**FRASER RIVER ACTION PLAN**

# Northwood Pulp Mill - Winter 1996 Resin Acids and 1994 - 1996 Chlorophenolic Compounds Summary Report

DOE FRAP 1997- 51

Canada

Environment Canada Environnement Canada

# Northwood Pulp Mill - Winter 1996 Resin Acids and 1994-1996 Chlorophenolic Compounds Summary Report


| | |
|---|---|
| Report Synthesis | - George Derksen (DOE) |
| Research Program | - George Kruzynski (DFO) |
| Analytical Chemistry | - Michael Ikonomou (DFO) |
| | - Brad Spencer (DOE) |
| | - Dale Hoover (AXYS) |


DOE FRAP 1997-51

March 1998

Any comments regarding this report should be forwarded to:

Technology and Pollution Prevention Section
Environment Canada
224 West Esplanade
North Vancouver, B.C.
V7M 3H7

# Table of Contents

# List of Tables

# List of Figures

# Summary

As part of a Northwood pulp mill winter 1996 chronic toxicity study on juvenile chinook salmon, the treated effluent was analyzed for resin acids and chlorophenolic compounds. A 1995 round robin analysis of a resin acid reference sample and Northwood's effluent showed that considerable variability existed among eight participating laboratories. In 1996, AXYS Analytical (AXYS), Pacific Environmental Science Centre (PESC) and Institute of Ocean Sciences (IOS) analyzed resin acids in each of ten 24-h composite effluent samples collected over the three month study. AXYS analyzed the effluent samples for chlorinated phenolic compounds and those results are also presented.

The effluent results demonstrated that two of the laboratories (AXYS and IOS) had closer overall study mean concentrations for pimaric acid (6.2 ug/L *vs* 12.7 ug/L), sandaracopimaric acid (0.6 ug/L *vs* 1.4 ug/L), isopimaric acid (5.8 ug/L *vs* 10.6 ug/L) and dehydroabietic acid (7.9 ug/L *vs* 18.0 ug/L). PESC had higher overall mean concentrations for the same resin acids (21.5 ug/L, 6.3 ug/L, 20.2 ug/L and 28.5 ug/L respectively).

Using the overall study mean resin acid effluent concentrations for each laboratory, the daily loading estimate for pimaric acid was 0.9 to 3 kg/d , sandaracopimaric acid 0.1 to 0.9 kg/d , isopimaric acid 0.8 to 2.8 kg/d and dehydroabietic acid 1.1 to 4 kg/d.

The effluent resin acid concentrations were well below 96h LC50 acute toxicity levels for salmonids (200 to 1700 ug/L at neutral pH). As little as a 5:1 dilution reduced even the highest dehydroabietic acid effluent concentration reported (64 ug/L) to within the surface water quality objective of 12ug/L and 13ug/L, at pH 7.5 and 8.0, respectively.

Of the forty-four chlorophenolic compounds analyzed, only nine were regularly detected and of those, six where mono-chlorophenolic compounds. The predominant compound was 6-Chlorovanillin (1.7 - 10 ug/L) and concentrations of other regularly detected compounds were less than 0.3 ug/L.

**Résumé**

Dans le cadre de l'étude de toxicité chronique portant sur le saumon quinnat qui a été effectuée pendant l'hiver de 1995 à l'usine de pâtes de Northwood, on a dosé les acides résiniques et les composés chlorophénoliques dans les effluents traités. En 1995, un test comparatif interlaboratoire d'un échantillon de référence d'acide résinique et d'un effluent de l'usine de Northwood a montré l'existence de fortes variations dans les résultats des huit laboratoires participants. En 1996, AXYS Analytical (AXYS), le Centre des sciences environnementales du Pacifique (CSEP) et l'Institut des sciences de la mer (ISM) ont analysé les acides résiniques de dix échantillons d'effluents composites de 24 h recueillis au cours de l'étude de trois mois. AXYS a dosé les composés phénoliques des échantillons d'effluents et ces résultats sont également présentés.

Les résultats obtenus pour les effluents ont montré que deux des laboratoires (AXYS et l'ISM) avaient obtenu, sur la durée totale de l'étude, des valeurs de concentrations moyennes plus rapprochées pour l'acide pimarique (6,2 µg/L contre 12,7 µg/L), l'acide sandaracopimarique (0,6 µg/L contre 1,4 µg/L), l'acide isopimarique (5,8 µg/L contre 10,6 µg/L) et l'acide déshydroabiétique (7,9 µg/L contre 18,0 µg/L). Le CSEP avait obtenu des concentrations moyennes plus élevées pour ces mêmes acides (21,5, 6,3, 20,2 et 28,5 µg/L, respectivement).

Selon les valeurs des concentrations moyennes d'acides résiniques dans les effluents sur toute la durée de l'étude, la charge quotidienne estimée était de 0,9 à 3 kg/jour pour l'acide pimarique, de 0,1 à 0,9 kg/jour pour l'acide sandaracopimarique, de 0,8 à 2,8 kg/jour pour l'acide isopimarique et de 1,1 à 4 kg/jour pour l'acide déshydroabiétique.

Les concentrations d'acides résiniques dans les effluents étaient bien inférieures aux valeurs de toxicité aiguë ($CL_{50}$ – 96 h) pour les salmonidés, puisqu'elles étaient comprises entre 200 et 1 700 µg/L à pH neutre. Une dilution de seulement 5:1 ramenait même la plus forte concentration d'acide déshydroabiétique signalée pour les effluents (64 µg/L) à une valeur respectant l'objectif de qualité de l'eau de surface (12 et 13 µg/L à des pH de 7,5 et 8,0, respectivement).

Des 44 composés chlorophénoliques analysés, seuls 9 étaient détectés de façon régulière et, de ceux-ci, six étaient des composés monochlorophénoliques. Le composé prédominant était la 6-chlorovanilline (de 1,7 à 10 µg/L) et les concentrations des autres composés détectés de façon régulière étaient inférieures à 0,3 µg/L.

# 1. INTRODUCTION

The Fraser River Action Plan, a six-year program, was initiated to assess the condition of the Fraser River ecosystem (FRAP, 1992). Determining the quality and quantity of wastewater discharges and estimating contaminant loadings was an integral component of the program.

In 1995, the three upper Fraser River bleached kraft pulp mills discharged approximately 400,000 $m^3$/d of secondary treated effluent into the river (Figure 1). The Department of Fisheries and Oceans (DFO) conducted on-site chronic sub-lethal continuous-flow bioassays on juvenile chinook salmon in the winter 1994-95 and again in 1995-96 at the Northwood pulp mill in Prince George. Northwood represents a state-of-the-art pulp mill and being the furthest upstream mill, potential effects resulting from background waterborne contaminants were reduced. Environment Canada participated in the project with funding to collect and analyze wastewater samples for selected chemical toxicants in both 1994-95 (Environment Canada, 1997) and 1995-96.

Levels of resin acids in untreated pulp mill effluents often exceed lethal limits. Chlorophenolic compounds, arising during the bleaching of pulp, are normally present at sublethal levels in untreated whole mill effluents (McLeay and Associates, 1987). To comply with federal and provincial acute fish toxicity and Biochemical Oxygen Demand ($BOD_5$) regulatory requirements, the upper Fraser River pulp mills treat their process water in Aerated Stabilization Basins (ASBs) (DFO, 1992; WMA, 1992). ASBs reduce resin acid concentrations, the major acute toxicity fraction, in wastewaters to non-acutely toxic conditions (generally zero mortality to rainbow trout over a 96-h exposure period). Recently, bleached kraft pulp mills have increased the substitution of elemental chlorine with chlorine dioxide to reduce dioxin levels (MELP, 1995). Studies have shown that this has also resulted in a change in the chemical profile and concentration of chlorophenolic compounds (Pryke et al., 1993; NCASI, 1993).

A round robin eight-laboratory assessment of the resin acid content of a quantitation standard sample and a sample of Northwood's effluent in 1995 demonstrated a high degree of inter-laboratory variability (Bicho et al., 1995). Based on the results of the round robin assessment it was decided to look at laboratory variability in more detail. Three of the laboratories which participated in the original round robin analyzed each of 10 effluent samples collected in the winter 1995-96 study. This report presents the resin acid results, some of the round robin results, and other relevant resin acid data collected recently at the three upper Fraser River pulp mills.

The results of samples analyzed for chlorinated compounds in the 1994-95 and 1995-96 studies by one of the two laboratories which tested for these compounds, are also presented.

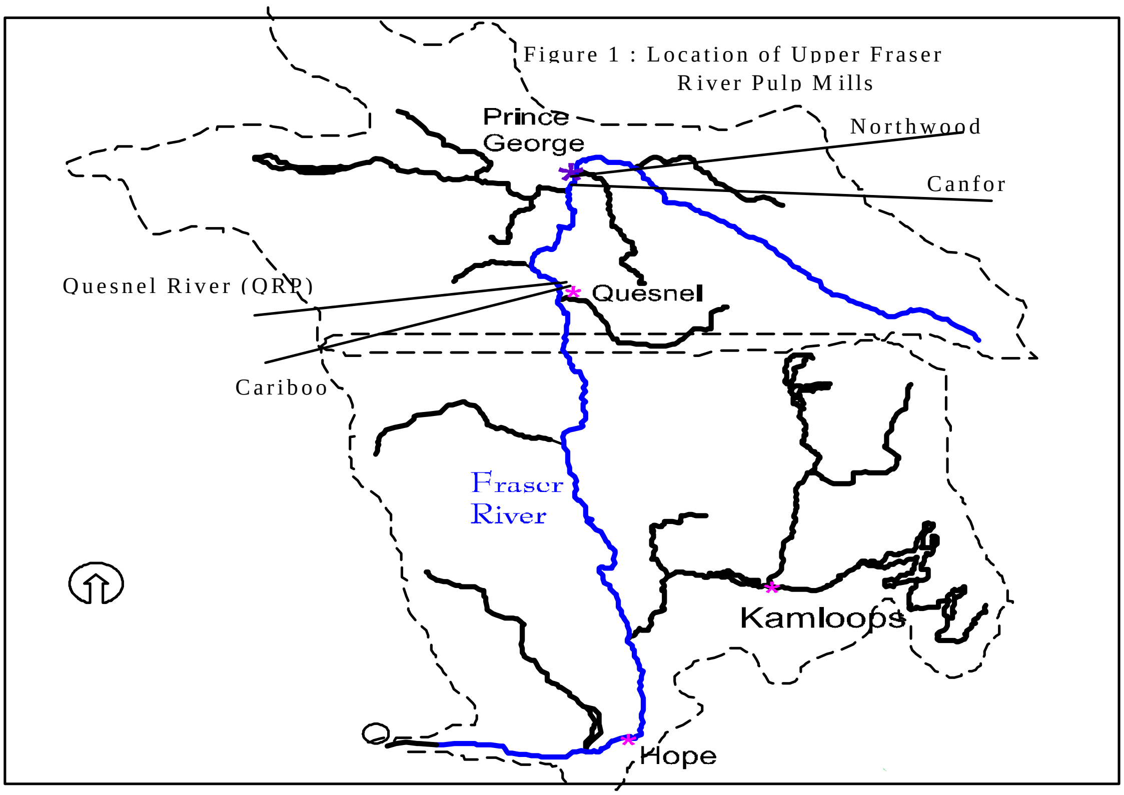


Figure 1 : Location of Upper Fraser River Pulp Mills

## 2. PULP MILL OPERATIONS

The upper Fraser pulp mills routinely collect effluent quality samples for conventional quality indicators. These data are submitted to Environment Canada and have been used in Section 4 to describe pulp mill operations during the study period. A description of each of the three upper Fraser River bleached kraft pulp mills is reported in Table 1.

