLUENT

Chlorophenols are among the most acutely toxic chemicals to fish and other aquatic life. Controlled laboratory studies of chlorophenols have established 96 hour LC_{50} values of 40-130 ppb for salmonids (8, 9, 10). Survival, growth, metabolism and reproduction of aquatic organisms may be impaired by prolonged exposure to concentrations of less than 10 ppb (8, 11, 12, 13, 14).

Application of laboratory derived LC_{50} values to field situations is often difficult. Bioassay tests performed with undiluted effluent provide more meaningful information concerning the potential for effect on the receiving environment.

7.1 Bioassay Procedures

The acute lethal static fish bioassays (LT_{50}*) were performed by the Environmental Protection Bioassay Laboratory in accordance with the Provincial Guidelines and Laboratory Procedures for Measuring Acute Lethal Toxicity of Liquid Effluents to Fish (15). Ten rainbow trout (*Salmo gairdneri*) ranging in size from 0.51 to 1.4 grams were placed in 20 litres of continuously aerated, undiluted storm water effluent. The bioassays were then observed at .08, .17, .33, .67, 1.33, 2.7, 24, 48, 72 and 96 hours. Mortality was recorded as the time to cessation of all movement by individual fish.

7.2 Results Mill #4 and Mill #6

A summary of the bioassay test conditions is presented in Table 6.

---

*The LT_{50} is the calculated lethal time to death of 50 percent of the test fish at a specified concentration of effluent.

TABLE 6 BIOASSAY TEST CONDITIONS - MILL #4, NOVEMBER 25, 1986

PARAMETER	UNITS	VALUE	RANGE
$\bar{x}$ Weight	g	0.72	0.51 - 1.4
$\bar{x}$ Length	cm	4.4	4.0 - 5.5
Loading Density	g/L	0.36	
Temperature	C	15	
pH		6.7	
Dissolved Oxygen	mg/L	12.0	
Conductivity	mS/cm	0.210	
PCP	ppb	440	
TTCP	ppb	810	

The concentration of PCP and TTCP in the bioassay sample were 440 ppb and 810 ppb respectively, exceeding the LC_{50} values by over 4 (PCP) and 8 (TTCP) times. While additional water quality data is not available for this sample, data from the same site, collected on November 25, 1986 indicate that all parameters fall within acceptable levels and would not be expected to contribute to the overall toxicity of the sample (Appendix I).

Results of the bioassay are summarized in Table 7.

TABLE 7 LT_{50} BIOASSAY RESULTS - MILL #4, NOVEMBER 25, 1986

TEST	CUMULATIVE MORTALITY AT TIME (hours)									
	.08	.17	.33	.67	1.33	2.7	24	48	72	96
Control	0	0	0	0	0	0	0	0	0	0
100% Effluent	0a	0b	0c	0d	10	-	-	-	-	-

a = coughing
b = eratic swimming
c = equilibrium failure
d = 10 fish moribund

When introduced into the test solution, the fish became excited. Within 5 minutes they exhibited a coughing response followed by erratic swimming within 10 minutes of exposure. By 20 minutes exposure time the fish had lost equilibrium, their opercular (gill cover) movements became irregular and they became unresponsive to movement or touch.

The 100% effluent LT_{50} was greater than 40 minutes but less than 80 minutes for rainbow trout underyearlings.

A summary of the bioassay test conditions for effluent from Mill #6 is provided in Table 8.

TABLE 8 BIOASSAY TEST CONDITIONS - MILL #6, JANUARY 23, 1987

PARAMETER	UNITS	VALUE	RANGE
$\bar{X}$ Weight	g	0.86	0.55 - 1.2
$\bar{X}$ Length	cm	4.7	4.1 - 5.2
Loading Density	g/L	0.43	
Temperature	C	15	
pH		7.9	
Dissolved Oxygen	mg/L	9.4	
Conductivity	mS/cm	-	
PCP	ppb	380	
TTCP	ppb	1,027	

The concentration of PCP and TTCP in the bioassay sample were 380 ppb and 1 027 ppb respectively, exceeding the LC_{50} values by approximately 4 (PCP) and 10 (TTCP) times. General water quality analyses were performed on this sample and results are presented in Appendix VI. These data indicate that the majority of parameters are within acceptable levels and would likely not contribute to the toxicity of the sample. Concentrations of aluminum, iron and silicon were elevated, however, and may have some effect on the overall toxicity of the sample.

Results of the bioassay are summarized in Table 9.

TABLE 9 LT_{50} BIOASSAY RESULTS - MILL #6, JANUARY 23, 1987

TEST	CUMULATIVE MORTALITY AT TIME (hours)									
	.08	.17	.33	.67	1.33	2.7	24	48	72	96
Control	0	0	0	0	0	0	0	0	0	0
100% Effluent	0	0	0a	0a	0b	10	-	-	-	-

a = surface swim b = severe stress and coughing

When introduced into the test solution, the fish became excited. Time checks to 40 minutes showed that the test fish were surface swimming. By 80 minutes exposure duration, the fish exhibited severe stress and coughing.

The 100% effluent LT_{50} was greater than 80 minutes but less than 120 minutes for rainbow trout underyearlings.

7.3 Toxicity of Pure Storm Water Effluent

The bioassay results for both mill sites demonstrate the high toxicity of the chlorophenol contaminated storm water effluent. Since some of the chemical could be expected to be adsorbed by the testing environment (suspended sediment, organic matter etc.), the test conditions could result in a low estimate of the toxicity (10, 16). Storm water effluent from the wood protection industry represents both an acute and chronic hazard to aquatic life in the receiving environment.

Figure 23 shows the total monthly precipitation averaged over thirty years for Vancouver Airport and Squamish. These represent the extremes in precipitation which can be expected in most B.C. Coastal areas. It is evident that rainfall occurs year round even in the driest month of July. An average of six days with rainfall (at 5mm/day) occur at Vancouver Airport during July. This daily accumulation is sufficient to produce significant quantities of runoff as demonstrated in sections 3 through 5.

The usage of the rivers by juvenile migratory fish is documented in Figure 24. The concern with respect to acute toxicity is for juvenile fish inhabiting the nearshore areas adjacent to treated lumber storage areas. These fish range in size from fry (4.0-6.0 cm) to smolts (10 to 15 cm) and are most likely to encounter a discharge of contaminated runoff during the downstream migration period which occurs from the beginning of March to the end of June (2).

Due to the small size of the fish it is conceivable that a local kill could occur after which the juveniles would be consumed by other fish, birds or be washed downstream with no visible evidence of the event occurring. Recent studies have found trace levels of chlorophenols in adult salmon migrating up the Fraser River (24). Mature eulachons have shown increases of chlorophenols in tissue during their migration from Steveston to the Port Mann Bridge (24).

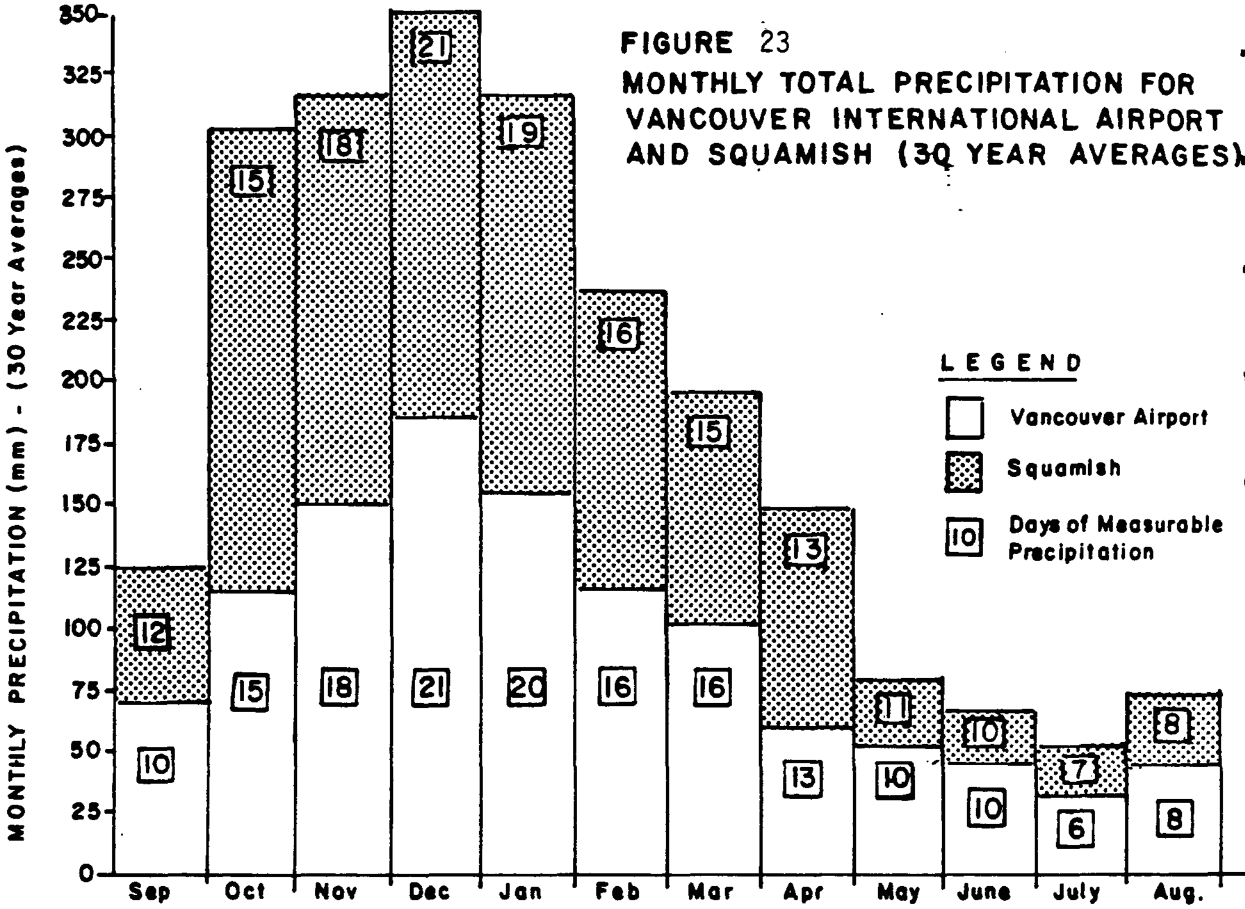


FIGURE 23
MONTHLY TOTAL PRECIPITATION FOR VANCOUVER INTERNATIONAL AIRPORT AND SQUAMISH (30 YEAR AVERAGES)

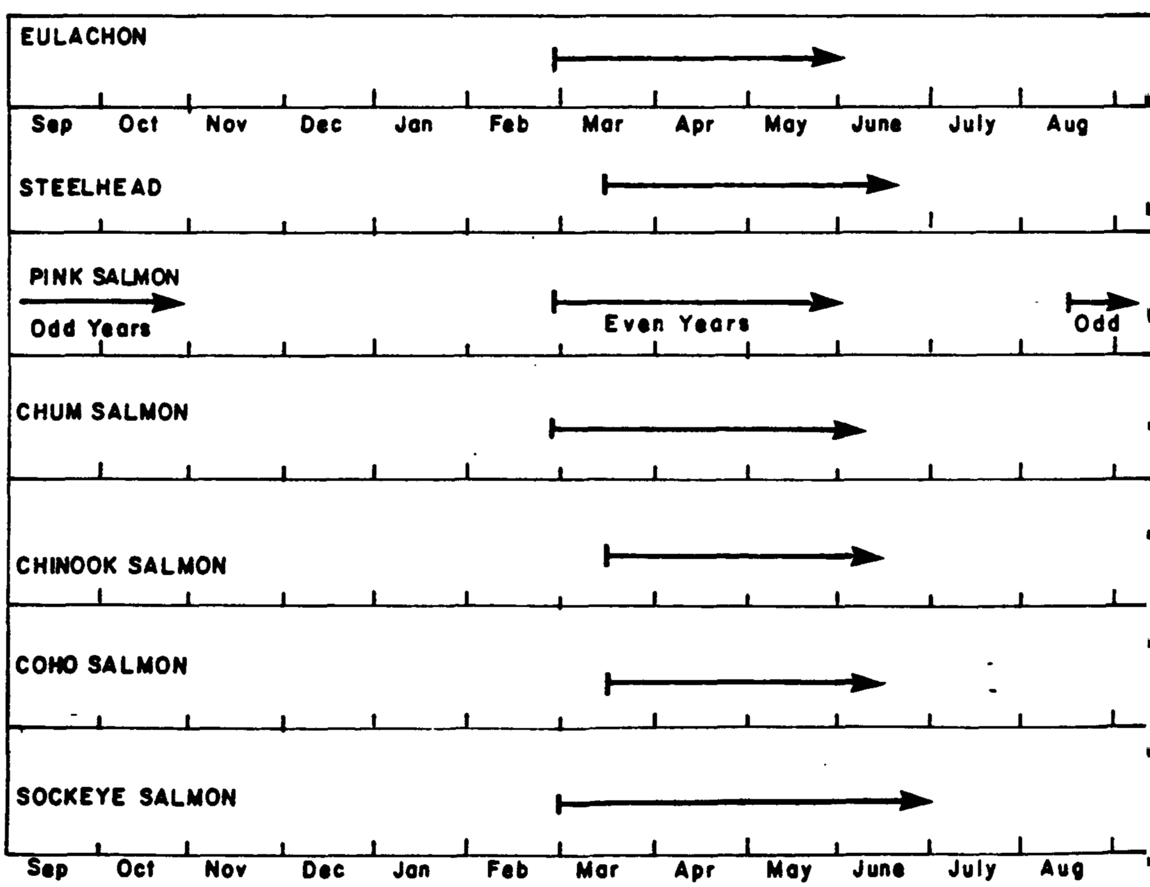


FIGURE 24
DOWNSTREAM MIGRATORY PERIODS OF FISH IN THE LOWER FRASER RIVER

7.4 Levels of Chlorophenols in Aquatic Organisms in the Fraser River

Table 10 provides a short summary of chlorophenol levels in aquatic organisms collected between 1973 and 1986 which are known to exist in the Fraser River and to which storm water discharges are expected to contribute.

TABLE 10 MAXIMUM TOTAL CHLOROPHENOL CONCENTRATIONS FOUND IN WATER, SEDIMENT AND AQUATIC ORGANISMS IN THE LOWER FRASER RIVER AND ESTUARY.(17)

Matrix	CONCENTRATION (PPb)		CONCENTRATION (PPB)
Water	1 000	Sediment	130
Organism			
Sculpin Muscle	575		
Whole Tissue	239		
Liver	1 550	Carp	308
Flounder	127	Eulachon	21
Squaw	130	Stickle Back	195
Sucker	370	Shrimp	3
Pea Mouth Chub	74	Clam	5
Smelt	30	Dungeness Crab	9
Flatfish	44	Crayfish	5
Rainbow Trout	60	Polycheates	2 500
Cutthroat Trout	60	Pelecypoda	30
Dolly Varden	55	Chironomids	90
White Sturgeon	130	Lampreys	60

REFERENCES

1. Hall, K., C. Jacobs, 1985. Use of Bioconcentration Capability of Hirudinea (Leeches) to Evaluate Chlorophenol Contamination of Water. Presented at the International Conference on New Directions and Research in Waste Treatment and Residuals Management, University of British Columbia, Vancouver, June 23-28, 1985, pp 774-788.

2. Northgate, T.G., 1974. Biology of Lower Fraser River: A Review. Westwater Research Center, University of British Columbia, Vancouver, B.C., Technical Report No. 3, May.

3. Blosser, R.O., 1986. Initial Review of Some Outfall Models and an Asymptotic Jet Dispersion Model for Use in River Systems. National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin NV 486, March.

4. CanTest Ltd., E.V.S. Consultants Ltd., 1979. Monitoring Environmental Contamination from Chlorophenol Contaminated Waste Generated in the Wood Preservation Industry. Prepared for Environmental Protection Service, Pacific and Yukon Region, Regional Program Report 79-24.

5. Cserjesi, A.J., et al., 1984. Simulated Rainfall Leaching of Chlorinated Phenols from Dip Treated Lumber. Forintek Contract No. 65-68-610, DSS Contract No. 06SB KE603-3-0221.

6. Konasewich, D.E., F.E. Henning, K.E. Wile and E. Gerincher, 1983. Chlorophenate Wood Protection, Recommmendations for Design and Operation. Environment Canada, B.C. Ministry of Environment.

7. Wilson, D.M. and S. Liu, 1986. Compliance Assessment Report on Wood Protection (Anti-Sapstain) Facilities in British Columbia (1984). Environment Canada, Conservation and Protection, Environmental Protection, Regional Program Report 86-08.

8. Webb, P.W. and J.R. Brett, 1973. Effects of Sublethal Concentrations of Sodium Pentachlorophenate on Growth Rate, Food Conversion Efficiency and Swimming Performance in Underyearling Sockeye Salmon. J. Fish. Res. Bd. Can., 30, pp 499-507.

9. Iwama, G.K. and G.L. Greer, 1979. Toxicity of Sodium Pentachlorophenate to Juvenile Chinook Salmon Under Conditions of High Loading Density and Continuous-Flow Exposure. Bull. Environ. Contam. Toxicol., 23, pp 711-716.

10. Jones, P.A., 1981. Chlorophenols and Their Impurities in the Canadian Environment. Environment Canada, Environmental Protection Service, EPS 3-EC-81-2, p 434.

11. Hodson, P.V. and B.R. Blunt, 1981. Temperature-Induced Changes in Pentachlorophenol Chronic Toxicity to Early Life Stages of Rainbow Trout. Aquat. Toxicol., 1 (2), pp 113-127.

12. Chapman, G.A. and D.L. Shumway, 1978. Effects of Sodium Pentachlorophenate in Survival and Energy Metabolism of Embryonic and Larval Steelhead Trout. In Pentachlorophenol: Chemistry, Pharmacology and Environmental Toxicology (ed. K. Rango Rao), Plenum Press, New York, pp 285-299.

13. Mathers, R.A., J.A. Brown and P.H. Johansen, 1985. The Growth and Feeding Behaviour Responses of Largemouth Bass Exposed to PCP. Aquat. Toxicol., 6 (3), pp 157-164.

14. Dominguez, S.E. and G.A. Chapman, 1984. Effect of Pentachlorophenol on the Growth and Mortality of Embryonic and Juvenile Steelhead Trout. Arch. Environ. Contam. Toxicol., 13 (6), pp 739-743.

15. Province of British Columbia, Bioassay Task Force, 1984. Provincial Guidelines and Laboratory Procedures for Measuring Acute Lethal Toxicity of Liquid Effluents to Fish, p 18.

16. Pierce, R.H. Jr. and D.M. Victor, 1983. The Fate of Pentachlorophenol in an Aquatic Ecosystem. In Pentachlorophenol: Chemistry, Pharmacology and Environmental Toxicology (ed. K. Rango Rao), Plenum Press, New York, pp 41-63.

17. Garrett, C.L. and J.A. Shrimpton, 1986. Chemicals in the Environment, Pacific and Yukon Region, V. Chlorophenols. Environment Canada, Conservation and Protection, Environmental Protecton, p 40.

18. Fact Sheet on Acid Rain in British Columbia and the Yukon. Atmospheric Environment Service, Environment Canada.

19. Cserjesi, A.J. and J.W. Roff, 1964. Retention of Pentachlorophenol in Lumber Dipped in Water Solutions. Canada Department of Forestry, Forest Products Research Branch, Contribution No. P-44, Forest Products Journal.

20. Government of Canada, 1979. Environmental Laboratory Manual. Department of Environment, Environmental Protection Service, Department of Fisheries and Oceans, Resource Services.

21. Wituschek, E., Personal Conversation.

22. Atmosphere and Environment Services (AES), Environment Canada, Pacific Yukon Region.

23. Carey, J., 1987. Unpublished data, Organic Pathways Section, National Water Research Institute, Environment Canada, (Call John Carey Re: Title and Results?)

24. Jim Servizi, Department of Fisheries and Oceans, Sweltzer Creek Station, Cultus Lake, B.C., Personal Communication, July 1987.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation of the following people and organizations for their assistance in the preparation of this report.

Les Swain -
B.C. Ministry of the Environment for partial funding of the analytical costs.

Tracey Wrubleski -
Environmental Protection for typing of the manuscript.

Paul Kluckner, Ron Leary, Randy Englar and Laboratory Support Staff -
West Vancouver Laboratory Services, Environmental Protection.
For their advice and participation in the Quality Control Program.

David Neufeld -
Environmental Protection, Equipment Preparation and Report Editing.

Lumber Mills and Management Of:

British Columbia Forest Products Ltd.
Sea Board International Terminals
West Coast Cellufiber Ltd.
Western Stevedoring Co. Ltd.
Doman Forest Products Ltd.
Squamish Terminals Ltd.
Canadian Forest Products Ltd.
Whonnock Lumber
Terminal Sawmill Ltd.
Weldwood Ltd.
Mainland Forest Products
Fraser River Planing Mills Ltd.
West Langley Forest Products

For providing access and security during the study period and co-operating with all requirements to provide sampling opportunities for good monitoring results. Their assistance was greatly appreciated.

APPENDIX I

WEST VANCOUVER LABORATORY SERVICES
ENVIRONMENTAL PROTECTION,
PROTOCOL FOR THE ANALYSIS OF
CHLOROPHENOLS IN FRESH WATER

-16

CHLORINATED PHENOLS V2.1 May, 1987

(Gas Chromatographic)

800-802

SCOPE AND APPLICATION

This method is applicable to the qualitative and quantitative gas chromatographic determination of Pentachlorophenol, 2,3,4,5-Tetrachlorophenol, 2,3,4,6-Tetrachlorophenol and 2,3,5,6-Tetrachlorophenol in natural and waste waters, sediments and biota. The minimum detectable concentration of Pentachlorophenol in waters and sediment/biota samples is 0.002 ug/l and 0.0001 ug/g respectively. The Tetrachlorophenols similarly provide 0.004 ug/l and 0.0002 ug/g as detection limits. These results were obtained using a packed column gas chromatograph with electron capture detector.