Table 1: Description of Upper Fraser River Bleached Kraft Pulp Mills

| Mill & Operation | Northwood | CanFor | Cariboo |
|---|---|---|---|
| Average 1995 Flow ($m^3/d$) | 145,000 | 145,000 | 98,100 |
| Average 1995 Production (ADt/d) | 1415 | 1471 | 909 |
| Bleach Sequence[1] | $D_{100}E_{Op}DE_pD$ (A & B mills) | $D_{100}E_{op}DED$ (Intercon & PGPC) | 50% $OCD_{50}E_{o(p)}DE_{(p)}D$<br>50% $OD_{100}E_{o(p)}DE_{(p)}D$ |
| Typical Wood Furnish<br>: Spruce or (Whitewood)<br>: Pine<br>: Fir | <br>50%<br>40%<br>10% | <br>45%<br>45%<br>10% | <br>(86-88%)<br>-<br>12-14% |
| ASB (days retention) | 8 | 6 | 8 |

(Whitewood) = Spruce,Pine,Balsam FIr

[1] D = Chlorine Dioxide; $E_{op}$ = hydrogen peroxide enhanced oxygen-caustic extraction; C = elemental chlorine; O = oxygen delignification

# 3. METHODS

## 3.1 Effluent Samples

The 1995-96 fish exposure experimental set-up was the same as in 1994-95 (Environment Canada, 1997). The 1996 sampling program occurred over two periods - January 08 to February 11 and again from February 12 to March 18. Effluent samples were collected at the final point of discharge, an overflow from a small mixing pond to the Fraser River. The pond receives wastewater from the mill's paired ASBs, each with a nominal 8-day retention.

Effluent samples were collected using a model PVS-DM9SD1-JX SIRCO liquid sampler equipped with an 8m 9.5mm ID teflon-lined intake line. This sampler was specifically selected because it can maintain liquid transport velocities in excess of 90 cm/sec and thus minimize sampling errors attributable to differential settling of suspended particulates common in treated bleach kraft mill effluent. Samples were drawn from a height of approximately 2m above the surface of the collection pond and the stainless steel intake was suspended 1m below the , surface in an area of high flow where the final effluent was being drawn into the diffuser intake for discharge into the Fraser River.

The sampler was programmed to composite hourly (350mL) samples over a period of 24h and to minimize possible temporal variation, sampling was conducted from noon Sunday to noon on Monday. Although the sampler was kept in a heated shed with the 9.5L glass collection vessel in a refrigerator immediately below, due to extreme weather conditions, the temperature was frequently less than the 4C setting resulting in samples being partially frozen on several occasions.

After transfer of the glass container from the sampling shed to the adjacent mobile laboratory, composite samples were thawed if necessary at room temperature, mixed vigorously with a clean PVC pipe to resuspend settled particulates and quickly poured into individual heat-treated 1L glass jars, resin acid samples pH adjusted to (~9.3) using 0.5N NaOH, temperature recorded and the jars sealed with hexane-washed aluminum foil and Teflon-lined caps. Sample jars were placed on ice packs in coolers and couriered overnight to analytical laboratories in North Vancouver and Sidney BC. Upon arrival, sample temperatures were recorded, pH adjusted to 9.5 if necessary, and then stored at 4C in the dark until extraction. Samples were processed within 24h of collection. The composite container was rinsed thoroughly with upstream Fraser River water before the next sampling period.

The chlorinated compounds samples were treated in the same manner except, the samples were adjusted to < pH 2 upon receipt at the laboratory. An additional sample was collected on each occasion for chloride, sulphate, bromide and nitrate analyses (PESC, 1995). Samples were placed in clean polyethylene containers and shipped with the other samples to North Vancouver.

## 3.2 Resin Acid Analyses

The laboratory methods for AXYS Analytical (AXYS), Pacific Environmental Science Centre (PESC) and Institute of Ocean Sciences (IOS) are summarized below. In addition to the effluent samples each laboratory was provided with an underivatized resin acid quantitation standard sample (RAQ1), prepared by PESC, to be analyzed (spike-in, derivatize and analyze) in the same manner as the effluent samples.

### 3.2.1 Extraction Step

AXYS - Methanol, surrogate standard and hydroxylamine hydrochloride were added and the sample was adjusted to pH 5 and extracted with 1:4 diethylether:hexane. The surrogate standard was O-methylpodocarpic acid. The extract was dried over anhydrous sodium sulphate and concentrated by rotary evaporation. The extract was transferred to a centrifuge tube with hexane, the solvent was evaporated and methanol was added to the residue. The laboratory recommended the effluent be adjusted to pH 9-9.5 in the field. The AXYS and IOS samples were shipped together and upon receipt of samples, AXYS checked and adjusted the pH for both laboratories and forwarded the samples to IOS.

PESC - The sample pH was adjusted to 9 and extracted with diethylether. The extract was dried over anhydrous sodium sulphate and concentrated by rotary evaporation. The extract residue was re-dissolved with methyl-t-butyl ether. The laboratory recommended effluent be adjusted to pH 9 upon receipt at the laboratory, thus avoiding problems with attaining accurate control of the pH adjustment under field conditions.

IOS - The sample was spiked with a surrogate standard and adjusted to pH 9 and extracted with 1:3 diethylether:dichloromethane (DCM) (3x). The extract was dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The extract was transferred to a centrifuge tube with DCM , the solvent was evaporated to dryness and methanol was added to the residue to reconstitute the sample. The laboratory recommended the effluent be adjusted to pH 9-10 in the field.

### 3.2.2 Derivatization Step

AXYS - Freshly generated diazomethane was added to the extract and allowed to react for 30 minutes, excess diazomethane was evaporated and hexane was added to the residue.

PESC - The extract was methylated with diazomethane for 30 minutes, evaporated to near dryness under nitrogen and the residue was re-dissolved in methyl t-butyl ether (MTBE).

IOS - Diazomethane was added to the extract and allowed to react for 2 hours at room temperature, excess diazomethane was evaporated to near dryness under nitrogen. An aliquot of MTBE was added to redissolve the residue.

3.2.3 Analysis

AXYS - The methylated extract was loaded onto a basic silica gel column. The column was eluted with hexane (discarded), followed by 5% diethylether:hexane (retained). The eluate was concentrated and an aliquot of recovery standard solution (d-12 chrysene) was added.

The final extract was analyzed by GC/MS using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 gas chromatograph with a CTC autosampler and a DG 10 Data system.

The chromatographic separation was carried out using a DB-5 column (30 m, 0.25 mm i.d., 0.25 um film thickness). A split/splitless injection sequence was used.

The mass spectrometer was operated in the EI mode using Multiple Ion Detection (MID) to enhance sensitivity, acquiring at least two characteristic ions for each target analyte and surrogate standard.

PESC - The re-dissolved residue was injected on a High Resolution Gas Chromatograph/ Low Resolution Mass Spectrometer (HRGC/LRMS) (Varian Saturn 3 system) for analysis.

The chromatographic separation was carried out using a DB-5 column (30 m, 0.25 mm i.d., 0.25 um film thickness). The mass spectrometer operated in EI mode.

The LRMS data is acquired in Total Ion Mode (TIM) and quantitation is performed using selected mass ions. A positive identification is made on the basis of a comparison of absolute retention times to those of the external standards and computer based mass spectral mass/intensity library matching routines.

IOS - The solution was analyzed by HRGC/HRMS. Analysis was carried out using a VG AUTOSpec high resolution mass spectrometer equipped with an HP 5890 Series II gas chromatograph.

The chromatographic separation was carried out on a DB-5 column (35 m, 0.25 mm i.d., 0.1 um film thickness). A splitless injection was used.

The mass spectrometer was operated in the positive EI mode and under Selected Ion Recording (SIR) conditions. Two characteristic ions for each target analyte and surrogate standard were monitored.

### 3.3 Chlorophenolic Compounds

The results reported herein are for AXYS. The 1994-95 results are based on effluent sample extracts provided by PESC upon which, an additional clean-up was made by AXYS to remove potential interferences.

An effluent sample, to which ascorbic acid had been added, was spiked with an aliquot of $^{13}C$-labelled surrogate standard solution (Appendix 1). The pH of the sample was adjusted to pH 9-9.5 with sodium hydroxide. Potassium carbonate solution and ascorbic acid were added to a separatory funnel containing the prepared sample and shaken vigorously. The solution was allowed to react for 5-minutes. The derivatized sample was extracted by shaking with hexane. The extract was dried over anhydrous sodium suphate and concentrated by rotary evaporation. An aliquot of the recovery standard (2,6-dibromophenol) was added. The final extract was transferred to an autosampler vial prior to analysis by GC/MS.

Sample extracts were analyzed using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler and a DG 10 data system. Chromatographic separation was achieved using a DB-5 capillary column (60m, 0.25mm i.d., 0.10 um film thickness). A split/splitless injection sequence was used. The mass spectrometer was operated in the EI mode using Multiple Ion Detection (MID) to enhance sensitivity, acquiring at least two characteristic ions for each target analyte and surrogate standard.

## 4. RESULTS

### 4.1 1995 Resin Acid Laboratory Round Robin

The participating laboratories were instructed to use their current “in-house” methodologies. The round robin analysis of an underivatized resin acid quantitation standard sample indicated that considerable potential inter-laboratory variability existed and that it varied with the analyte (Table 2a). In this case, most of the laboratories (at least 6 of the 8 participating laboratories) determined dehydroabietic acid, isopimaric acid and sandaracopimaric acid to be within 30% of the expected value. However, considering this variability extends either as an under estimation or an over estimation, there was considerable discrepancy among the laboratories.

The analysis of the 24h composite treated pulp mill effluent sample also indicated a high level of inter-laboratory variability (Table 2b). In this case the difference between the minimum and maximum concentration reported for the two resin acids with the lowest coefficient of variation (CV) was 179 ug/l for dehydroabietic acid and 117 ug/L for pimaric acid.

Table 2: Resin Acid Round Robin - (a) Comparison of Resin Acid Quantitation Sample Percentage Differences from Expected Values and (b) Pulp Mill Effluent Concentrations

(a) Quantitation Standard Sample Tested by all Laboratories

| Resin Acid/ Laboratory | Pimaric 1016 ug/ml | Sandaracopimaric 813 ug/ml | Isopimaric 924 ug/ml | Dehydroabietic 1905 ug/ml | Abietic 1405 ug/ml | Palustric 821 ug/ml |
|---|---|---|---|---|---|---|
| a | +87(%) | +60 | +84 | +89 | +64 | +46 |
| b | -12 | +9 | +3 | +7 | -59 | -65 |
| c | -34 | -24 | -35 | -26 | -57 | - |
| d | -26 | -3 | +12 | -29 | +4 | +18 |
| e | -1 | +13 | -18 | -22 | +47 | -47 |
| f | +12 | +16 | +10 | -15 | +189 | +30 |
| g | +46 | +47 | +12 | -22 | +14 | +95 |
| h | -4 | +13 | -16 | -16 | +99 | -66 |
| # of Labs within 30% of expected value | 5/8 | 6/8 | 6/8 | 7/8 | 2/8 | 2/7 |

(b) Pulp Mill Effluent Sample Tested by all Laboratories*

| Resin Acid/ Laboratory | Pimaric ug/L | Sandaracopimaric ug/L | Isopimaric ug/L | Dehydroabietic ug/L | Abietic ug/L |
|---|---|---|---|---|---|
| a | 45 | 5 | 56 | 107 | 90 |
| b | 35 | 12 | 0 | 89 | 53 |
| c | 33 | 5 | 47 | 91 | 206 |
| d | 109 | 109 | 208 | 180 | 174 |
| e | 60 | 10 | 78 | 107 | 182 |
| f | 87 | 27 | 0 | 193 | 38 |
| g | 150 | 18 | 129 | 268 | 298 |
| h | 48 | 6 | 56 | 95 | 740 |
| Overall Average & %CV | 71 (55%) | 24 (137%) | 72 (90%) | 141 (43%) | 222 (95%) |

* Average of triplicate analysis. Samples were not pH adjusted at time of collection but adjusted to pH 9 upon receipt at the coordinating laboratory, prior to shipment to participating laboratories.
CV (%) = Coefficient of Variation = standard deviation/mean x 100.

## 4.2 Mill Operations During the 1996 Study Period

The variability in daily pulp mill production on a weekly basis is shown on Figure 2. The average pulp production was lower during the first sample period (1350 t/d) than the second period (1500 t/d). The mill actually stopped production on March 15 1996 for scheduled maintenance, four days prior to the last effluent sampling. With the exception of nitrate, the process indicators (chloride, sulphate, $BOD_5$, effluent flow) showed the two sample periods to be similar (Table 3). Nitrate concentrations were clearly higher during the first sample period (average = 1600 mg/L) than the second period (average = 116 mg/L) when nitrate was generally below detectable levels. This appears to be inversely reflected by the TSS loading which was higher during the first period (average = 10,400 kg/d) than the second period (average = 8500 kg/d).