SAMPLE CONDITION

Note: All glassware, aluminum foil and sampling equipment that comes in contact with the sample must be acetone rinsed and heat treated at 325 C for a minimum of 12 hr.

1. Water samples should be collected in an all glass system and stored at 4 C or just above the freezing point. If Teflon lined caps are not available for the sampling containers then treated aluminum foil must be used as a liner. Sample volume should be at least 1 litre.
2. Sediment and biota samples should be collected and frozen immediately in an all glass system. Treated aluminum foil may also be used to wrap the samples for storage. If Teflon lined caps are not available for the sampling containers then treated aluminum foil must be used as a liner. Sample weight collected should be at least 25 grams.

METHOD PRINCIPLE

Aqueous samples are acidified to pH 2 with conc. H2SO4 and the chlorinated phenols extracted with ethyl ether. After concentration the extract is methylated using ethereal diazomethane. The extract is cleaned up using a Florisil column then treated successively with activated copper, conc. H2SO4 and mercury to remove interferences.
Sediment and biota (after homogenization) are acetone extracted using a wrist action shaker and then treated as above.
Alternately, sediment samples are soxhlet extracted with acetone and then treated as above. Biota samples are digested overnight with 50% sulfuric acid in a benzene-hexane solution and treated in the manner outlined for the water samples. The samples are then analyzed by packed column gas chromatography.

INTERFERENCES

1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatographs. All of these materials must be demonstrated to be free of interferences under the conditions of analysis.

2. Organochlorine pesticides, certain organophosphorous pesticides, other halogenated compounds, phthalate esters and elemental sulphur constitute interferences in the determination of CP's. Most of these are eliminated by the method described below.

3. Petroleum hydrocarbons may create analytical problems, such as quenching of the EC detector, especially when their concentration considerably exceeds the CP content. Petroleum hydrocarbons are usually destroyed by the sulfuric acid clean-up step detailed in this procedure.

4. Difficulties may be encountered in the analysis of pulp mill waste due to the interference of chlorinated degradation products of lignin.

5. 2,3,4.6-tetrachlorophenol is not resolved from 2,3,5,6-tetrachlorophenol with the recommended gas chromatographic columns.

PRECISION AND ACCURACY

Recovery of Chlorinated Phenols from 750 ml of Fortified Wastewater

Chlorinated Phenol	Fortification Level (ug/l)	Average Recovery (%)	Coefficient of variation (%)
2,3,5.6-Tetrachlorophenol	1.0	91	3.6
2,3,4,5-Tetrachlorophenol	1.0	90	4.3
2,3,4.6-Tetrachlorophenol	------- No Data Available --------		
Pentachlorophenol	1.0	96	2.4

APPARATUS

All glassware must be washed with heavy-duty soap, rinsed with distilled water, rinsed with acetone and then heat treated at 325 C for at least 12 hours prior to use. The glassware amust be stored in an area protected from chemical contamination.

1. Rotary evaporator.
2. Soxhlet extraction apparatus.
3. Extraction thimbles.
4. Boiling flasks. 125-ml, 250-ml.
5. Separatory funnels, 125-ml, 250-ml, 500-ml.
6. Vials. 7-ml. with tin liners on caps.
7. Volumetric flasks. 2-ml, 5-ml.
8. Brinkman Polytron homogenizer.
9. Homogenizer tubes, 5-cm X 5-cm X 12-cm.
10 Screw top centrifuge tubes, 100-ml.
11. Magnetic stirrer or wrist-action shaker.
12. Diazald kit. Aldrich #Z10,025-0.
12. Gas chromatograph, with dual EC detectors and on-column injectors.
13. Gas chromatographic columns - 180 cm x 4 mm ID.
    (a) Primary - 4% OV-101/6% OV-210 on 80/100 Chromosorb W.
    (b) Confirmation - 3% OV-1 on on 80/100 Chromosorb W.

GAS CHROMATOGRAPHIC CONDITIONS

GAS CHROMATOGRAPH CONDITIONS

Oven temp - 160 C
Inlet temp - 220 C
Detector temp - 350 C

Carrier gas - 95% argon/5% methane
Detector temp - 60 ml/min

REAGENTS

NOTE: All reagents must be shown to contain no interfering substances by running the appropriate blanks.

1. Hexane, pesticide grade.
2. Acetone, pesticide grade.
3. Benzene, pesticide grade.
4. Diethyl ether, pesticide grade.
5. Ethanol, 95%, pesticide grade.
6. Methanol, pesticide grade.
7. Iso-octane, pesticide grade.
8. Sulfuric acid, conc.
9. Hexane extracted tap water.
   - extract 1500 ml of tap water with 200 ml of hexane in a 2 l sep. funnel
   - let separate 15 min then discard hexane fraction
   - repeat extraction two more times
10. Sodium sulfate, anhydrous.
    - heat treated for 12 hr at 325 C
    - wash with pesticide grade solvent of choice prior to use
11. Sodium chloride.
    - heat treated for 12 hr at 325 C
    - wash with pesticide grade solvent of choice prior to use
12. Sodium chloride solution, 2%.
    - make up using hexane extracted tap water
13. Sodium hydroxide.
14. Potassium hydroxide.
15. Copper, activated.
    - rinse the copper powder with 2N HCL for 30 sec then filter and rinse quickly with DI water until the wash is of neutral pH.
    - wash with acetone 4 times and air dry.
    - wash with hexane 3 times.
    - store under hexane in a closed jar. It should be shiny for optimum effectiveness.
16. Mercury.
17. Diazald (N-methyl-N-nitroso-p-toluenesulfonamide), Aldrich #D2,800-0.
18. Diazomethane, ethereal alcoholic solution
    - glassware is assembled according to the instructions contained in Aldrich Technical Information Bulletin #AL-131.
    - diazomethane is generated from the Diazald reagent. The following is extracted from Aldrich Technical Information Bulletin #AL-113.

****

CAUTION: USE ONLY THE GLASSWARE SUPPLIED WITH THE DIAZALD KIT. THE USE OF STANDARD GROUND GLASS JOINTS WILL CREATE AN EXTREME EXPLOSION HAZARD.

DIAZOMETHANE MUST BE GENERATED ONLY IN AN EFFICIENT FUME HOOD AND BEHIND A SAFETY SHIELD.

****

-a 250-ml distilling flask is fitted with a dropping funnel and an efficient condenser set for downwards distillation. The condenser is fitted to 2 receiving flasks in series, the second of which contains 30 ml of diethyl ether. The inlet tube of the second receiver dips below the surface of the ether and both receivers are cooled in a water-ice bath. Heat is supplied by a constant temperature water bath set to 65 C. The heated portion of the glassware is covered with aluminum foil to promote faster distillation.
-using the 250-ml distilling flask dissolve 5 g KOH in 8 ml DI water.
-add 25 ml 95% ethanol.
-add 21.4 g (0.1 mole) Diazald to 200 ml diethyl ether, dissolve and add to the dropping funnel.
-over a period of 25 minutes add this to the alkali solution. The rate of addition should equal the rate of distillation.
-when the dropping funnel is empty slowly add another 40 ml of diethyl ether and continue distillation until the distillate is colourless.
-the combined ethereal distillates should contain about 3 g of diazomethane.
-store diazomethane over ether-washed NaOH in a glass bottle with a teflon top (NOT a ground glass top).
-store the prepared diazomethane in the freezer compartment of an explosion proof refrigerator.

19. Pentachlorophenol.
20. 2,3.5,6-Tetrachlorophenol.
21. 2,3,4,5-Tetrachlorophenol.
22. 2,3,4,6-Tetrachlorophenol.
23. 2,3,6-Trichlorophenol.
24. 2,4,6-Trichlorophenol.

PROCEDURE - GENERAL

1. Blanks are required for each new batch of reagents.
2. Duplicates and spiked samples must be run on a routine basis.
3. Standards should be injected frequently as a check on the stability of operating conditions, detector and column.

PROCEDURE - WATER SAMPLES

1. Place 300 ml of the shaken sample in a 500-ml separatory funnel. If the sample is suspected to contain high CP levels then consider using a smaller volume and diluting it to 300 ml at this point.
2. Carefully acidify the sample to pH 2 with 2N H2SO4.
3. Add 60 ml of diethyl ether to the graduated cylinder used to measure the aqueous aliquot, rinse and transfer to the separatory funnel.
4. Shake vigorously for 2 min.
5. Drain the ether fraction into a 250-ml rotary evaporator flask.
6. Repeat steps 3, 4 and 5 twice more (Notes 1 and 2).
7. Add 1 ml iso-octane to the ether extract as a keeper.
8. Proceed to the "COMMON TO ALL EXTRACTS" section. PCB's may also be determined from this extract.

PROCEDURE - SEDIMENTS AND BIOTA USING SHAKER EXTRACTION

7. Repeat the hexane extraction two more times.

8. Add 1 ml iso-octane to the hexane extract as a keeper.
9. Dry the extract over 5 g anhydrous sodium sulfate then transfer with washing into a clean 250-ml rotary evaporator flask.
10. Proceed to the "COMMON TO ALL EXTRACTS" section.

PROCEDURE - COMMON TO ALL EXTRACTS

1. Concentrate to about 5 ml on a rotary evaporator. Caution - do not evaporate to dryness. Water bath temperature must not exceed 35 C.
2. Quantitatively transfer the sample to a Florisil column and clean up using the following procedure:

   Calibrate each batch of Florisil with PCB and CP standard to assure complete recovery. The procedure below assumes that all PCB's and CP'S are eluted with 150 ml of hexane.
   -the column used is 30 cm x 25 mm I.D. with a 250 ml reservoir, teflon stopcock and a glass wool plug at the bottom.
   -add 70 ml of hexane then 30 g of 2% Florisil pre-slurried with hexane to the column.
   -add 1 cm of heat treated Na_2SO_4 to the top of the column.
   -pre-rinse the column with 2 x 50 ml portions of hexane.
   -just before exposure of the Na_2SO_4 layer, add the sample and then elute with 2 x 75 ml hexane.
   -collect the extract in 250 ml rotary evaporator flask.
   -add 1 ml of iso-octane as a keeper then evaporate (water temperature less than 35 C) to about 1 ml.
   -quantitatively transfer the extract to a 5 ml volumetric with hexane and make up to volume OR, if PCB analysis is required, to a 10 ml volumetric.
3. Transfer a 2 ml aliquot of the sample to a 7 ml vial with tin lined cap or if high CP levels are suspected then use an appropriate dilution.
4. Evaporate to very near dryness by placing vial at an angle in a fume-hood and lowering the door such that a gentle air current flows over the vial mouth.
5. Add 0.25 ml of methanol and mix.
6. IN A FUME HOOD AND WITH EXTREME CAUTION add 2 ml of diazomethane, cap and let stand for 30 min in the fume hood. If the yellow colour does not persist then repeat the methylation.
7. Open the cap and let the sample evaporate to near dryness in the fume hood.
8. Add exactly 2.00 ml hexane and dissolve.