**Figure 2 : Northwood Pulp Mill Pulp Production - January to March 1996**

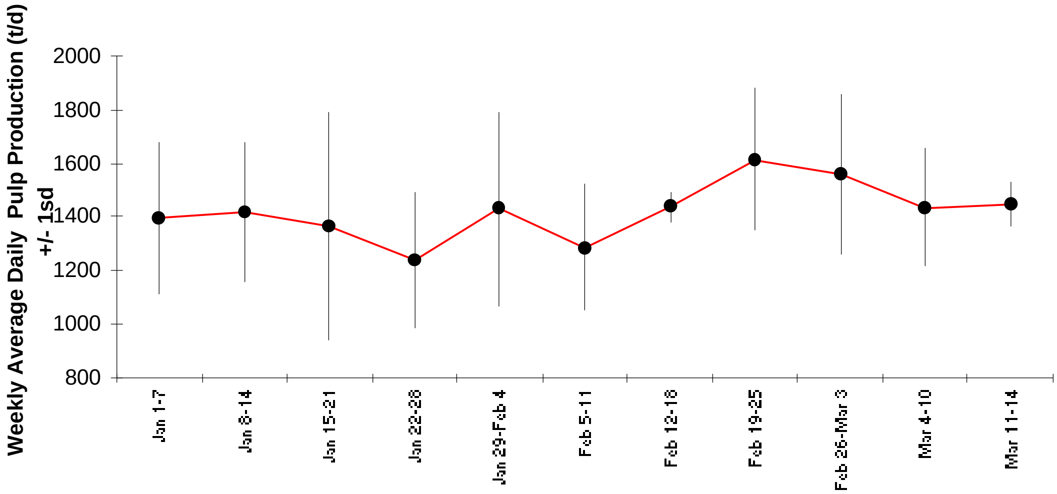



Table 3: Northwood Pulp Mill Operational and Wastewater Characteristics - January to March 1996

| 1996 | Chloride (mg/L) | Sulphate (mg/L) | Nitrate (ug/L) | Flow ($m^3$/d x 1000) | $BOD_5$ (kg/d) | TSS (kg/d) | Pulp Prod. (ADt/d) | Chloride (kg/d) |
|---|---|---|---|---|---|---|---|---|
| Jan 15 | 220 | 486 | <2 | 135.2 | 3245 | 8382 | 1693 | 29744 |
| Jan 22 | 220 | 433 | 2111 | 133.1 | 4392 | 11447 | 1155 | 29282 |
| Jan 24 | 218 | 509 | 1602 | 137.8 | 4410 | 9922 | 731 | 30040 |
| Jan 29 | 209 | 437 | 2371 | 160.6 | 5621 | 11242 | 826 | 33565 |
| Feb 05 | 173 | 436 | 2005 | 138.3 | 5532 | 10787 | 1293 | 23926 |
| mean | 208 | 460 | 1618 | 141.0 | 4640 | 10356 | 1140 | 29312 |
| sd | 20 | 35 | 945 | 11.2 | 977 | 1250 | 386 | 3458 |
| CV(%) | 10 | 8 | 58 | 8 | 21 | 12 | 34 | 12 |
| Feb 19 | 183 | 381 | <2 | 140.4 | 3931 | 8705 | 1735 | 25693 |
| Feb 26 | 226 | 406 | <2 | 144.1 | 4611 | 7781 | 1717 | 32567 |
| Mar 04 | 238 | 416 | 457 | 128.7 | 5019 | 8108 | 1140 | 30631 |
| Mar 11 | 214 | 464 | <2 | 133.7 | 3744 | 9493 | 1498 | 28612 |
| Mar 18 | 156 | 385 | <2 | 59.7 | 1015 | 2507 | 0 | 9313 |
| mean* | 215 | 417 | 116 | 136.7 | 4326 | 8522 | 1523 | 29376 |
| sd | 24 | 35 | 228 | 6.9 | 593 | 752 | 277 | 2938 |
| CV(%) | 11 | 8 | 197 | 5 | 14 | 9 | 18 | 10 |
| Overall mean* | 211 | 441 | 950 | 139.1 | 4501 | 9541 | 1310 | 29340 |
| sd | 21 | 40 | 1045 | 9.2 | 798 | 1388 | 379 | 3036 |
| CV(%) | 10 | 9 | 110 | 7 | 18 | 15 | 29 | 10 |

* mean does not include March 18 sample date.

## 4.3 Resin Acid Sample Tracking

The QC check on the field pH adjustment showed that for the first three samples, of the first sample period, samples were received at a pH lower than the desired level (Table 4). Subsequent samples were generally received close to the desired pH. Samples were generally received by the laboratory the day after being collected. The sample temperatures upon receipt at the laboratory were higher (range 5°C - 11°C) than the desired 4°C (Table 4). Samples were stored at the laboratories in the dark, at 4°C.

Table 4: Field Sample Quality Control Tracking

**Sample pH**

| Sample Date(1996) | Effluent pH | Field adjusted pH | AXYS pH Received | pH adjustment | PESC pH Received | pH adjustment |
|---|---|---|---|---|---|---|
| Jan-15 | - | - | - | - | 7 | 9.5 |
| Jan-22 | 7.5 | 9.2 | 7.5 | 9.5 | 8 | 10 |
| Jan-24 | 7.9 | 9.2 - 9.3 | 7.5 | 9.5 - 10 | 7.5 | 9 |
| Jan-29 | 7.9 | 9.8 - 9.9 | 8.5 | 9.5 | 9.5 | none |
| Feb-05 | 7.9 | 9.8 - 9.9 | 9 | 9.5 | 9 | none |
| Feb-19 | 7.9 | 9.7 - 9.9 | 9 | 9.5 | 8.5 | 9.5 |
| Feb-26 | 8 | 9.7 - 9.8 | 9 | 9.5 | 8 | 9 |
| Mar-04 | 8 | 9.9 | 9 | 9.5 | 8.5 | 9 |
| Mar-11 | 8 | 9.9 - 10 | 9 | 9.5 | 9 | none |
| Mar-18 | 8 - 8.8 | 10 - 10.6 | 9.5 | none | 8.9 | none |

**Sample Temperature** / **Sample Transit**

| Sample Date(1996) | Effluent Sample °C | AXYS Received | PESC Received | Sample Date(1996) | AXYS Received | PESC Received |
|---|---|---|---|---|---|---|
| Jan-15 | - | - | 8 | Jan-15 | - | Jan-16 |
| Jan-22 | 3 | 5 | 8 | Jan-22 | Jan-22 | Jan-23 |
| Jan-24 | 3.8 | 10 | 5 | Jan-24 | Jan-25 | Jan-25 |
| Jan-29 | 4.1 | 6.5 | 4 | Jan-29 | Jan-30 | Jan-30 |
| Feb-05 | 8 | 8.5 | 7 | Feb-05 | Feb-07 | Feb-07 |
| Feb-19 | 8.3 | 8.5 | 11 | Feb-19 | Feb-20 | Feb-20 |
| Feb-26 | 5.2 | 7.5 | 7.5 | Feb-26 | Feb-28 | Feb-28 |
| Mar-04 | 6.3 | 8 | 7.5 | Mar-04 | Mar-05 | Mar-05 |
| Mar-11 | 9 | 6.5 | 10 | Mar-11 | Mar-12 | Mar-12 |
| Mar-18 | 6.4 | 5 | 8 | Mar-18 | Mar-19 | Mar-19 |

The recommended maximum sample holding time of 30 days before analysis was achieved with the exception of the March 12 (44 days) and March 19 (37 days) samples at PESC (Table 5).

## 4.4 Resin Acid Quantitation Standard Sample RAQ1

AXYS analyzed the quantitation standard sample RAQ1 three times and PESC analyzed the sample four times over the course of the study (Appendix 2). IOS analyzed the sample once but, in triplicate. AXYS routinely reports surrogate recovery (o-Methylpodocarpic acid) corrected results, but in the following discussion both corrected and unadjusted results are presented. The surrogate recovery corrected results are identified by a SRC notation, otherwise, the results reported are for unadjusted samples.

For pimaric acid, sandaracopimaric acid, isopimaric acid and dehydroabietic acid, based on average values, AXYS unadjusted concentrations tended to over estimate (31% to 51%) the expected value (Table 6). PESC tended to under estimate (-5% to - 34%) the expected value. With the results corrected for surrogate recovery, AXYS then more closely reflected the expected values (-10% to 3%). Based on a triplicate analysis of one sample, IOS concentrations varied between -12% to 14% from the expected values. AXYS and PESC under estimated the neoabietic acid concentration by approximately -33% and IOS by -4%.

Table 5: Sample Analysis and  Holding Times

| Sample Date(1996) | AXYS Received | Extraction | Analysis | # days stored | PESC Received | Extraction | Analysis | # days stored |
|---|---|---|---|---|---|---|---|---|
| Jan-15 | Jan-16 | Jan-29 | Jan-31 | 13 | Jan-16 | Jan-30 | Jan-31 | 14 |
| Jan-22 | Jan-22 | Jan-29 | Jan-31 | 7 | Jan-23 | Jan-30 | Jan-31 | 7 |
| Jan-24 | Jan-25 | Jan-29 | Jan-31 | 4 | Jan-25 | Jan-30 | Jan-31 | 5 |
| Jan-29 | Jan-30 | Feb-08 | Feb-10 | 9 | Jan-30 | Jan-30 | Jan-31 | 0 |
| Feb-05 | Feb-07 | Feb-08 | Feb-10 | 1 | Feb-07 | Feb-07 | Feb-15 | 0 |
| Feb-19 | Feb-20 | Mar-20 | Mar-25 | 29 | Feb-20 | Mar-07 | Mar-11 | 16 |
| Feb-26 | Feb-28 | Mar-20 | Mar-25 | 21 | Feb-28 | Mar-07 | Mar-12 | 8 |
| Mar-04 | Mar-05 | Mar-20 | Mar-25 | 15 | Mar-05 | Mar-07 | Mar-12 | 2 |
| Mar-11 | Mar-12 | Mar-20 | Mar-25 | 8 | Mar-12 | Apr-25 | Apr-26 | 44 |
| Mar-18 | Mar-19 | Mar-20 | Mar-25 | 1 | Mar-19 | Apr-25 | Apr-26 | 37 |
| **Sample Date(1996)** | **IOS Received** | **Extraction** | **Analysis** | **# days stored** | | | | |
| Jan-15 | Jan-16 | Jan-31 | Feb-01 | 15 | | | | |
| Jan-22 | Jan-23 | Jan-31 | Feb-01 | 9 | | | | |
| Jan-24 | Jan-25 | Feb-01 | Feb-03 | 7 | | | | |
| Jan-29 | Jan-31 | Feb-14 | Feb-19 | 15 | | | | |
| Feb-05 | Feb-07 | Feb-14 | Feb-19 | 7 | | | | |
| Feb-19 | Feb-21 | Mar-05 | Mar-11 | 14 | | | | |
| Feb-26 | Feb-28 | Mar-05 | Mar-11 | 6 | | | | |
| Mar-04 | Mar-05 | Mar-06 | Mar-11 | 1 | | | | |
| Mar-11 | Mar-12 | Mar-20 | Mar-22 | 8 | | | | |
| Mar-18 | Mar-19 | Mar-20 | Mar-22 | 1 | | | | |

Shaded areas reflect samples which were analyzed as a sample batch.

AXYS reported that the isomerization of neoabietic and palustric acids to form abietic acid has been documented and while analysis conditions were controlled to minimize this, sample data for these compounds should be interpreted with caution. For AXYS, the first RAQ1 analysis clearly had a lower abietic acid concentration and higher palustric and neoabietic concentrations than the third sample tested (Appendix 2). This was also evident in the PESC results for the first three analyses.

Table 6: Comparison of Average Resin Acid Concentrations for Quantitation Standard Sample RAQ1 as a Percentage of Expected Value

| Resin Acid Expected Concentration & Laboratory | Pimaric 121 ug/ml | Sandaracopimaric 58.1 ug/ml | Isopimaric 53.5 ug/ml | Dehydroabietic 139 ug/ml | Abietic 90.2 ug/ml | Palustric 45.6 ug/ml | Neoabietic 101 ug/ml |
|---|---|---|---|---|---|---|---|
| AXYS (n=3) ** | +2 (%) | +3 | -10 | -1 | +25 | -10 | -55 |
| AXYS (n=3) (unadjusted) | +50 | +51 | +31 | +41 | +74 | +36 | -34 |
| PESC (n=4) | -19 | -7 | -5 | -34 | -35 | -21 | -33 |
| IOS* | +14 | -5 | -12 | -4 | -45 | +1 | -4 |

* Triplicate analysis of single sample; ** SRC = Surrogate Recovery Corrected

## 4.5 Effluent Resin Acids

The effluent sample results are reported in Appendix 3. IOS analyzed all samples in triplicate. AXYS and PESC each analyzed three samples in duplicate to assess analytical precision (Appendix 4). The coefficient of variation for the effluent samples for pimaric acid, sandaracopimaric acid, isopimaric acid, and dehydroabietic acid are summarized in Table 7. The higher CV range for IOS likely reflects the larger number of samples tested as well as being analyzed in triplicate.

Table 7: Comparison of Coefficient of Variation (CV) for Replicate Effluent Resin Acid Samples

| Resin Acid/ Laboratory | Number of Samples Tested in Duplicate | Pimaric CV (%) | Sandaracopimaric CV (% | Isopimaric CV (%) | Dehydroabietic CV (%) |
|---|---|---|---|---|---|
| AXYS** | 3 | 0-18 | 1-9 | 5-10 | 4-9 |
| PESC | 3 | 12-64 | 0-20 | 10-14 | 8-19 |
| IOS* | 10 | 7-29 | 6-25 | 9-29 | 8-30 |

C* Based on triplicate analysis; **SRC = Surrogate Recovery Corrected.

The mean concentration of pimaric acid, sandaracopimaric acid, isopimaric acid and dehydroabietic acid for PESC is distinctly higher than for AXYS and IOS (Table 8, Figure 3a-d). For sandaracopimaric acid this is largely a result of PESC's higher detection limit of 5ug/L. Abietic acid, palustric acid and neoabietic acid concentrations are summarized in Table 8. However, with reported potential isomerization of neoabietic and palustric acids to form abietic acid, these results should be interpreted with caution. Based on a comparison between the AXYS calibration standard and a standard provided by PESC for comparison, AXYS adjusted the concentration of abietic acid by a factor of 0.5 for the samples collected during the first exposure period.

**Figure 3: Laboratory Differences in Northwood Pulp Mill Effluent Winter 1996 Mean Resin Acid Concentrations**

**Figure 3a: Northwood Pulp Mill Pimaric Acid - Jan to Mar 1996**

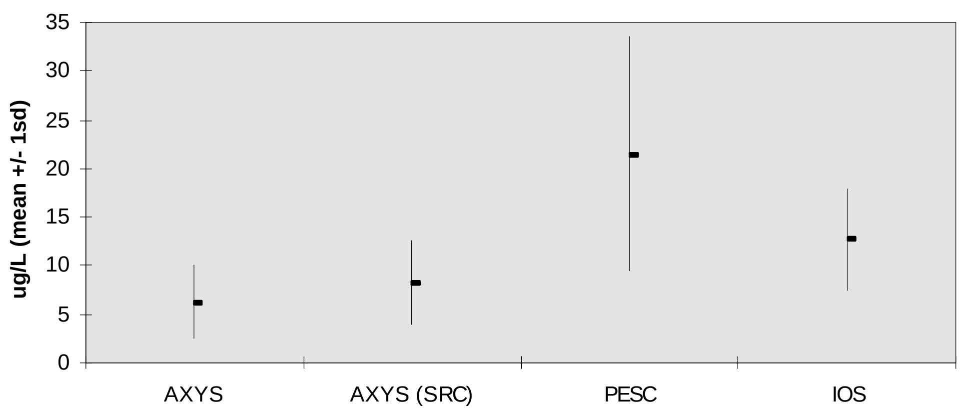



**Figure 3b: Northwood Pulp Mill Sandaracopimaric Acid - Jan to Mar 1990**

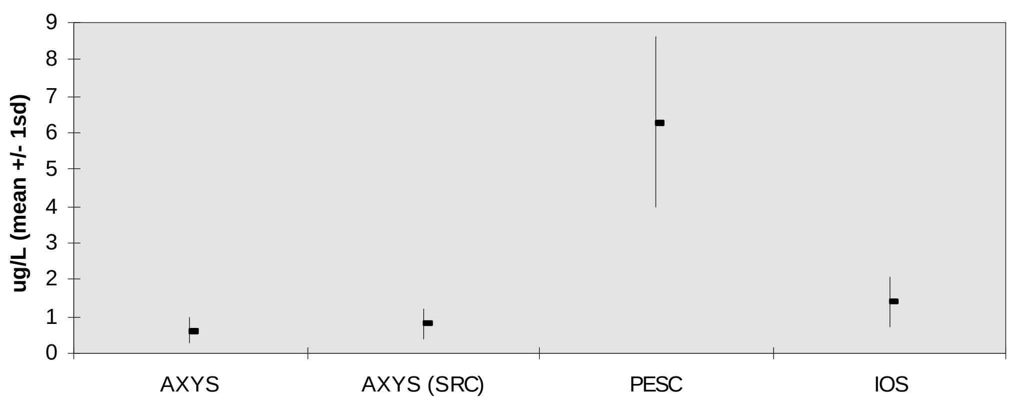


**Figure 3c: Northwood Pulp Mill Isopimaric Acid - Jan to Mar 1996**

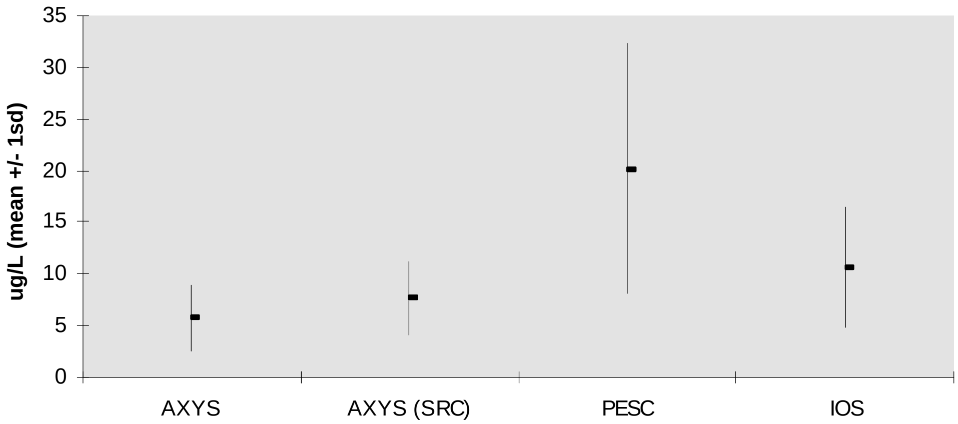
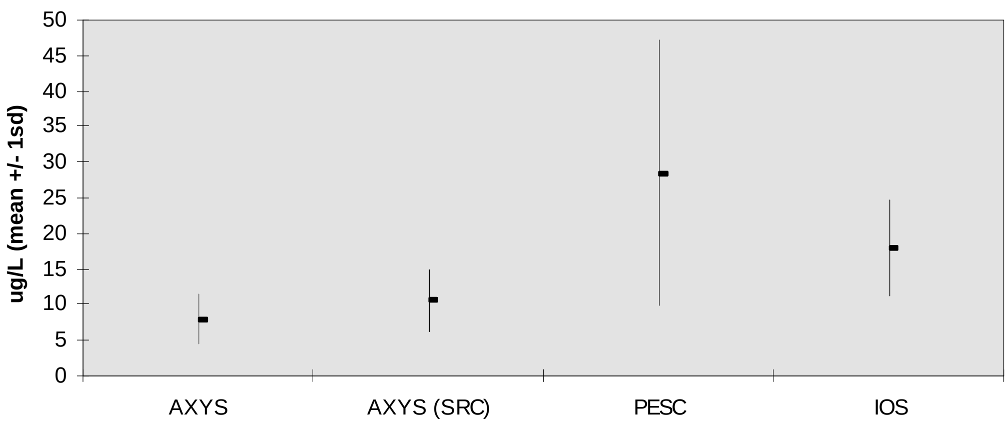



**Figure 3d: Northwood Pulp Mill Dehydroabietic Acid - Jan to Mar 1996**




## 4.6 Effluent Chlorophenolic Compounds

The chlorophenolic sample results for the 1994-95 (five samples) and 1995-96 (ten samples) studies are reported in Appendix 5. Quality assurance results are reported in Appendix 6. As of June 1993, the Northwood pulp mill had completely converted to 100% chlorine dioxide substitution.

Of the forty-four compounds identified in Appendix 6, only nine appeared to be regularly detected and even then, at low ng/L levels (Table 9).

Table 8: Summary of Northwood Effluent - Winter 1996 Resin Acid Results

| | | Pimaric Acid (ug/L) | (96h LC50 of 320 to 1200 ug/L)** | | Sandara-copimaric Acid (ug/L) | (96h LC50 of 360 ug/L) |
|---|---|---|---|---|---|---|
| **Sample Period and Laboratory** | **AXYS*** | **PESC** | **IOS** | **AXYS*** | **PESC** | **IOS** |
| **Period 1** | | | | | | |
| Mean | 8.3 | 22.8 | 11.6 | 0.8 | 7.0 | 1.1 |
| sd | 4.0 | 13.2 | 3.0 | 0.4 | 3.1 | 0.4 |
| CV | 49 | 58 | 26 | 52 | 44 | 35 |
| **Period 2** | | | | | | |
| Mean | 4.2 | 20.2 | 13.9 | 0.5 | 5.6 | 1.7 |
| sd | 2.1 | 12.4 | 7.0 | 0.2 | 0.9 | 0.9 |
| CV | 50 | 61 | 51 | 45 | 16 | 51 |
| **Overall** | | | | | | |
| Mean | 6.2 | 21.5 | 12.7 | 0.6 | 6.3 | 1.4 |
| sd | 3.7 | 12.1 | 5.3 | 0.3 | 2.3 | 0.7 |
| CV | 59 | 57 | 41 | 54 | 36 | 51 |
| | | **Isopimaric Acid (ug/L)** | **(96h LC50 of 220 to 1000 ug/L)** | | **Dehydro-abietic Acid (ug/L)** | **(96h LC50 of 500 to 2100 ug/L)** |
| **Sample Period and Laboratory** | **AXYS*** | **PESC** | **IOS** | **AXYS*** | **PESC** | **IOS** |
| **Period 1** | | | | | | |
| Mean | 7.6 | 21.2 | 8.0 | 10.3 | 25.8 | 16.9 |
| sd | 3.4 | 15.9 | 4.0 | 3.3 | 17.5 | 3.9 |
| CV | 45 | 75 | 50 | 32 | 68 | 23 |
| **Period 2** | | | | | | |
| Mean | 4.0 | 19.2 | 13.1 | 5.6 | 31.2 | 19.0 |
| sd | 1.7 | 8.5 | 6.6 | 2.1 | 21.7 | 9.1 |
| CV | 41 | 44 | 50 | 38 | 69 | 48 |
| **Overall** | | | | | | |
| Mean | 5.8 | 20.2 | 10.6 | 7.9 | 28.5 | 18.0 |
| sd | 3.1 | 12.1 | 5.8 | 3.6 | 18.8 | 6.7 |
| CV | 54 | 60 | 55 | 45 | 66 | 37 |
| | | **Abietic Acid (ug/L)** | **(96h LC50 of 200 to 1500 ug/L)** | | **Palustric Acid (ug/L)** | **(96h LC50 of 500 to 600 ug/L)** |
| **Sample Period and Laboratory** | **AXYS*** | **PESC** | **IOS** | **AXYS*** | **PESC** | **IOS** |
| **Period 1** | | | | | | |
| Mean | 20.4 | 24.4 | 15.0 | 3.7 | 12.6 | 6.2 |
| sd | 7.1 | 14.3 | 6.3 | 1.6 | 9.2 | 2.6 |
| CV | 35 | 58 | 42 | 44 | 73 | 42 |
| **Period 2** | | | | | | |
| Mean | 27.5 | 54.6 | 17.0 | 1.2 | 5.8 | 7.0 |
| sd | 11.7 | 42.1 | 7.8 | 0.6 | 1.3 | 3.0 |
| CV | 42 | 77 | 46 | 50 | 22 | 43 |
| **Overall** | | | | | | |
| Mean | 24.0 | 39.5 | 16.0 | 2.4 | 9.2 | 6.6 |
| sd | 9.9 | 33.7 | 6.8 | 1.8 | 7.1 | 2.7 |
| CV | 41 | 85 | 42 | 72 | 78 | 41 |

* For comparative purposes, AXYS unadjusted for surrogate recovery results are presented - see Appendix 3 for surrogate recovery corrected (SRC) results.
** 96h LC50 values reported for comparative purposes: Source Taylor et al., 1988.