9. Clean Up Procedure Using Activated Copper, conc. Sulfuric Acid and Mercury.
   -add 2 ml of sample and 200 mg activated copper to a 7 ml vial.
   -seal the vial and ultrasonicate the sample for 60 min.
   -centrifuge at 2000 rpm for 10 min.
   -decant the sample into a clean 7 ml vial.
   -add 1 ml of conc. H_2SO_4, vortex mix for 1 min then centrifuge.
   -repeat the above treatment until the acid layer is colourless then transfer the sample to a clean vial.
   -add 2 drops of mercury to the extract and ultrasonicate for 30 min.
   -centrifuge and decant the sample into a clean 7 ml vial. Repeat the procedure as necessary.
10. The sample is now ready for GC analysis.
11. Inject a known amount of sample on the gas chromatograph. Identification of the individual chlorinated phenols present is based on a comparison of the retention time with that of the corresponding methylated chlorinated phenol standards (Notes 3 and 4).
12. Comparison of retention times on the confirmation column is used to confirm identification.

NOTES

1. If an emulsion forms, add a few drops of a saturated sodium sulfate

NOTES

1. If an emulsion forms, add a few drops of a saturated sodium sulfate solution. Gentle agitation of the contents may further help to break t emulsion. If the emulsion persists then transfer the sample to glass centrifuge tubes and centrifuge for 30 min at 2500 rpm.
2. If the combined extract appears to contain a significant amount of suspended water, it should be centrifuged as above and the aqueous lay discarded.
3. If you identify only Pentachlorophenol and no Tetrachlorophenol be awa that PCP might not be present. Some pesticides elute in this area.
4. Fatty acid methyl esters may interfere but are destroyed by the conc. H2SO4 treatment. Additional H2SO4 treatments may be required for comp removal.
5. While the 2,3,4,6- and 2,3,5,6-Tetrachlorophenol isomers co-elute thei response factors are quite different. It is extremely important to identify which and to maintain consistency in the isomer used for the standard calculations. In wood preservatives, the common source of CP samples submitted, 2,3,4,6-Tetrachlorophenol has been identified as th isomer present, thus result should be quantitated on the basis of this isomer.

CALCULATIONS

The chlorinated phenol concentration is determined by direct comparison of peak area with a standard, providing the sample and standard are within th linear range of the GC detector. Results are reported to three significan figures.

[CONC] = ([A][C][D][E][F]) / [B] units

A = Sample Peak Area/ul Injected
B = Standard Peak Area/ul Injected
C = Conc. of Standard in ug/ml
D = Volume of hexane extract made up to
E = Dilution Factor (if any)
F = for Water Samples = [1000]/[Volume Sample extracted - in ml]
= for Sediment Samples = [1]/[Dry Wt. Sample extracted - in g]
= for Biota Samples = [1]/[Received Wt. Sample extracted - in

Reporting Units = for Water Samples = ug/l
= for Sediment Samples = ug/g
= for Biota Samples = ug/g [W]

REFERENCES

[1] L. Rudling, Water Research, 4, P533-537, (1970).
[2] G.R. Higginbotham, J. Ress, and A. Rockne, JAOAC, 53, P673-676, (1970)
[3] A.S.Y. Chau and J.A. Coburn, JAOAC, 57, P389-393, (1974).
[4] L.L. Lamparski et al., Gas Liquid Chromatographic Determination of Chlorinated Benzene and Phenols in Selected Biological Matrices, Anal. Chem., Vol. 63, No. 1, (1980).
[5] Tetra Tech, Inc. Recommended Protocols for Measuring Organic Compounc in Puget Sound Sediment and Tissue Samples. Prepared for U.S. E.P.A., Final Report TC-3991-04, December, 1986.

APPENDIX II

CANTEST LTD. ANALYSIS OF STORM WATER RUNOFF FROM CHLOROPHENATE WOOD PROTECTION FACILITIES

ANALYSIS OF STORM WATER RUNOFF FROM CHLOROPHENATE WOOD PROTECTION FACILITIES

MAY 1987

REPORTED TO:

ENVIRONMENT CANADA

ENVIRONMENTAL PROTECTION SERVICE

SUITE 200 - 1523 WEST 3RD AVENUE,
VANCOUVER, BRITISH COLUMBIA V6J 1J8
TELEPHONE (604) 734-7276
TELEX 04-54210

can test ltd.

TABLE OF CONTENTS

1.0 EXECUTIVE SUMMARY

Three hundred and forty two water samples of storm water runoff from chlorophenate wood protection facilities were analyzed for chlorinated phenols using gas-chromatography with electron capture detection. The results of the analysis showed the presence of pentachlorophenol and 2,3,4,6-tetrachlorophenol in all the water samples, with pentachlorophenol ranging from 1.30 to 273,000 ug/L and tetrachlorophenol ranging from 0.21 to 340,000 ug/L. Details of the results are listed in Table II of this report.

2.0 INTRODUCTION

Environmental Protection Service (EPS) of Environment Canada has undertaken a study of chlorinated phenols content in stormwater runoff from various chlorophenate wood protection facilities located in the B.C. Lower Mainland. As a part of this study, Can Test Ltd. was responsible for the quantitative analysis of the water samples for pentachlorophenol (PCP) 2,3,4,6-tetrachlorophenol (2,3,4,6-TTCP), 2,4,6-trichlorophenol, (2,4,6-TCP) and 2,3,6-trichlorophenol (2,3,6-TCP).

This report describes the method, chromatographic conditions, quality control (QC) and results for three hundred and forty two water samples for chlorinated phenols.

3.0 APPARATUS AND MATERIALS

3.1 Apparatus and Materials

3.1.1 Grab sample bottle - Amber glass, one-liter volume, fitted with screw caps lined with foil. The bottles were consecutively rinsed with acetone and hexane and baked in an oven at 100°C before use.

3.1.2 Separatory funnel - 1000 mL, with Teflon stopcock.

3.1.2.1 All glassware was rinsed as soon as possible after use with dichloromethane (DCM). This was followed by washing with hot detergent solution (Decon 75 Concentrate) and rinsing until all the soap disappears. Glassware was then rinsed with 0.2N NaOH and then rinsed thoroughly with hot water. Glassware was drained dry and heated in an oven at 150°C for 15 - 30 minutes. Finally, dishes were taken out of the oven, cooled and consecutively rinsed with acetone, hexane and DCM.

3.1.3 Round bottom flasks - 250 mL.

3.1.4 Graduated cylinders -500 mL and 5 mL.

3.1.5 Graduated test tubes - 10 mL or 25 mL.

3.1.6 Flash evaporator with water bath - temperature setting at 29°C .

3.1.7 Heating block and nitrogen gas connection to blow samples.

3.1.8 Gas Chromatograph (GC) (see instrumentation).

3.1.9 GC vials with caps and septum.

3.1.10 Column for derivatized phenols - 3% OV17 on Chromosorb W, High Performance 80/100 mesh

3.1.11 Detectors - Electron Capture Detector (ECD) was used for determining the derivatized chlorinated phenols

3.2 Reagents

3.2.1 Deionized water- reagent water for blanks and solutions.

3.2.2 Sodium hydroxide solution (0.2N) (J.T. Baker) - Dissolve 32 g NaOH in reagent water and dilute to 4 L.

3.2.3 Acetone, hexane, methanol, dichloromethane, isooctane (2,2,4-Trimethylpentane) - glass distilled, pesticide grade (BDH Chemicals).

3.2.4 1000 ppm stock solutions of PCP, 2,3,4,6-TTCP, 2,3,6-TCP, and 2,4,6-TCP are prepared from authentic standards obtained from Agriculture Canada, Laboratory Service Division, Ottawa. Weigh out 5 mg of each accurately, dissolve in benzene and dilute to 5 mL in a 5 mL volumetric flask.

3.2.5 Derivatization reagent: N-Methyl-N^1-nitro-N-nitrosoguanidine, 97% - Aldrich

3.2.6 Preparation & Generation of Diazomethane (derivatization reagent)

3.2.6.1 Wash generator apparatus first with distilled H_2O, then acetone and then ethyl ether. Let it air dry.

3.2.6.2 This operation is carried out in a fume hood. Weigh into generator 200 mg of N-methyl-N^1-nitro-N- nitrosoguanidine. Add 20 mL of ether into the outer tube, 2.0 mL ether into the inner tube of the generator. Cap the generator tight. With a syringe, inject into the inner tube 2 mL of 50% KOH. Wrap the generator surface with aluminum foil and let it sit overnight. Strength of diazomethane is directly related to its yellowish-green color intensity.

Diazomethane is freshly prepared every day and is stored at 4°C, protected from light with aluminum foil.

Caution: Diazomethane is carcinogenic and preparation could be explosive if contents in the generator contact ground glass joints.

3.3 Calibration

3.3.1 To calibrate the GC-ECD for the analysis of chlorinated phenols, set gas chromatographic operating parameters equivalent to those indicated in Table 1.

3.3.2 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. One external standard should represent a concentration near but above the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

3.3.3 Derivatize, then inject 2 uL of each calibration standard, and tabulate peak response against the amount (nanograms) injected. The results can be used to prepare a calibration curve.

TABLE 1

GC-ECD Parameters

Oven: Temperature: 165°C isothermal
Injection Temperature: 230°C
Aux/Detector Temperature: 320°C
Detector: Electron Capture Detector (ECD)
Carrier gas: 5% methane/95% Argon
Flow rate: 30 mL/min.
GC: Hewlett Packard 5840A Gas Chromotograph
Autosampler: Hewlet Packard 7671A Automatic Sampler

3.4 Quality Control

Each day a batch of samples (reagent blanks, spikes and samples) was analyzed in the following order:

1. Spike #1 (High Level)
2. Method Blank
3. Sample #1
4. Sample #2
5. Sample #3
6. Sample #4
7. Spike #2 (Low Level)
8. Sample #5
9. Sample #6
10. Sample #7
11. Sample #8
12. Duplicate of any of the above samples.

3.4.1 Method Blank

A 0.5 litre aliquot of reagent blank water was analyzed to monitor that all glassware and reagent interferences were under control.

3.4.2 Spikes

Spike samples were prepared by the Quality Assurance Officer.

The high spike levels were: 1 ppm PCP, 1 ppm 2,3,4,6-TTCP and 0.1 ppm levels of both 2,3,6-TCP and 2,4,6-TCP. The low spike levels were: 2 ppb PCP and 2 ppb 2,3,4,6-TTCP.

3.4.3 Duplicates

Duplicates were analyzed on 10% of the samples.

3.5 Extraction Procedure

All samples received in the laboratory were logged and kept refrigerated at 4°C prior to extraction.

3.5.1 Shake samples (after samples achieved room temperature) for one minute and transfer 500 mL of sample into a 1 litre separatory funnel. For concentrated samples, 5 mL of sample is transferred into a 1 litre separatory funnel containing 495 mL of reagent water.

3.5.2 Adjust all samples to a pH of 1-2 with concentrated HCL (approx. 1 mL).

3.5.3 Add 50 mL of dichloromethane to the sample, stopper and shake funnel with periodic venting to release pressure. Shake all six samples and by the time you reach the first one again, the solvent will have separated from the water phase. Collect the dichloromethane portion (bottom layer) in a 250 mL round bottom flask.

3.5.4 Add a second 50 mL volume of DCM to the sample and repeat the extraction procedure a second time combining the extracts in the round bottom flask. Perform a third extraction in the same manner.

3.5.5 Before evaporation, rinse around the neck of the round bottom flask with approximately 1 mL of isooctane.

3.5.6 Set the flash evaporator water bath temperature to 29°C and reduce sample volume down to approximately 1 mL.

3.5.7 Quantitatively transfer sample extract with 5 mL of Hexane into a graduated test tube.

3.5.8 The sample is now ready to be derivatized. Add 0.5 mL of isooctane. Dry down contents to 0.5 mL again with a flow of nitrogen. Add to the contents 1.0 mL of diazomethane, mix and let sit for one hour at room temperature. After an hour, add 0.5 mL of isooctane to the derivatized contents and dry down contents to 0.5 mL with nitrogen. Make up sample to 5 mL final volume with isooctane, vortex, dilute and proceed with electron capture gas chromatographic analysis.

4.0 RESULTS AND DISCUSSION

4.1 Results of Analysis

The results of chlorinated phenols found in the water samples are shown in Table II. Details of sample identification are also included in the table. Using the described methodology, the detection limit of PCP, 2,3,4,6-TTCP and the TCPs is 0.1 ug/L. A total of three hundred sixty-six samples were received at our laboratory; however, only three hundred and forty two samples were analyzed. As requested by EPS some of the extra samples were composited to reduce the total number of samples for analysis. In the table, each sample was also recorded as to degree of visual clarity. The samples were rated from 1 to 4 as the clarity of the sample decreases from clear (rated as 1), to either cloudy (as 2), or to contain fine sediment (as 3) or large sediment (as 4).

Of the 342 samples, all were found to contain some levels of PCP and 2,3,4,6-TTCP. The ranges of PCP and 2,3,4,6-TTCP found were from less than 1 ug/L to more than 100 mg/L. Levels of 2,4,6-TCP and 2,3,6-TCP were found to have a lower range (9 ug/L to less than 0.1 ug/L). Approximately one half of the samples did not contain any detectable amount of 2,4,6-TCP.

4.2 Quality Control

As stated in our proposal (Appendix D, Section 8.1) a QC program must consist of an initial demonstration of laboratory capability. This was established by the completion of the qualification samples submitted to Mr. Paul Kluckner dated September 9, 1986.

An ongoing analysis of reagent water blanks (Appendix D, Section 8.1.3) with each processing batch of samples was carried out throughout the whole period of this project. The results of the reagent blanks did not indicate any significant chromatographic peaks that might cause inteference in the chlorinated phenol analysis (see Figure 1). Approximately 30 reagent blanks were analyzed throughout the four month project.

It was our intention at the beginning of the project to analyze 10% matrix spikes as stated in our proposal (Appendix D, Section 8.3). However, due to the vast range in the concentration of the chlorinated phenols found in the samples (i.e., ranging from less than 0.1 ug PCP/L to greater than 100 mg PCP/L), and the time constraints of the project, our laboratory had to resort to the use of in-house quality control (QC) fortified samples at various concentrations (Appendix D, Section 8.2) and duplicate analysis of some actual samples to monitor the accuracy and precision of our analysis. A summary of the QC fortified sample recoveries is listed in Table 3, showing dates of analysis, levels of spike (in water), and recoveries of different chlorinated phenols. A summary of the duplicate analysis is listed in Table 4. There were 20 fortified samples and 32 duplicate analysis included in this project for quality control.

Since the ratio of the electron capture detector response to the amount of chlorinated phenols injected (calibration factor) is constant over the working range (from 0.02 - 0.20 ng "on column"), the calibration factor of each chlorinated phenol was used for quantification as recommended in EPA Method 604. Instrument performance was also monitored in measuring the daily response of the detector to a fixed amount of the phenols. Thus, any sudden change in sensitivity of the system would be easily recognized.

4.3 GC/MS Confirmation

Three samples were selected for the confirmatory analysis of PCP and 2,3,4,6-TTCP using a Finnigan 4500 gas chromatograph/mass spectrometer (GC/MS). The samples were CTL#145, #288 and #364. The derivatized extracts of the samples were injected into the GC/MS followed by the injection of the derivatized analytical standards of PCP and TTCP. Both PCP and TTCP were confirmed to be present in the three samples analysed.

APPENDIX III

SAMPLING AND ANALYSIS QUALITY CONTROL

APPENDIX III SAMPLING AND CHEMICAL ANALYSIS QUALITY CONTROL

A laboratory prequalification study was run in order to determine the contract laboratory capable of performing the analysis. After the laboratory was selected an internal quality control program was combined with a series of blind split samples to be analysed by both the contract laboratory and the Environment Canada Water Quality Laboratory.

1.1 Laboratory Demonstration Test - Prequalification Study

An industrial "real world" storm water sample was collected from a working drive in dip tank operation which was subject to flooding by rainfall. The tank was selected to provide a concentrated solution from which stock solutions would be formulated for the contract lab qualification study.

The working solution in the drive in tank would contain the typical contaminant matrix of chemical and yard debris which would be found in rain water runoff from a production mill site. The working stock solution was formulated from the stock solution at approximately 1 000 000 ppb PCP. PCP was the major target chemical for the purpose of making up standards and TTCP was selected as the minor target chemical that would have concentrations in the stock dilutions proportional to the PCP concentration. Two laboratory stock solutions of simulated rainfall were made up at concentrations of 1.0 ppb and 100 ppb PCP. From these two stock solutions the following split sample solutions were made to represent the estimated range of concentrations expected in storm water runoff:

Solution #1: 18 mls of 100 ug/L into 6.0 L = $\frac{1\ 800\ \text{ug}}{6\ \text{L}}$ 300 ug/L (ppb)

Solution #2: 150 mls of 100 ug/L into 6.0 L = $\frac{15\ 000\ \text{ug}}{6\ \text{L}}$ 2 500 ug/L (ppb)

Solution #3: 0.3 mls of 1.0 ug/L into 6.0 L = $\frac{0.3\ \text{ug}}{6.0\ \text{L}}$ 0.05 ug/L (ppb)

Solution #4: 6.0 mls of 1.0 ug/L into 6.0 L = $\frac{6.0\ \text{ug}}{6.0\ \text{L}}$ 1.0 ug/l (ppb)

These samples were analysed by West Vancouver Laboratory Services - Environmental Protection Water Quality Laboratory and the results are reported in Table 1 (see also Appendix I, Chlorophenol Analysis Protocol).

TABLE 1 **WEST VANCOUVER LABORATORY SERVICES - ENVIRONMENTAL PROTECTION, WATER QUALITY LABORATORY ANALYTICAL RESULTS FOR PCP and 2, 3, 4, 6 - TTCP CONCENTRATIONS (PPB) in BLIND SAMPLES SUBMITTED TO COMMERCIAL LABORATORIES**

SAMPLE #	PCP TARGET CONCEN-TRATION PPB	1ST ANALYSIS (86/08/13) PCP	2ND ANALYSIS (86/09/16) PCP	1ST ANALYSIS (86/08/13) TTCP	2ND ANALYSIS (86/08/16) TTCP
1	300	387	318	1 070	803
2	2 500	4 070	3 830	10 200	10 300
3	0.05	0.058	--	0.118	--
4	1.00	1.13	1.08	2.89	2.56

One liter aliquots of each stock solution was submitted to the six candidate private laboratories for analysis in the numerical order listed. This order was specified to test for cross sample contamination in the analytical procedure.

Cantest Ltd. was selected as the contract laboratory based on analytical performance and price/sample criteria. Test protocol used by Cantest Ltd. is reported in Appendix II.

2 CANTEST LTD. - IN HOUSE QUALITY CONTROL - FORTIFIED SAMPLES

Table 2 lists the recoveries of inhouse samples fortified with known quantities of chlorophenols. The spiking concentrations range from 0.2-5 000 ppb. Recoveries of chlorophenols averaged 102.4 ± 15.8 ppb for PCP and 96 ± 19 % for TTCP for 20 samples. Recoveries for 2,3,6-Trichlorophenols averaged 101.2 ± 12.8 % for five samples.

2.2.1 **Duplicate Analysis.** A total of 38 field stormwater samples (11% of the total quantity) were analyzed in duplicate to check for precision in the analytical procedure. The total mean difference was 1.9% for TTCP and 1.6% for PCP indicating good repeatability of analysis within a short time frame.

TABLE 2 CANTEST LTD. IN-HOUSE QUALITY CONTROL FORTIFIED SAMPLE RESULTS

DATE OF ANALYSIS	LEVEL OF SPIKING (ppb)	PERCENT RECOVERIES		
		PCP	TTCP	TCP (2,3,6-)
86/11/28	2.0	72	130	110
86/12/18	4.0	110	94	80
87/01/29	0.2	75	135	NA
87/02/04	5000	108	103	NA
87/02/05	5000	97	85	NA
87/02/06	1000	90	85	NA
87/02/09	1000	116	77	NA
87/02/11	1000	118	104	NA
87/02/15	2.0	120	100	NA
87/02/15	1000	120	113	108
87/02/16	1000	98	125	NA
87/02/18	1000	120	94	98
87/02/19	2.0	120	100	110
87/02/20	2.0	94	86	NA
87/02/25	1000	122	108	NA
87/02/25	2.0	97	80	NA
87/02/26	1000	88	75	NA
87/02/27	2.0	83	70	NA
87/02/27	2.0	104	86	NA
87/02/28	2.0	95	70	NA
		$\overline{x}$ = 102.4 ± 15.8	$\overline{x}$ = 96 ± 19	$\overline{x}$ = 1012 ± 12.8

2.2 Storm Water Runoff - Split Sample Analysis Results.

A total of 29 split samples (8% of the total field samples collected) were submitted to both the Environment Canada (EP) and the Cantest Ltd. Laboratories. The samples were split by two methods, either two bottles were filled simultaneously at the storm drain or several samples were composited and then divided into equal volumes for submission to each laboratory.

During the early stages of the sampling program an anomaly between the labs was discovered in that the EP lab analysis of samples taken at a site in mid November were in the 20 000-40 000 ppb range while the contract lab analysis for the same samples were in the 1 000 to 2 600 ppb range. All new sample analysis was stopped until the cause(s) for the anomalies were determined.

At the Contract Laboratory it was found that at concentrations above 1 500 ppb all the conversion reagent (diazomethane) used to derivatize the chlorophenols was consumed at concentrations above 1 500 ppb and excess chlorophenol would not be "seen" by the gas chromatograph detector. A total of 50 samples at 1 000 ppb or greater were then re-analyzed by the contract lab for the correct value. The quality control procedure was then revised by increasing the number of blind split samples and blind spike samples. The number of technicians performing the analysis was also reduced. A total of four weeks was lost before the regular sample analysis could begin. Due to the late start in the monitoring program, field sampling was continued during the retesting period and a backlog of six weeks analysis occurred at the contract lab. All samples submitted to the EP lab were analyzed as submitted so that an average of 4 to 6 weeks developed between analytical times for the QC splits for each laboratory. Sample analysis was continued at the EP lab in order to reduce the potential for sample deterioration and provide a reference for the contract lab results.

The revised quality control procedure demonstrated that the lack of derivatization chemical was the cause of the discrepancies in the initial samples and there was good agreement between laboratories after this problem was corrected.