Table 8 cont'd: Summary of Northwood Effluent - Winter 1996 Resin Acid Results

| Sample Period and Laboratory | AXYS* | Neoabietic Acid (ug/L) PESC | (96h LC50 of 600 to 700 ug/L) IOS | AXYS* | 12/14 Chloro-dehydroabietic acid (ug/L) PESC | IOS |
|---|---|---|---|---|---|---|
| **Period 1** | | | | | | |
| Mean | 2.3 | 11.4 | 2.1 | 0.6 | - | - |
| sd | 1.5 | 8.1 | 1.0 | 0.3 | | |
| CV | 65 | 71 | 49 | 41 | | |
| **Period 2** | | | | | | |
| Mean | 0.7 | 5.2 | 1.9 | 0.3 | - | - |
| sd | 0.4 | 0.4 | 0.8 | 0.2 | | |
| CV | 55 | 9 | 43 | 74 | | |
| **Overall** | | | | | | |
| Mean | 1.5 | 8.3 | 2.0 | 0.5 | - | - |
| sd | 1.3 | 6.3 | 0.9 | 0.3 | | |
| CV | 90 | 76 | 44 | 64 | | |

Table 9: Chlorophenolic Compounds Routinely Detected in Northwood Pulp Mill Effluent

| Chlorophenolic Compound | Number of Positive Sample Identifications* | Concentration Range (ng/L) | Chlorophenolic Effect Concentration (ng/L) |
|---|---|---|---|
| 6-Chlorovanillin | 10/10 | 1,700 - 10, 000 | 107,000*** |
| 5-Chlorovanillin | 6/10 | 8.4 - 18 | - |
| 4-Chloroguaiacol | 9/15 | 110 - 200 | - |
| 5-Chloroguaiacol | 14/15 | 8.8 - 210 | - |
| 4-Chlorocatechol | 10/15 | 12 - 43 | 79,000*** |
| 4,5-Dichlorocatechol | 9/15 | 33 - 310 | 44,500*** |
| 3,4,5,6-Tetrachlorocatechol | 10/15 | 2.2 - 32 | 7,300*** |
| 4-Chlorophenol | 6/15 | 13 - 23 | 700**<br>650,000*** |
| 2,4,6-Trichlorophenol | 13/15 | 5.3 - 170 | pH <7.5 =120**<br>pH $\geq$7.5 = 500**<br>3,200*** |

* results that were reported as NDR (not detected - incorrect ratio) are not included.
** MELP, 1997: maximum concentration to protect aquatic life.
*** NCASI, 1994: Lowest of two chronic effect level concentrations reported in NCASI Table 1.

# 5. DISCUSSION

## 5.1 Resin Acids

The underivatized quantitation standard sample for pimaric acid, sandaracopimaric acid, isopimaric acid and dehydroabietic acid indicated that while PESC appeared to under estimate the expected concentration, it reported higher effluent resin acid concentrations. For AXYS, correcting the results based on surrogate recovery reduced the over estimation of the quantitation standard sample expected values. Effluent sample concentrations increased slightly with surrogate correction. Irrespective of surrogate recovery adjustment, AXYS and

IOS effluent results were quite similar. The reasons for the differences in resin acid quantification by the three laboratories was not evaluated as part of this report.

### 5.1.1 Resin Acid Concentration Comparison - Acute Toxicity and Water Quality Guidelines

The resin acid concentrations determined by the three laboratories were well below reported 96h-LC50 concentrations for salmonids (see Table 8). Acute lethality of individual resin acids seems to fall within a narrow range of 200 to 1700 ug/L at neutral pH (Taylor et al., 1988). A single high value reported by PESC for abietic acid (112 ug/L) was still only about one-half of the lower end of the acute toxicity range.

Taylor et al., 1988 established a dehydroabietic acid surface water quality guideline based on pH. At pH 7.5 and 8.0 the guideline for dehydroabietic acid was 12 ug/L and 13 ug/L respectively. The Northwood effluent pH is typically in this range, as is the Fraser River at Prince George. The number of effluent samples greater than 13 ug/L was one (14.4 ug/L) for AXYS (unadjusted for surrogate recovery results), ten (18ug/L to 64 ug/L) for PESC and seven (14.3 ug/L to 31.2 ug/L) for IOS. The results demonstrate that at the point of effluent discharge to the Fraser River the dehydroabietic acid guideline concentration is already met or, with minimal dilution (5:1), the guideline concentration would be expected to be quickly achieved.

### 5.1.2 Resin Acid Loading Estimates

The overall higher mean concentration reported by PESC is reflected in the loading estimates. The average daily loading are pimaric acid (0.87 to 2.99 kg/d), sandaracopimaric acid (0.09 to 0.88 kg/d), isopimaric acid (0.81 to 2.81 kg/d) and dehydroabietic acid (1.11 to 3.96 kg/d) (Table 10).

### 5.1.3 Other Recent Sources of Resin Acid Data

The Upper Fraser pulp mills included effluent resin acid analyses in their Environmental Effects Monitoring (EEM) cycle one study (Hatfield Consultants, 1996). The samples were reported to be analyzed using an earlier version of the method used by PESC, but with extraction of an acidified sample with dichloromethane and derivatization with diazomethane. The results for the four pulp mills involved in the study are reported in Table 11. For the Northwood samples, the results indicated concentrations that are not unlike this study and most similar to PESC. The results also suggested that there are similarities between the two Prince George kraft pulp mills but that the Quesnel kraft pulp mill effluent (Cariboo) is quite different in resin acid content.

Table 10: Estimated Daily Loading of Four Resin Acids Based on the Results of Three Laboratories.

| kg/d* | Pimaric | Sandaracopimaric | Isopimaric | Dehydroabietic |
|---|---|---|---|---|
| **AXYS** | **0.87** | **0.09** | **0.81** | **1.11** |
| **PESC** | **2.99** | **0.88** | **2.81** | **3.96** |
| **IOS** | **1.77** | **0.19** | **1.47** | **2.50** |

*** Loading estimated from mean study concentration (see Table 8) and mean flow for the same dates and period.**

Table 11: Pulp Mill Effluent Resin Acid Concentrations Reported in Upper Fraser Pulp Mill EEM Study

| Resin Acid/ Pulp Mill (1995) | Pimaric (ug/L) | Sandaracopimaric (ug/L) | Isopimaric (ug/L) | Dehydroabietic (ug/L) | Abietic (ug/L) |
|---|---|---|---|---|---|
| Northwood | | | | | |
| Aug 14 | 10 | <2 | 12 | 18 | 27 |
| Sep 11 | 15 | 3 | 14 | 22 | 99 |
| Oct 16 | 36 | 4 | 33 | 64 | 167 |
| Nov 06 | 24 | 3 | 22 | 54 | 100 |
| (Mean) | 21 | 3 | 20 | 40 | 98 |
| This Study (Mean) | | | | | |
| AXYS | 6.2 | 0.6 | 5.8 | 7.9 | 24.0 |
| PESC | 21.5 | 6.3 | 20.2 | 28.5 | 39.5 |
| IOS | 12.7 | 1.4 | 10.6 | 18.0 | 16 |
| Canfor | | | | | |
| Aug 14 | 36 | 5 | 37 | 51 | 72 |
| Sep 11 | 170 | 30 | 110 | 110 | 520 |
| Oct 02 | 32 | 17 | 30 | 37 | <2 |
| Nov 06 | 33 | 4 | 28 | 37 | 60 |
| (Mean) | 68 | 14 | 51 | 59 | 164 |
| QRP* | | | | | |
| Aug 21 | <2 | 3 | 70 | 6 | 5 |
| Sep 18 | <2 | <2 | 35 | 3 | <2 |
| Oct 23 | 4 | <2 | 6 | 38 | 22 |
| Nov 20 | <2 | <2 | 126 | 23 | 12 |
| (Mean) | - | - | 59 | 18 | 10 |
| Cariboo | | | | | |
| Aug 21 | <2 | <2 | 4 | <2 | <2 |
| Sep 18 | 3 | <2 | 3 | 3 | <2 |
| Oct 16 | <2 | <2 | 3 | <2 | <2 |
| Nov 20 | <2 | <2 | <2 | <2 | <2 |
| (Mean) | - | - | 3 | - | 10 |

*CTMP pulp mill located at Quesnel

## 5.2 Chlorophenolic Compounds

Only a few chlorophenolic compounds were regularly identified in the pulp mill effluent samples and even then, at concentrations well below environmental effect levels (Table 9). The effluent chlorophenolic compounds profile changes since full implementation of chlorine dioxide substitution are illustrated by the reduction in the tri- and tetra- chlorophenolic compounds (Table 12). For example, the average 3,4,5-Trichloroguaicol concentration was reduced from 41,000 ng/L, to 3,440 ng/L to less than detectable levels. Servizi et al., 1993 monitored effluent quality in 1989 prior to the Northwood's chlorine dioxide substitution program which started in 1991. Prahacs et al., 1996 monitored the mill's effluent during the transition period which was completed in June 1993.

Similar findings have been reported previously. Pryke et al., 1993 reported that increasing chlorine dioxide substitution decreased the formation of chlorinated phenolic compounds. For example, they reported that final effluent concentrations of 3,4,5-trichloroguaiacol at 70% substitution (3600 - 14,000 ng/L) were virtually eliminated (<100 ng/L) after 100% substitution. They reported that at 100% substitution, 4-chloroguaiacol concentrations ranged between 400-800 ng/L, not unlike the concentrations reported herein of 72-200 ng/L.

Table 12: Change in Chlorophenolic Compounds with Introduction of Chlorine Dioxide Substitution

| Chlorophenolic Compounds (range - ng/L) | Servizi et al., 1993 | Prachacs et al., 1996* | This Study |
|---|---|---|---|
| 3,4,5-Trichloroguaiacol [mean] | 18,700 - 81,300 [41,000] | 1,900 - 6,450 [3,440] | < detection or NDR |
| TeCGuaiacol | 8700 - 92,700 [44,300] | 320 - 1,490 [730] | < detection or NDR |
| TeCCatechol | 1,900 - 61,200 [24,800] | <30 - 240 [110] | < 2.9 - 32 [14] |
| 2,4,6-Trichlorophenol | 2,500 - 10,500 [6,800] | 460 - 1,610 [850] | 5.3 - 170 [36] |
| Pentachlorophenol | 600 - 1800 | <20 - <50 | <4.2 - 14 |

* see Appendix 6, individual mill results provided courtesy of K. Hall, UBC.

# REFERENCES

Bicho, P.A., R. Strub and J.N. Saddler. 1995. Resin Acid Analysis Laboratory Round Robin. In DOE FRAP 1997-10 (Appendix A).

DFO, 1992. Department of Fisheries and Oceans. Pulp and Paper Effluent Regulations. Canada Gazette, Part II. May 20, 1992.

Environment Canada. 1997. Fraser River Pulp Mill Effluents: Interpretation of Northwood Effluent Characterization Data. Final Report. DOE FRAP 1997-10.

FRAP, 1992. Fraser River Action Plan. Proceedings of the Federal/Provincial Information Session January 14, 1992. Government of Canada and Province of British Columbia.

Hatfield Consultants, 1996. Fraser River Environmental Effects Monitoring (EEM) Cycle One Interpretive Report. Appendices Volume 3.

McLeay and Associates. 1987. Aquatic Toxicity of Pulp and Paper Mill Effluent: A Review. Report EPS 4/PF/1.

MELP, 1995. B.C.'s Pulp Mills: Effluent Status Report. 1994 Update. Ministry of Environment Lands and Parks.

NCASI, 1993. Aquatic Community Effects of Biologically Treated Bleached Kraft Mill Effluent Before and After Conversion to Increased Chlorine Dioxide Substitution: Results Form Experimental Streams Study. National Council of the Paper Industry for Air and Stream Improvement. Technical Bulletin NO. 653.

NCASI, 1994. An Assessment of the Significance of Discharge of Chlorinated Phenolic Compounds from Bleached Kraft Pulp Mills. National Council of the Paper Industry for Air and Stream Improvement. Technical Bulletin NO. 658.

PESC, 1995. Anions/Ion Chromatography Method. October 1995. Pacific Environmental Science Centre.

Prahacs, S.M., K. J. Hall and W. Duncan. 1996. Leeches as *In Situ* Biomonitors of Chlorinated Compounds Part 2: Pulp Mill Investigations. Wat. Res 30: 2301-2308.

Pryke, D.C., P. Winter, G. R. Bourree and C. Mickowski. 1993. The Impact of Chlorine Dioxide Delignification on Pulp Manufacturing and Effluent Characteristics at Grand Prairie, Alberta. Presented at 1993 Spring Conference. Canadian Pulp & Paper Association.

Servizi, J.A., R.W. Gordon, D.W. Martens, W.L. Lockhart, D.A. Metner, I.H. Rogers, J.R. McBride and R.J. Norstrom. 1993. Effects of Biotreated Bleached Kraft Mill Effluent on Fingerling Chinook Salmon (*Oncorhynchus tshawytscha*). Can. J. Fish. Aquat. Sci. 50: 846-857.

Taylor, B.R., K.L. Yeager, S.G. Abernethy, and G.F. Westlake. 1988. Scientific Criteria Document for the Development of Provincial Water Quality Objectives and Guidelines - Resin Acids. Environment Ontario..

WMA, 1992. Waste Management Act. Pulp Mill and Pulp and Paper Mill Liquid Effluent Control Regulation. B.C. Reg 470/90. March 2/92.

## ACKNOWLEDGEMENTS

The efforts of John Rex, Dan Dunlop, Terri McClymont and Jordan Beblow for effluent sampling and field support under very difficult conditions is greatfully acknowledged. Jack Nylund (Northwood Pulp Mill) provided advice and support throughout the study.

# APPENDICES

Appendix 1: Surrogate Recovery Codes for Chlorophenolic Compounds

| CODE | SURROGATE-$^{13}C$ | Compound |
|---|---|---|
| A | 4-CHLOROPHENOL | 4-Chlorophenol |
| B | 2,4-DICHLOROPHENOL | 2,6-Dichlorophenol<br>2,4/2,5-Dichlorophenol<br>3,5-Dichlorophenol<br>2,3-Dichlorophenol<br>3,4-Dichlorophenol |
| C | 4-CHLOROGUAIACOL | 6-Chloroguaiacol<br>4-Chloroguaiacol<br>5-Chloroguaiacol |
| D | 2,4,6-TRICHLOROPHENOL | 2,4,6-Trichlorophenol<br>2,3,6-Trichlorophenol<br>2,3,5-Trichlorophenol |
| E | 2,4,5-TRICHLOROPHENOL | 2,4,5-Trichlorophenol<br>2,3,4-Trichlorophenol<br>3,4,5-Trichlorophenol<br>3-Chlorocatechol<br>4-Chlorocatechol |
| F | 5-CHLOROVANILLIN | 5-Chlorovanillin<br>6-Chlorovanillin |
| G | 2,3,4,5-TETRACHLOROPHENOL | 4,6-Dichloroguaiacol<br>3,4-Dichloroguaiacol<br>4,5-Dichloroguaiacol<br>2,3,5,6-Tetrachlorophenol<br>2,3,4,5-Tetrachlorophenol<br>2,3,4,6-Tetrachlorophenol<br>3,5-Dichlorosyringol |
| H | 4,5-DICHLOROCATECHOL | 3,6-Dichlorocatechol<br>3,5-Dichlorocatechol<br>3,4-Dichlorocatechol<br>4,5-Dichlorocatechol<br>3,4,6-Trichlorocatechol<br>3,4,5-Trichlorocatechol |
| I | 4,5,6-TRICHLOROGUAIACOL | 3,4,6-Trichloroguaiacol<br>3,4,5-Trichloroguaiacol<br>4,5,6-Trichloroguaiacol |
| J | PENTACHLOROPHENOL | 5,6-Dichlorovanillin<br>Pentachlorophenol<br>2-Chlorosyringaldehyde<br>2,6-Dichlorosyringaldehyde |
| K | 3,4,5,6-TETRACHLOROGUAIACOL | 3,4,5,6-Tetrachloroguaiacol<br>3,4,5-Trichlorosyringol |
| L | 3,4,5,6-TETRACHLOROCATECHOL | 3,4,5,6-Tetrachlorocatechol |

## Appendix 2: Resin Acid Quantitation Standard Sample RAQ1

| Compound (ug/ml) | Prepared (Jan 23/96) | AXYS (surrogate recovery corrected) AXYS (i) Jan-31 | AXYS (ii) Feb-10 | AXYS (iii) Mar-25 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|
| Pimaric | 121 | 140 | 140 | 89 | 123 | 29 | 24 |
| Sandaracopimaric | 58.1 | 63 | 63 | 55 | 60 | 5 | 8 |
| Isopimaric | 53.5 | 53 | 48 | 43 | 48 | 5 | 10 |
| Dehydroabietic | 139 | 130 | 130 | 150 | 137 | 12 | 8 |
| Abietic | 90.2 | 80 | 90 | 170 | 113 | 49 | 44 |
| Palustric | 45.6 | 54 | 48 | 22 | 41 | 17 | 41 |
| Neoabietic | 101 | 99 | 28 | 6.7 | 45 | 48 | 108 |

| Compound (ug/ml) | Prepared (Jan 23/96) | AXYS (unadjusted for surrogate recovery) AXYS (i) Jan-31 | AXYS (ii) Feb-10 | AXYS (iii) Mar-25 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|
| Pimaric | 121 | 94 | 85 | 74 | 84 | 10 | 12 |
| Sandaracopimaric | 58.1 | 42 | 38 | 46 | 42 | 4 | 9 |
| Isopimaric | 53.5 | 36 | 29 | 36 | 33 | 4 | 11 |
| Dehydroabietic | 139 | 87 | 79 | 125 | 97 | 24 | 25 |
| Abietic | 90.2 | 54 | 55 | 141 | 83 | 50 | 60 |
| Palustric | 45.6 | 36 | 29 | 18 | 28 | 9 | 32 |
| Neoabietic | 101 | 66 | 17 | 6 | 30 | 32 | 109 |
| Surrogate Recovery (%) | | 67 | 61 | 83 | | | |

**Appendix 2 cont'd..**

**PESC**

| | Prepared (Jan 23/96) | PESC (i) Feb-02 | PESC (ii) Feb-15 | PESC (iii) Mar-08 | PESC (iv) May-15 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|---|
| Pimaric | 121 | 63.5 | 117 | 119 | 91.7 | 98 | 26 | 27 |
| Sandaracopimaric | 58.1 | 40.8 | 66.8 | 61 | 48.8 | 54 | 12 | 22 |
| Isopimaric | 53.5 | 39.3 | 73.8 | 42.4 | 46.6 | 51 | 16 | 31 |
| Dehydroabietic | 139 | 56.8 | 49.7 | 144 | 119 | 92 | 46 | 50 |
| Abietic | 90.2 | 31.1 | 42.1 | 112 | 52.4 | 59 | 36 | 61 |
| Palustric | 45.6 | 35.1 | 46.4 | 22.2 | 40.5 | 36 | 10 | 29 |
| Neoabietic | 101 | 62.7 | 59.6 | 54.6 | 95.3 | 68 | 18 | 27 |

**IOS***

| | Prepared (Jan 23/96) | IOS (ia) Feb-01 | IOS (ib) Feb-01 | IOS (ic) Feb-01 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|
| Pimaric | 121 | 134 | 133 | 145.8 | 138 | 7 | 5 |
| Sandaracopimaric | 58.1 | 50.9 | 53.7 | 61.1 | 55 | 5 | 10 |
| Isopimaric | 53.5 | 42.7 | 44.3 | 54.7 | 47 | 7 | 14 |
| Dehydroabietic | 139 | 127.8 | 125.1 | 145.4 | 133 | 11 | 8 |
| Abietic | 90.2 | 44.1 | 50.5 | 53.9 | 50 | 5 | 10 |
| Palustric | 45.6 | 39.1 | 46.8 | 52.8 | 46 | 7 | 15 |
| Neoabietic | 101 | 90.4 | 103.7 | 96.8 | 97 | 7 | 7 |

* Replicate analysis of single sample versus single analysis of multiple samples by AXYS and PESC

Appendix 3: Resin Acids - Northwood Pulp Mill (a)

Compound: Pimaric

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 5.5 | 27 | 6.2 | 5.6 | 8.2 | 6.7 |
| Jan-22 | 16 | 38 | 11 | 11.7 | 14.1 | 12.3 |
| Jan-24 | 13 | 31 | 13.8 | 12.4 | 12.1 | 12.8 |
| Jan-29 | 11 | 9 | 16.2 | 13.2 | 15.3 | 14.9 |
| Feb-05 | 6.8 | 9 | 8.9 | 15 | 9.9 | 11.3 |
| mean | 10.5 | 22.8 | 11.2 | 11.6 | 11.9 | 11.6 |
| sd | 4.3 | 13.2 | 3.9 | 3.6 | 2.9 | 3.0 |
| CV (%) | 42 | 58 | 35 | 31 | 25 | 26 |
| Feb-19 | 3.1 | 15 | 3.5 | 3.7 | 5.6 | 4.3 |
| Feb-26 | 6.3 | 26 | 11.9 | 11.8 | 15.6 | 13.1 |
| Mar-04 | 11 | 39 | 22.3 | 25.1 | 20.7 | 22.7 |
| Mar-11 | 4.1 | 8 | 9.9 | 9.7 | 13.3 | 11.0 |
| Mar-18 | 5.5 | 13 | 17.1 | 16.7 | 20.9 | 18.2 |
| mean | 6.0 | 20.2 | 12.9 | 13.4 | 15.2 | 13.9 |
| sd | 3.1 | 12.4 | 7.1 | 8.0 | 6.3 | 7.0 |
| CV (%) | 51 | 61 | 55 | 60 | 41 | 51 |
| OVERALL | | | | | | |
| mean | 8.2 | 21.5 | 12.1 | 12.5 | 13.6 | 12.7 |
| sd | 4.2 | 12.1 | 5.5 | 5.9 | 4.9 | 5.3 |
| CV (%) | 52 | 57 | 46 | 48 | 36 | 41 |
| -1sd | 4.0 | 9.4 | 6.6 | 6.6 | 8.6 | 7.5 |
| +1sd | 12.5 | 33.6 | 17.6 | 18.4 | 18.5 | 18.0 |
| Loading mean (g/d) | 1145 | 2991 | 1680 | 1737 | 1888 | 1768 |