APPENDIX IV

ADDITIONAL WATER QUALITY PARAMETERS

APPENDIX IV ADDITIONAL WATER QUALITY PARAMETERS

The primary objective of the storm water study was to monitor the concentration of chlorophenol in runoff at wood protection mill sites. As the terms of reference were developed it was recognized that other stormwater constituents should be monitored. A limited number of samples were collected and a variety of water quality tests were performed to provide information regarding the potential impact they may have on the receiving environment.

1.1 Results and Discussion

Water quality parameter data for all monitored sites is presented in Appendix I-VII. To illustrate general trends and correlations in the stormwater effluent, as discussed below, water quality data from samples collected at Mill #6 on December 22, 1986 are presented here (Figures 1-6).

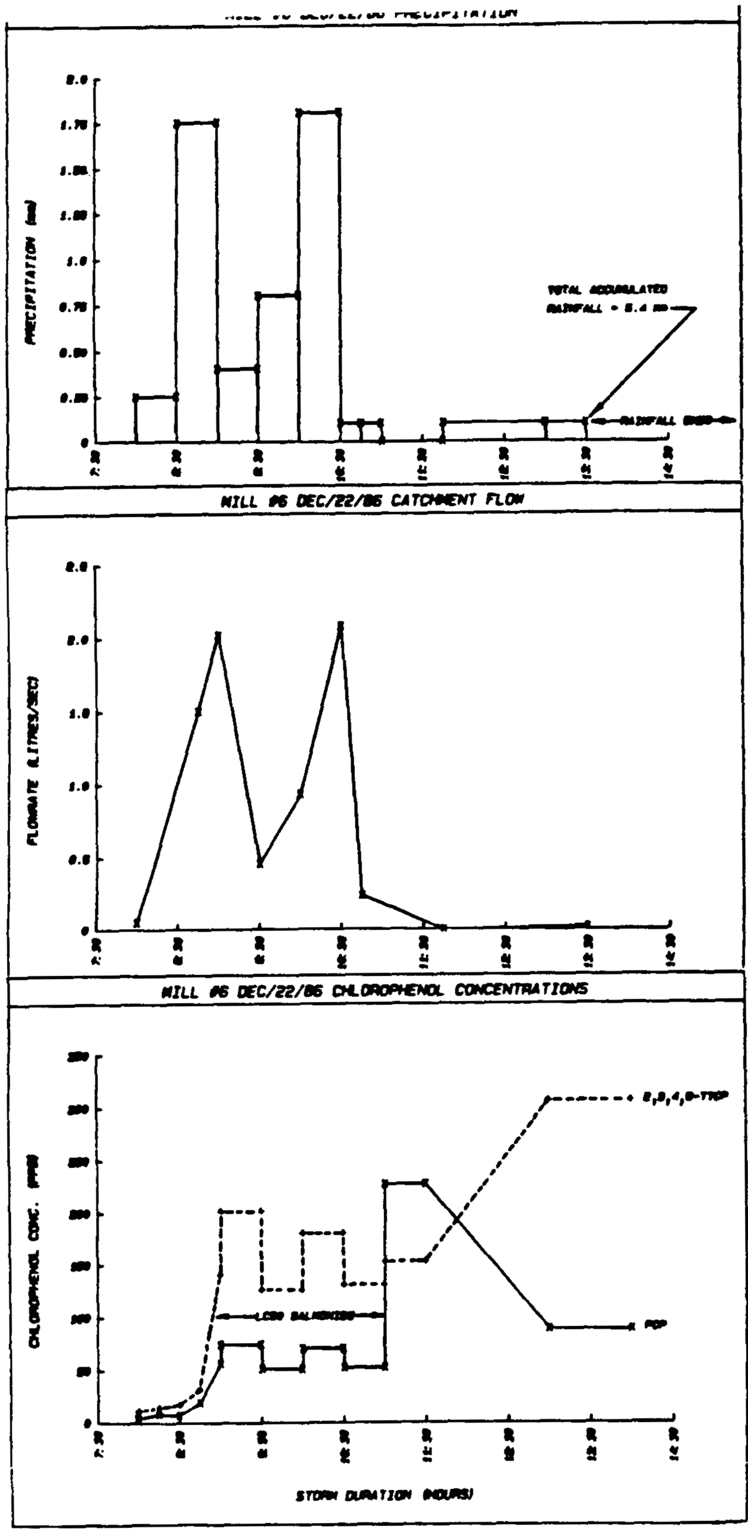
1.1 Temperature

The temperature of the stormwater effluent at all of the mills ranged from 3.9°C to 14.5°C depending on the time of year sampling was performed and the individual storm conditions. Little variation in temperature was evident during an individual storm event.

1.2 Dissolved Oxygen

Storm water effluent was generally well aerated, with concentrations ranging from 7.7 mg/l to 13.8 mg/l at all of the mills. A strong positive correlation exists between rainfall and D.O. concentration. In all cases, as rainfall intensity increased, the stormwater became more highly aerated. The intensity of the storm therefore, determined the variation in dissolved oxygen concentration over the individual storm event.

It should also be noted that the highest dissolved oxygen concentrations occur at the lowest water temperatures, as would be expected given the physics of gas solubility in water.



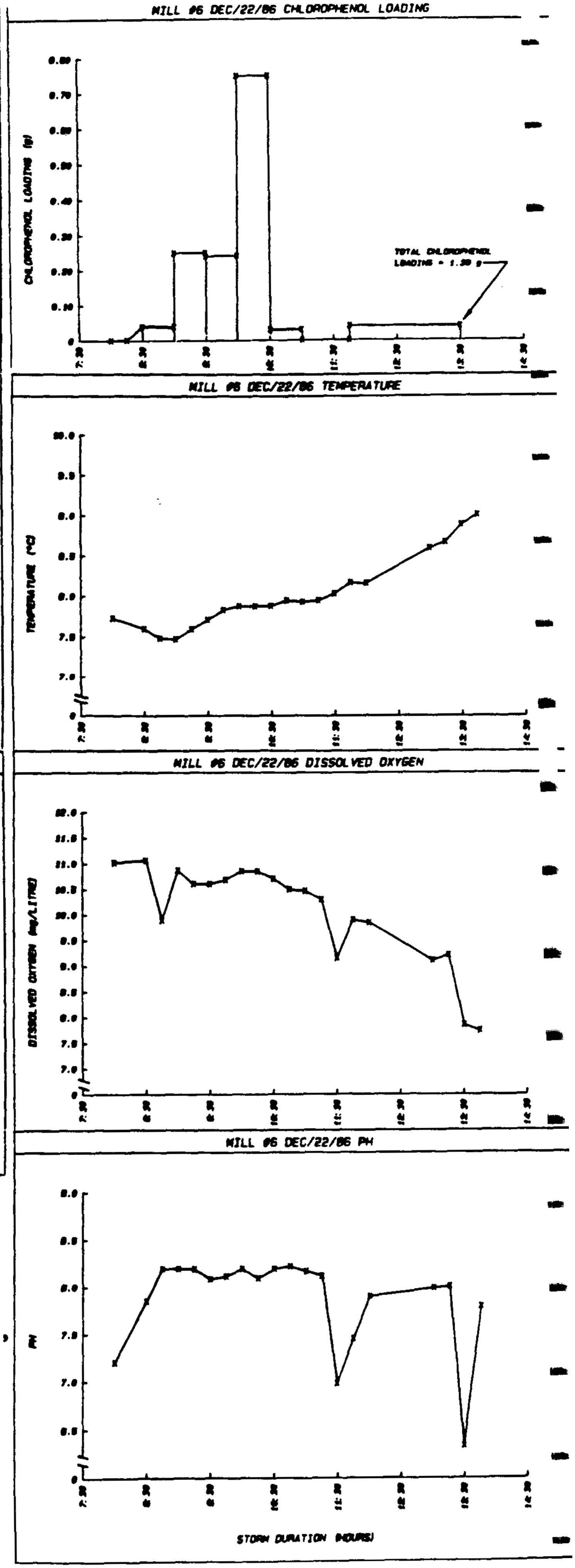


FIGURE 1 MILL #6 - DECEMBER 22,1986

PRECIPITATION, FLOW, CHLOROPHENOL CONCENTRATION, CHLOROPHENOL LOADING, TEMPERATURE, DISSOLVED OXEGEN, AND pH.