Compound: Sandaracopimaric

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 0.6 | 5 | 0.4 | 0.5 | 0.4 | 0.4 |
| Jan-22 | 1.6 | 8 | 0.9 | 1 | 1.2 | 1.0 |
| Jan-24 | 1.2 | 12 | 1.4 | 1.3 | 1.1 | 1.3 |
| Jan-29 | 0.82 | 5 | 1.5 | 1.2 | 1.4 | 1.4 |
| Feb-05 | 0.61 | 5 | 1 | 1.5 | 1 | 1.2 |
| mean | 1.0 | 7.0 | 1.0 | 1.1 | 1.0 | 1.1 |
| sd | 0.4 | 3.1 | 0.4 | 0.4 | 0.4 | 0.4 |
| CV (%) | 44 | 44 | 42 | 35 | 37 | 35 |
| Feb-19 | 0.3 | 5 | 0.4 | 0.5 | 0.6 | 0.5 |
| Feb-26 | 0.66 | 6 | 1.6 | 1.7 | 2.1 | 1.8 |
| Mar-04 | 0.9 | 7 | 2.5 | 2.6 | 2.3 | 2.5 |
| Mar-11 | 0.49 | 5 | 1 | 1 | 1.4 | 1.1 |
| Mar-18 | 1.1 | 5 | 2.3 | 2.2 | 2.8 | 2.4 |
| mean | 0.7 | 5.6 | 1.6 | 1.6 | 1.8 | 1.7 |
| sd | 0.3 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| CV (%) | 46 | 16 | 56 | 54 | 47 | 51 |
| OVERALL | | | | | | |
| mean | 0.8 | 6.3 | 1.3 | 1.4 | 1.4 | 1.4 |
| sd | 0.4 | 2.3 | 0.7 | 0.7 | 0.8 | 0.7 |
| CV (%) | 47 | 36 | 55 | 50 | 53 | 51 |
| -1sd | 0.4 | 4.0 | 0.6 | 0.7 | 0.7 | 0.7 |
| +1sd | 1.2 | 8.6 | 2.0 | 2.0 | 2.2 | 2.1 |
| Loading mean (g/d) | 115 | 876 | 181 | 188 | 199 | 189 |

Note: shaded values are less than detection limit, detection limit used in mean calculaation

Appendix 3: Resin Acids - Northwood Pulp Mill (b)

Compound: Isopimaric

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 5.8 | 17 | 2.5 | 1.7 | 2.9 | 2.4 |
| Jan-22 | 15 | 32 | 5.1 | 5.2 | 6.3 | 5.5 |
| Jan-24 | 11 | 43 | 10.4 | 13 | 11.8 | 11.7 |
| Jan-29 | 9.6 | 7 | 12.7 | 9.8 | 11.9 | 11.5 |
| Feb-05 | 6.5 | 7 | 6.2 | 11.2 | 9.9 | 9.1 |
| mean | 9.6 | 21.2 | 7.4 | 8.2 | 8.6 | 8.0 |
| sd | 3.7 | 15.9 | 4.1 | 4.6 | 3.9 | 4.0 |
| CV (%) | 39 | 75 | 56 | 57 | 45 | 50 |
| Feb-19 | 2.5 | 11 | 3 | 3.1 | 4.9 | 3.7 |
| Feb-26 | 5.4 | 23 | 13 | 13.4 | 17.8 | 14.7 |
| Mar-04 | 8.3 | 30 | 19 | 20.8 | 17.4 | 19.1 |
| Mar-11 | 4.5 | 10 | 8.3 | 8.2 | 11.3 | 9.3 |
| Mar-18 | 7.9 | 22 | 17.4 | 17.1 | 21.6 | 18.7 |
| mean | 5.7 | 19.2 | 12.1 | 12.5 | 14.6 | 13.1 |
| sd | 2.4 | 8.5 | 6.6 | 7.0 | 6.6 | 6.6 |
| CV(%) | 42 | 44 | 54 | 56 | 45 | 50 |
| OVERALL | | | | | | |
| mean | 7.7 | 20.2 | 9.8 | 10.4 | 11.6 | 10.6 |
| sd | 3.6 | 12.1 | 5.8 | 6.1 | 6.0 | 5.8 |
| CV (%) | 47 | 60 | 59 | 59 | 52 | 55 |
| -1sd | 4.1 | 8.1 | 4.0 | 4.3 | 5.6 | 4.8 |
| +1sd | 11.2 | 32.3 | 15.5 | 16.4 | 17.6 | 16.4 |
| Loading mean (g/d) | 1064 | 2810 | 1358 | 1440 | 1611 | 1469 |

Compound: Dehydroabietic

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 8.1 | 26 | 8.3 | 8.5 | 13.7 | 10.2 |
| Jan-22 | 18 | 33 | 18.3 | 25.3 | 16.9 | 20.2 |
| Jan-24 | 13 | 51 | 19.4 | 17.5 | 16.8 | 17.9 |
| Jan-29 | 16 | 10 | 15.4 | 17.6 | 22.7 | 18.6 |
| Feb-05 | 11 | 9 | 13.7 | 22.8 | 17.2 | 17.9 |
| mean | 13.2 | 25.8 | 15.0 | 18.3 | 17.5 | 16.9 |
| sd | 3.9 | 17.5 | 4.4 | 6.5 | 3.3 | 3.9 |
| CV (%) | 30 | 68 | 29 | 35 | 19 | 23 |
| Feb-19 | 4 | 21 | 6 | 6.4 | 8.3 | 6.9 |
| Feb-26 | 7.4 | 42 | 17.7 | 17.6 | 24.3 | 19.9 |
| Mar-04 | 12 | 64 | 30.2 | 35.5 | 28 | 31.2 |
| Mar-11 | 6.7 | 11 | 13.1 | 12.8 | 17.1 | 14.3 |
| Mar-18 | 9.9 | 18 | 21 | 20.9 | 25.5 | 22.5 |
| mean | 8.0 | 31.2 | 17.6 | 18.6 | 20.6 | 19.0 |
| sd | 3.1 | 21.7 | 9.0 | 10.9 | 8.0 | 9.1 |
| CV(%) | 38 | 69 | 51 | 58 | 39 | 48 |
| OVERALL | | | | | | |
| mean | 10.6 | 28.5 | 16.3 | 18.5 | 19.1 | 18.0 |
| sd | 4.3 | 18.8 | 6.8 | 8.4 | 6.0 | 6.7 |
| CV (%) | 41 | 66 | 42 | 46 | 31 | 37 |
| -1sd | 6.3 | 9.7 | 9.5 | 10.1 | 13.1 | 11.3 |
| +1sd | 14.9 | 47.3 | 23.1 | 26.9 | 25.0 | 24.6 |
| Loading mean (g/d) | 1476 | 3964 | 2269 | 2572 | 2650 | 2497 |

Appendix 3: Resin Acids - Northwood Pulp Mill (C)

Compound: Abietic (ug/L)

| 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 13 | 35 | 8.1 | 9.8 | 3.5 | 7.1 |
| Jan-22 | 36 | 44 | 16.1 | 22.6 | 32.5 | 23.7 |
| Jan-24 | 25 | 17 | 14.3 | 15.2 | 12.9 | 14.1 |
| Jan-29 | 33 | 14 | 19.9 | 15.9 | 19 | 18.3 |
| Feb-05 | 25 | 12 | 15.1 | 7.7 | 12.2 | 11.7 |
| mean | 26.4 | 24.4 | 14.7 | 14.2 | 16.0 | 15.0 |
| sd | 8.9 | 14.3 | 4.3 | 5.8 | 10.7 | 6.3 |
| CV (%) | 34 | 58 | 29 | 41 | 67 | 42 |
| Feb-19 | 18 | 33 | 4.4 | 4.5 | 7.3 | 5.4 |
| Feb-26 | 34 | 86 | 19.8 | 19.9 | 25.1 | 21.6 |
| Mar-04 | 50 | 112 | 23.3 | 21.7 | 21.3 | 22.1 |
| Mar-11 | 32 | 14 | 11.3 | 10.6 | 15.2 | 12.4 |
| Mar-18 | 62 | 28 | 21.5 | 20.6 | 27.9 | 23.3 |
| mean | 39.2 | 54.6 | 16.1 | 15.5 | 19.4 | 17.0 |
| sd | 17.1 | 42.1 | 8.0 | 7.6 | 8.3 | 7.8 |
| CV(%) | 44 | 77 | 50 | 49 | 43 | 46 |
| OVERALL | | | | | | |
| mean | 32.8 | 39.5 | 15.4 | 14.9 | 17.7 | 16.0 |
| sd | 14.5 | 33.7 | 6.1 | 6.4 | 9.2 | 6.8 |
| CV(%) | 44 | 85 | 39 | 43 | 52 | 42 |
| Loading mean (g/d) | 4562 | 5494 | 2139 | 2066 | 2461 | 2222 |

Compound: Palustric (ug/L)

| 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 2.6 | 9 | 2.1 | 2.3 | 2.8 | 2.4 |
| Jan-22 | 7.6 | 18 | 6 | 6.6 | 8.4 | 7.0 |
| Jan-24 | 5 | 26 | 8.4 | 9.9 | 8.9 | 9.1 |
| Jan-29 | 4.4 | 5 | 8.2 | 6.7 | 7.9 | 7.6 |
| Feb-05 | 4 | 5 | 6.5 | 3.5 | 4.7 | 4.9 |
| mean | 4.7 | 12.6 | 6.2 | 5.8 | 6.5 | 6.2 |
| sd | 1.8 | 9.2 | 2.5 | 3.0 | 2.7 | 2.6 |
| CV (%) | 39 | 73 | 41 | 52 | 41 | 42 |
| Feb-19 | 0.59 | 5 | 2.1 | 2.2 | 3.2 | 2.5 |
| Feb-26 | 1.1 | 8 | 7.4 | 7.3 | 9.4 | 8.0 |
| Mar-04 | 2.3 | 5 | 10.3 | 9.6 | 9.5 | 9.8 |
| Mar-11 | 1.7 | 5 | 5.3 | 5 | 6.6 | 5.6 |
| Mar-18 | 2.7 | 6 | 8.7 | 8.4 | 10.5 | 9.2 |
| mean | 1.7 | 5.8 | 6.8 | 6.5 | 7.8 | 7.0 |
| sd | 0.9 | 1.3 | 3.2 | 2.9 | 3.0 | 3.0 |
| CV (%) | 51 | 22 | 47 | 45 | 38 | 43 |
| OVERALL | | | | | | |
| mean | 3.2 | 9.2 | 6.5 | 6.2 | 7.2 | 6.6 |
| sd | 2.1 | 7.1 | 2.7 | 2.8 | 2.7 | 2.7 |
| rsd | 66 | 78 | 42 | 46 | 38 | 41 |
| Loading mean (g/d) | 445 | 1280 | 904 | 855 | 1000 | 920 |

Appendix 3: Resin Acids - Northwood Pulp Mill (d)

Compound: Neoabietic

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 1.8 | 8 | 1.1 | 1.5 | 1.2 | 1.3 |
| Jan-22 | 5.2 | 15 | 2.5 | 2.6 | 4.8 | 3.3 |
| Jan-24 | 4 | 24 | 2.9 | 3.1 | 2.9 | 3.0 |
| Jan-29 | 1.5 | 5 | 1.8 | 1.3 | 1.7 | 1.6 |
| Feb-05 | 1.8 | 5 | 1.4 | 1.1 | 1 | 1.2 |
| mean | 2.9 | 11.4 | 1.9 | 1.9 | 2.3 | 2.1 |
| sd | 1.6 | 8.1 | 0.8 | 0.9 | 1.6 | 1.0 |
| CV (%) | 58 | 71 | 39 | 46 | 68 | 49 |
| Feb-19 | 0.35 | 5 | 0.3 | 0.4 | 0.9 | 0.5 |
| Feb-26 | 0.57 | 6 | 2.5 | 2 | 2.6 | 2.4 |
| Mar-04 | 1.4 | 5 | 3.4 | 1.3 | 2.5 | 2.4 |
| Mar-11 | 0.87 | 5 | 1.7 | 1.4 | 1.9 | 1.7 |
| Mar-18 | 1.6 | 5 | 2.2 | 2.1 | 2.8 | 2.4 |
| mean | 1.0 | 5.2 | 2.0 | 1.4 | 2.1 | 1.9 |
| sd | 0.5 | 0.4 | 1.1 | 0.7 | 0.8 | 0.8 |
| CV (%) | 56 | 9 | 57 | 47 | 36 | 43 |
| OVERALL | | | | | | |
| mean | 1.9 | 8.3 | 2.0 | 1.7 | 2.2 | 2.0 |
| sd | 1.5 | 6.3 | 0.9 | 0.8 | 1.2 | 0.9 |
| CV)%) | 80 | 76 | 46 | 47 | 52 | 44 |
| Loading mean (g/d) | 266 | 1155 | 275 | 234 | 310 | 273 |