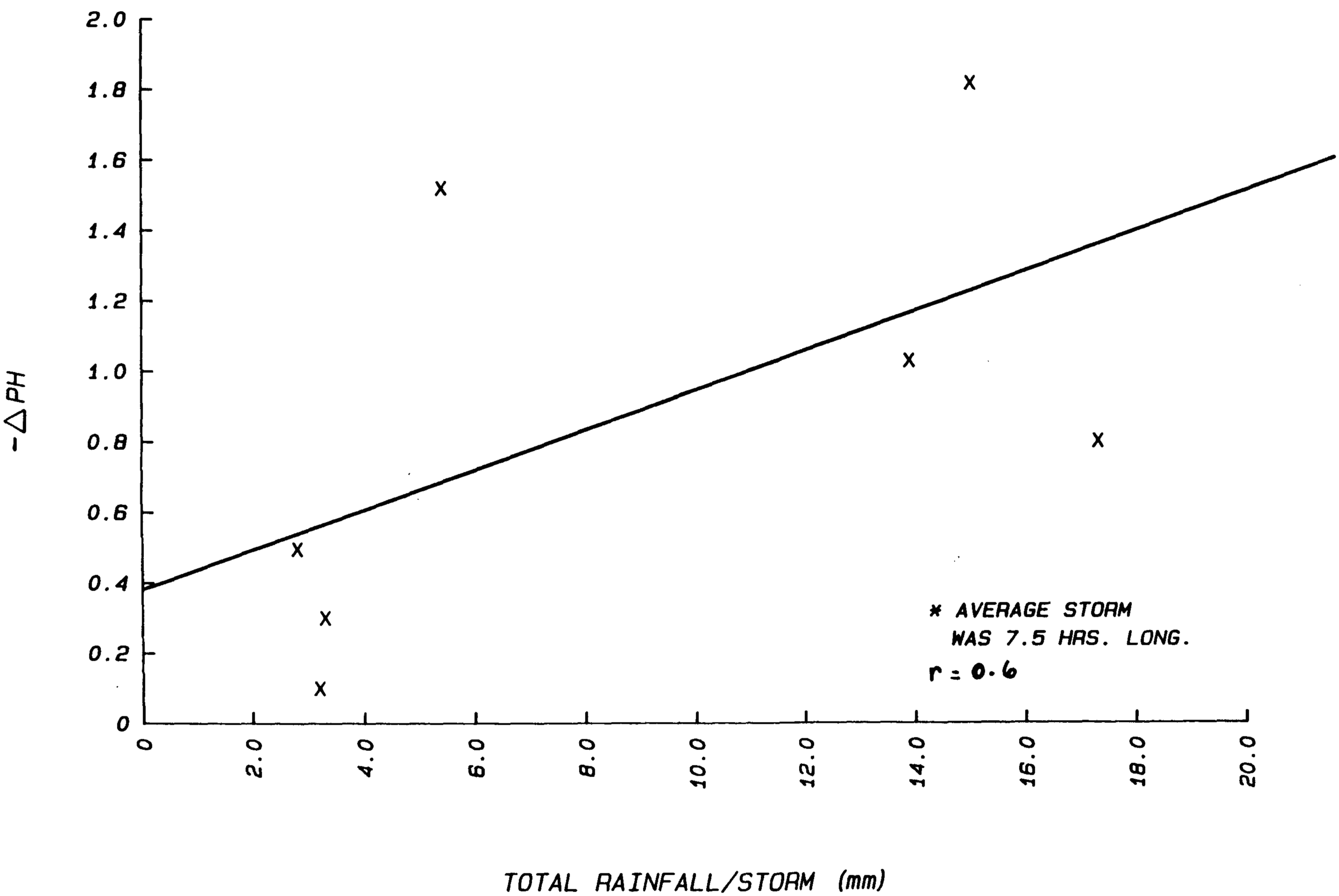
1.3 pH

The pH of the storm water effluent at all sites ranged from 4.3 to 8.9. Most of the storm water monitored however, was in the pH 6 to pH 7 range. During individual storm events, pH rarely fluctuated more than one unit. While the data show some anomalies, pH appears to be most directly dependent on rainfall, both intensity and cumulative amount. In general, the pH at the beginning of a storm event was higher than at the end of the storm. The data indicate that the buffering agents in the treatment solution which keep the chlorophenols in the chlorophenate form, buffer the stormwater for a length of time. As the storm progresses and the buffering capacity diminishes, the pH of the storm water approaches that of rainfall (average pH 4.77). Storm dynamics, the treatment formulation and the amount of treated lumber and/or contaminated areas on the site create a complex set of variables that will affect storm water pH. Based on data from seven storm events which average 7.5 hours long the decrease in pH with total rainfall can be approximated by the relationship $pH = 0.06R + 0.39$ where R is the total accumulated rainfall in mm (Figure 26).

1.4 Conductivity

Conductivity values ranged from 0.017 millisiemens/cm (mS/cm) to 0.55 mS/cm at all sites. Conductivity tended to be elevated at the start of the storm as the initial overland flow contributed dissolved materials to the storm water. After the "first flush", an inverse correlation between conductivity and flow became evident, due to dilution and concentration effects created by the storm. Conductivity was sensitive to variations in all dissolved solids and therefore could not be directly correlated to concentrations of specific storm water components.

FIGURE 2 - TOTAL RAINFALL PER STORM VS ΔPH



1.5 Phenolics

Phenolic concentrations in the storm water effluent were high, ranging from 0.02 mg/l to 22 mg/l. Levels fluctuated over the storm duration but exhibited a trend for high initial concentrations corresponding with the "first flush", and a decline as each storm progressed.

1.6 Total and Suspended Solids

Values of total and suspended solids varied considerably between mills, depending on site specific characteristics. Mill #6 sampled on December 22, 1986 had the highest levels of total solids at 20,000 mg/l, corresponding to the "first flush" at a site where the paved yard was deteriorated and covered with dirt from vehicles operating at an adjacent construction project. Initially high concentrations of solids were generally followed by a decline as the storm progressed. Occasional elevations in levels were correlated to increased flows.

1.7 Total Organic Carbon

Concentrations of total organic carbon ranged from 6 mg/l to 52 mg/l at the two mills where samples were collected. Total organic carbon levels were elevated at the start of the storm and declined rapidly as the storm progressed. At the end of the storm TOC levels began to rise slightly.

1.8 Oils and Grease

Concentrations of oil and grease in the mill storm water effluent from all sites ranged from 2.0 mg/l to 53 mg/l. A general trend of high initial levels declining and plateauing as the storms progessed, was established.

1.9 Nitrogen (NO_2, NO_3 and NH_3)

Concentrations of nitrates and nitrites ranged from 0.035 mg/l to 1.9 mg/l at the three sites monitored. Ammonia concentrations were monitored at only one site, (Mill #5 January 29, 1987) where they ranged between 0.01 mg/l and 0.16 mg/l. Nitrate/nitrite and ammonia data exhibit a tendency for elevated initial values corresponding to the "first flush" with an overall decline by the storms end.

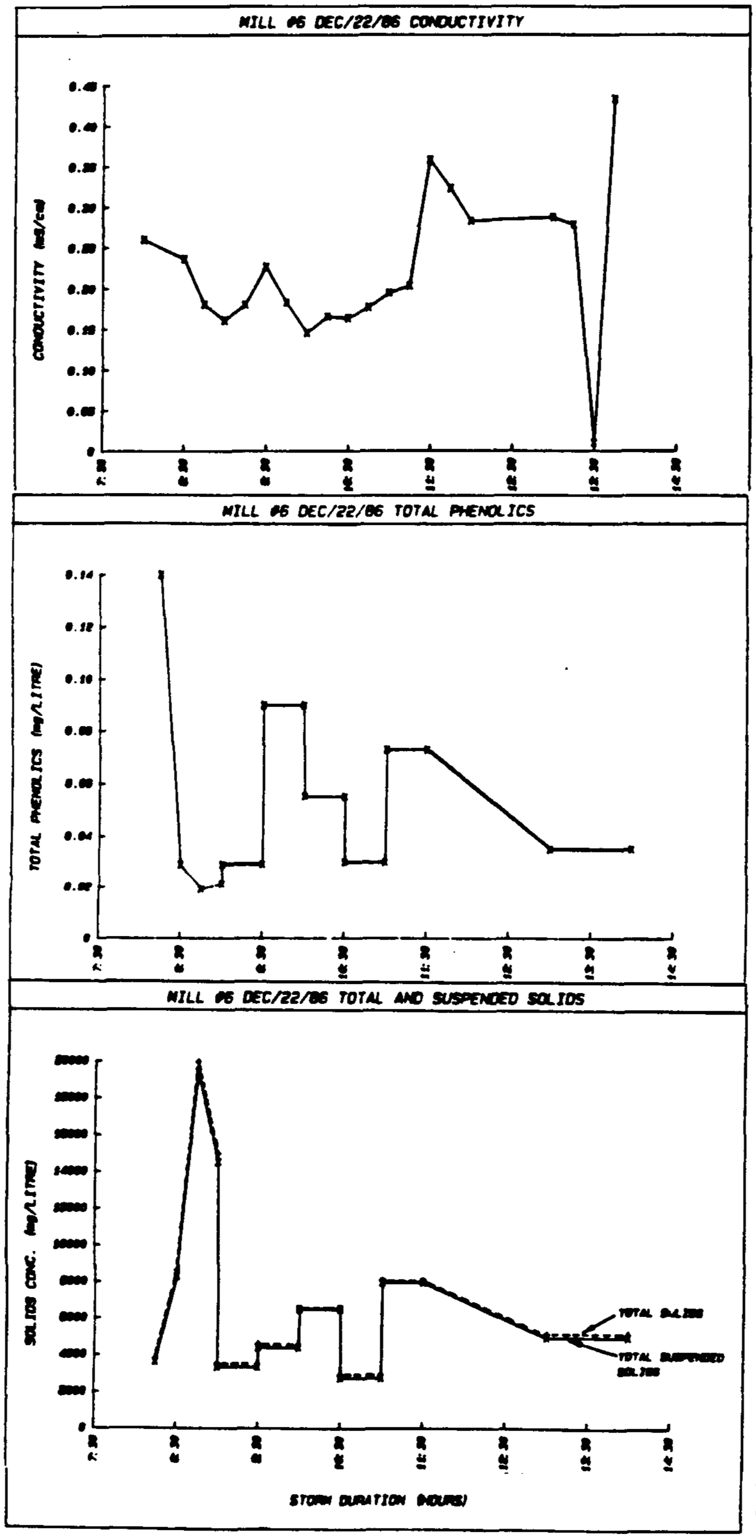
1.10 Metals

Ranges in the concentration of total metals in mill storm water effluent is presented in Table 6. Concentrations of antimony, arsenic, beryllium, bismuth, nickel, silver and tin were below detectable levels in all samples. Concentrations of barium, boron, cadmium, calcium, cobalt, copper, iron, magnesium, molybdenum, potassium, sodium, strontium, titanium, vanadium and zinc were all within acceptable ranges. Some elevated concentrations of aluminum, chromium, lead, manganese, phosphorus and silicon were exhibited.

Metal concentrations were generally highest at the beginning of the storm, corresponding to the "first flush". As the storm progressed, the higher metal concentrations declined and showed decreased variation. A trend toward higher concentration of the metals in the storm water was also seen when rainfall diminished or stopped.

TABLE 6 RANGES IN CONCENTRATION OF TOTAL METALS IN STORM WATER EFFLUENT MILL #6, DECEMBER 22, 1986

PARAMETER	# OF SITES MONITORED	RANGE IN VALUES (mg/l)	PARAMETER	# OF SITES MONITORED	RANGE IN VALUES (mg/l)
Aluminum	4	0.6 - 380	Magnesium	4	2.5 - 160
Antimony	4	< DL	Manganese	4	0.45 - 10.0
Arsenic	4	< DL	Molybdenum	4	< DL - 0.7
Barium	4	0.01 - 3.2	Nickel	4	< DL
Beryllium	4	< DL	Phosphorus	4	1.0 - 40.0
Bismuth	2	< DL	Potassium	2	7.0 - 24.0
Boron	4	< DL - 0.4	Silicon	4	1.5 - 460
Cadmium	4	< DL - 0.05	Silver	2	< DL
Calcium	4	5.5 - 650	Sodium	4	18.0 - 75.0
Chromium	4	< DL - 0.6	Strontium	4	0.02 - 2.1
Cobalt	4	< DL - 2.3	Tin	4	< DL
Copper	4	< DL - 1.65	Titanium	4	< DL - 20.0
Iron	4	1.2 - 430	Vanadium	4	< DL - 1.0
Lead	4	< DL - 1.9	Zinc	4	0.15 - 4.5



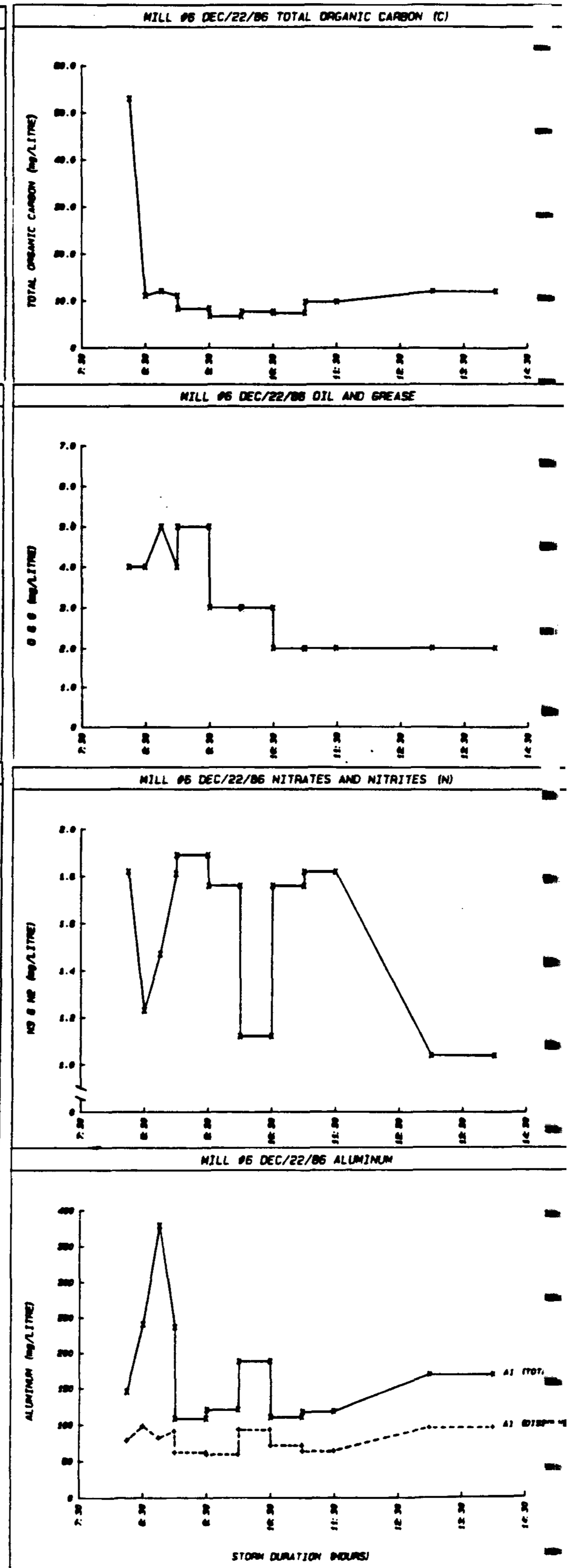
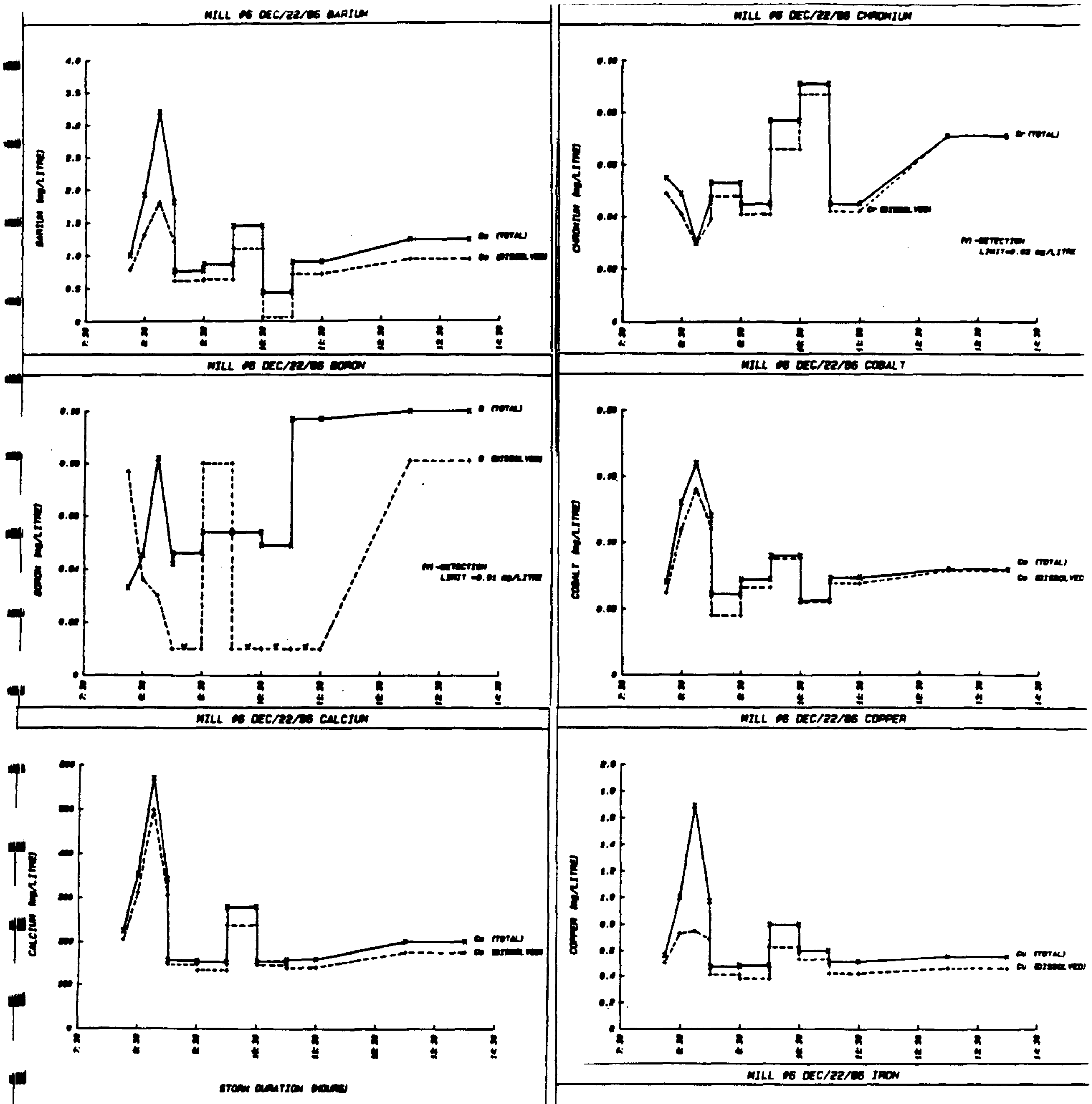


FIGURE 3 MILL #6 - DECEMBER 22, 1986
CONDUCTIVITY, PHENOLICS, TOTAL AND SUSPENDED SOLIDS, TOTAL ORGANIC CARBON, OIL AND GREASE, NITRATES AND NITRITES, AND ALUMINIUM.



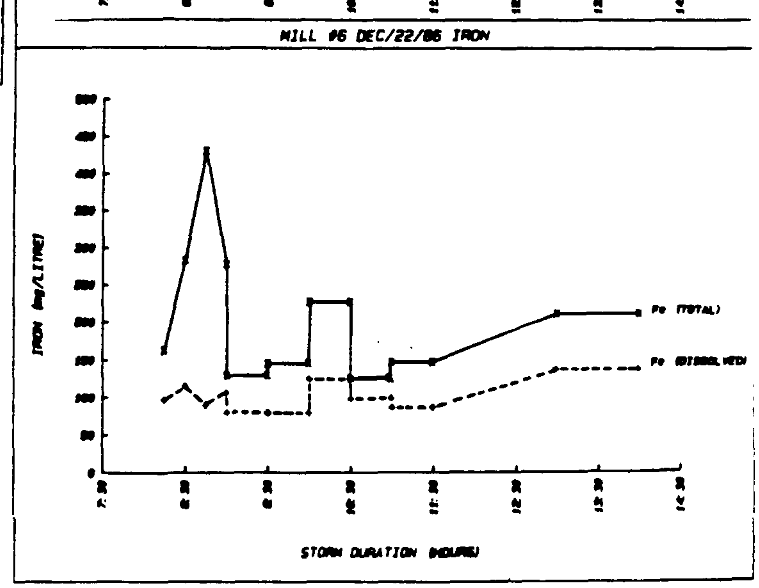


FIGURE 4 MILL #6 - DECEMBER 22, 1986
BARIUM, BORON, CALCIUM, CHROMIUM, COBALT,
COPPER, AND IRON.

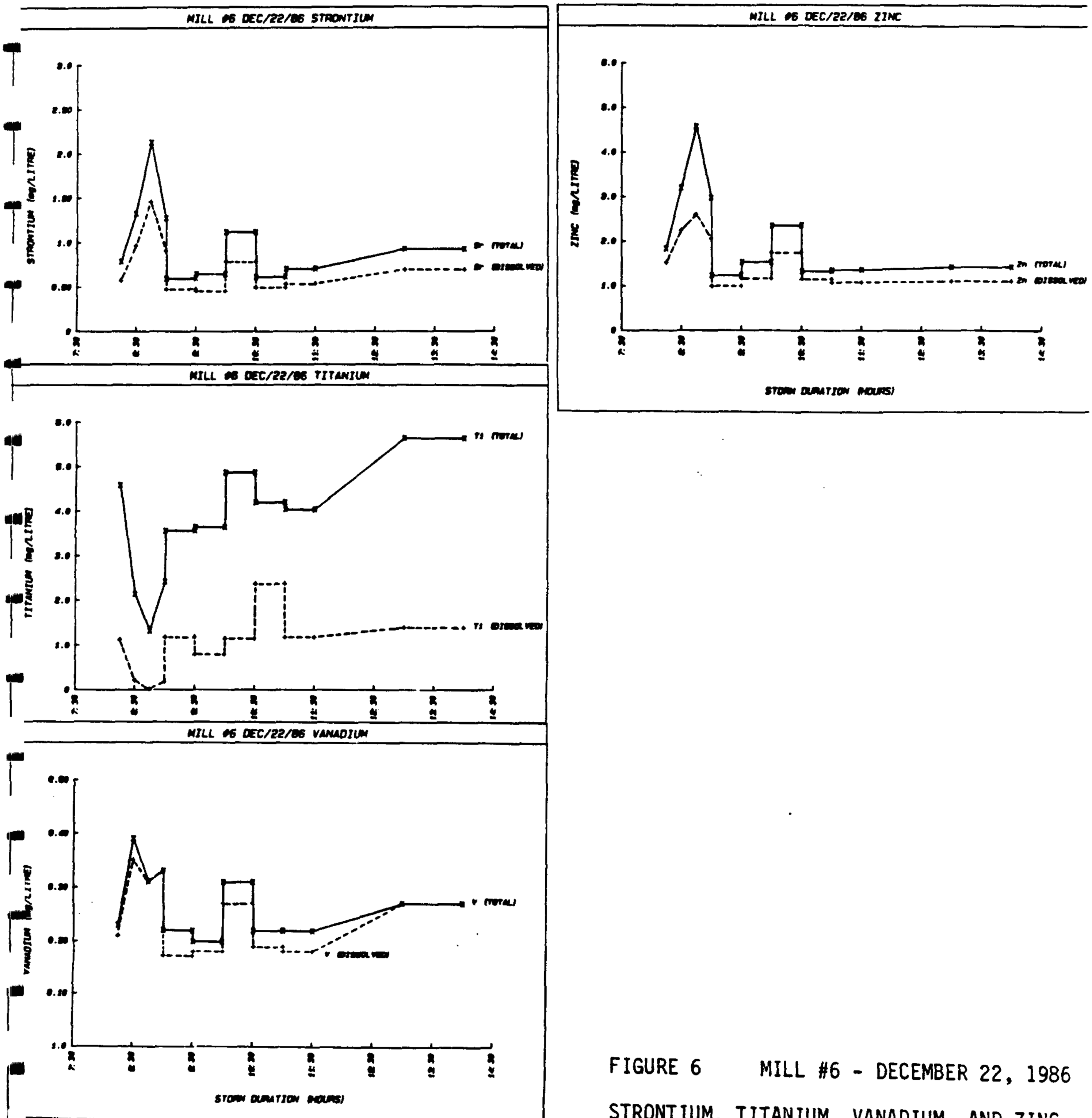


FIGURE 6 MILL #6 - DECEMBER 22, 1986

STRONTIUM, TITANIUM, VANADIUM, AND ZINC.