Compound: 12/14 Chlorodehydroabietic

| (ug/L) 1996 | AXYS (SRC) | PESC | IOS (i) | IOS (ii) | IOS (iii) | IOS mean |
|---|---|---|---|---|---|---|
| Jan-15 | 0.48 | | | | | |
| Jan-22 | 1.3 | | | | | |
| Jan-24 | 0.76 | | | | | |
| Jan-29 | 0.86 | | | | | |
| Feb-05 | 0.69 | | | | | |
| mean | 0.8 | | | | | |
| sd | 0.3 | | | | | |
| CV(%) | 37 | | | | | |
| Feb-19 | 0.16 | | | | | |
| Feb-26 | 0.65 | | | | | |
| Mar-04 | 0.76 | | | | | |
| Mar-11 | 0.19 | | | | | |
| Mar-18 | 0.19 | | | | | |
| mean | 0.4 | | | | | |
| sd | 0.3 | | | | | |
| CV (%) | 74 | | | | | |
| OVERALL | | | | | | |
| mean | 0.6 | | | | | |
| sd | 0.4 | | | | | |
| CV (%) | 60 | | | | | |
| Loading mean (g/d) | 84 | | | | | |

**Appendix 3: Resin Acids - Northwood Pulp Mill - AXYS Unadjusted For Surrogate Recovery (e)**

| Compound: (ug/L) | Pimaric | | Compound: (ug/L) | Sandaracopimaric |
|---|---|---|---|---|
| 1996 | AXYS | AXYS Surrogate Recovery (%) | 1996 | AXYS |
| Jan-15 | 4.2 | 77 | Jan-15 | 0.5 |
| Jan-22 | 12.8 | 80 | Jan-22 | 1.3 |
| Jan-24 | 12.1 | 93 | Jan-24 | 1.1 |
| Jan-29 | 7.6 | 69 | Jan-29 | 0.6 |
| Feb-05 | 4.7 | 69 | Feb-05 | 0.4 |
| mean | 8.3 | | mean | 0.8 |
| sd | 4.0 | | sd | 0.4 |
| CV (%) | 49 | | CV (%) | 52 |
| Feb-19 | 2.1 | 69 | Feb-19 | 0.2 |
| Feb-26 | 4.4 | 70 | Feb-26 | 0.5 |
| Mar-04 | 7.7 | 70 | Mar-04 | 0.6 |
| Mar-11 | 3.0 | 74 | Mar-11 | 0.4 |
| Mar-18 | 3.8 | 69 | Mar-18 | 0.8 |
| mean | 4.2 | | mean | 0.5 |
| sd | 2.1 | | sd | 0.2 |
| CV (%) | 50 | | CV (%) | 45 |
| OVERALL | | | OVERALL | |
| mean | 6.2 | | mean | 0.6 |
| sd | 3.7 | | sd | 0.3 |
| CV (%) | 59 | | CV (%) | 54 |
| -1sd | 2.5 | | -1sd | 0.3 |
| +1sd | 10.0 | | +1sd | 1.0 |
| Loading mean (g/d) | 869 | | Loading mean (g/d) | 87 |

Appendix 3: Resin Acids - Northwood Pulp Mill - AXYS Unadjusted For Surrogate Recovery (f)

Compound: Isopimaric

| (ug/L) 1996 | AXYS | AXYS Surrogate Recovery (%) |
|---|---|---|
| Jan-15 | 4.5 | 77 |
| Jan-22 | 12.0 | 80 |
| Jan-24 | 10.2 | 93 |
| Jan-29 | 6.6 | 69 |
| Feb-05 | 4.5 | 69 |
| mean | 7.6 | |
| sd | 3.4 | |
| CV (%) | 45 | |
| Feb-19 | 1.7 | 69 |
| Feb-26 | 3.8 | 70 |
| Mar-04 | 5.8 | 70 |
| Mar-11 | 3.3 | 74 |
| Mar-18 | 5.5 | 69 |
| mean | 4.0 | |
| sd | 1.7 | |
| CV (%) | 41 | |
| OVERALL | | |
| mean | 5.8 | |
| sd | 3.1 | |
| CV (%) | 54 | |
| -1sd | 2.6 | |
| +1sd | 8.9 | |
| Loading mean (g/d) | 805 | |

Compound: Dehydroabietic

| (ug/L) 1996 | AXYS |
|---|---|
| Jan-15 | 6.2 |
| Jan-22 | 14.4 |
| Jan-24 | 12.1 |
| Jan-29 | 11.0 |
| Feb-05 | 7.6 |
| mean | 10.3 |
| sd | 3.3 |
| CV (%) | 32 |
| Feb-19 | 2.8 |
| Feb-26 | 5.2 |
| Mar-04 | 8.4 |
| Mar-11 | 5.0 |
| Mar-18 | 6.8 |
| mean | 5.6 |
| sd | 2.1 |
| CV (%) | 38 |
| OVERALL | |
| mean | 7.9 |
| sd | 3.6 |
| CV (%) | 45 |
| -1sd | 4.4 |
| +1sd | 11.5 |
| Loading mean (g/d) | 1106 |

Appendix 3: Resin Acids - Northwood Pulp Mill - AXYS Unadjusted For Surrogate Recovery (g)

| Compound: (ug/L) | Abietic | |
|---|---|---|
| 1996 | AXYS | AXYS Surrogate Recovery (%) |
| Jan-15 | 10.0 | 77 |
| Jan-22 | 28.8 | 80 |
| Jan-24 | 23.3 | 93 |
| Jan-29 | 22.8 | 69 |
| Feb-05 | 17.3 | 69 |
| mean | 20.4 | |
| sd | 7.1 | |
| CV (%) | 35 | |
| Feb-19 | 12.4 | 69 |
| Feb-26 | 23.8 | 70 |
| Mar-04 | 35.0 | 70 |
| Mar-11 | 23.7 | 74 |
| Mar-18 | 42.8 | 69 |
| mean | 27.5 | |
| sd | 11.7 | |
| CV (%) | 42 | |
| OVERALL | | |
| mean | 24.0 | |
| sd | 9.9 | |
| CV (%) | 41 | |
| -1sd | 14.1 | |
| +1sd | 33.8 | |
| Loading mean (g/d) | 3335 | |

| Compound: (ug/L) | Palustric |
|---|---|
| 1996 | AXYS |
| Jan-15 | 2.0 |
| Jan-22 | 6.1 |
| Jan-24 | 4.7 |
| Jan-29 | 3.0 |
| Feb-05 | 2.8 |
| mean | 3.7 |
| sd | 1.6 |
| CV (%) | 44 |
| Feb-19 | 0.4 |
| Feb-26 | 0.8 |
| Mar-04 | 1.6 |
| Mar-11 | 1.3 |
| Mar-18 | 1.9 |
| mean | 1.2 |
| sd | 0.6 |
| CV (%) | 50 |
| OVERALL | |
| mean | 2.4 |
| sd | 1.8 |
| CV (%) | 72 |
| -1sd | 0.7 |
| +1sd | 4.2 |
| Loading mean (g/d) | 340 |

**Appendix 3: Resin Acids - Northwood Pulp Mill - AXYS Unadjusted For Surrogate Recovery** **(h)**

| Compound: (ug/L) | Neoabietic | |
|---|---|---|
| 1996 | AXYS | AXYS Surrogate Recovery (%) |
| Jan-15 | 1.4 | 77 |
| Jan-22 | 4.2 | 80 |
| Jan-24 | 3.7 | 93 |
| Jan-29 | 1.0 | 69 |
| Feb-05 | 1.2 | 69 |
| mean | 2.3 | |
| sd | 1.5 | |
| CV (%) | 65 | |
| Feb-19 | 0.2 | 69 |
| Feb-26 | 0.4 | 70 |
| Mar-04 | 1.0 | 70 |
| Mar-11 | 0.6 | 74 |
| Mar-18 | 1.1 | 69 |
| mean | 0.7 | |
| sd | 0.4 | |
| CV (%) | 55 | |
| OVERALL | | |
| mean | 1.5 | |
| sd | 1.3 | |
| rsd | 90 | |
| -1sd | 0.1 | |
| +1sd | 2.8 | |
| Loading mean (g/d) | 207 | |

| Compound: (ug/L) | 12/14 Chlorodehydroabietic |
|---|---|
| 1996 | AXYS |
| Jan-15 | 0.4 |
| Jan-22 | 1.0 |
| Jan-24 | 0.7 |
| Jan-29 | 0.6 |
| Feb-05 | 0.5 |
| mean | 0.6 |
| sd | 0.3 |
| CV (%) | 41 |
| Feb-19 | 0.1 |
| Feb-26 | 0.5 |
| Mar-04 | 0.5 |
| Mar-11 | 0.1 |
| Mar-18 | 0.1 |
| mean | 0.3 |
| sd | 0.2 |
| CV (%) | 74 |
| OVERALL | |
| mean | 0.5 |
| sd | 0.3 |
| CV (%) | 64 |
| -1sd | 0.2 |
| +1sd | 0.7 |
| Loading mean (g/d) | 63 |

## Appendix 4: Replicate Effluent Samples Analyses for AXYS and PESC

| Resin Acid (ug/L) | AXYS (i) Jan-22 | AXYS (ii) Jan-22 | mean | sd | CV (%) | AXYS (i) Jan-29 | AXYS (ii) Jan-29 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Pimaric | 16 | 15 | 16 | 1 | 5 | 11 | 11 | 11 | 0 | 0 |
| Sandaracopimaric | 1.6 | 1.5 | 1.6 | 0.1 | 5 | 0.82 | 0.81 | 0.82 | 0.01 | 1 |
| Isopimaric | 15 | 14 | 15 | 1 | 5 | 9.6 | 8.6 | 9.1 | 0.7 | 8 |
| Dehydroabietic | 18 | 17 | 18 | 1 | 4 | 16 | 14 | 15 | 1 | 9 |
| Abietic | 36 | 34 | 35 | 1 | 4 | 33 | 30 | 32 | 2 | 7 |
| Palustric | 7.6 | 6.6 | 7.1 | 0.7 | 10 | 4.4 | 1.9 | 3.2 | 1.8 | 56 |
| Neoabietic | 5.2 | 5.4 | 5.3 | 0.1 | 3 | 1.5 | 0.63 | 1.1 | 0.6 | 58 |

**AXYS results Surrogate Recovery corrected**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Recovery (%)** | 80 | 70 | 75 | 7 | 9 | 69 | 66 | 68 | 2 | 3 |

| | AXYS (i) Mar-11 | AXYS (ii) Mar-11 | mean | sd | CV (%) | PESC (i) Jan-22 | PESC (ii) Jan-22 | mean | sd | CV (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Pimaric | 4.1 | 5.3 | 4.7 | 0.8 | 18 | 88 | 33 | 61 | 39 | 64 |
| Sandaracopimaric | 0.49 | 0.56 | 0.53 | 0.05 | 9 | 8 | 6 | 7 | 1 | 20 |
| Isopimaric | 4.5 | 5.2 | 4.9 | 0.5 | 10 | 32 | 27 | 30 | 4 | 12 |
| Dehydroabietic | 6.7 | 7.4 | 7.1 | 0.5 | 7 | 33 | 29 | 31 | 3 | 9 |
| Abietic | 32 | 36 | 34 | 3 | 8 | 44 | 45 | 45 | 1 | 2 |
| Palustric | 1.7 | 1.6 | 1.7 | 0.1 | 4 | 18 | 16 | 17 | 1 | 8 |
| Neoabietic | 0.87 | 0.88 | 0.88 | 0.01 | 1 | 15 | 13 | 14 | 1 | 10 |

**AXYS results Surrogate Recovery corrected**

| | | | | | |
|---|---|---|---|---|---|
| **Recovery (%)** | 70 | 69 | 70 | 1 | 1 |

**Appendix 4 cont'd..: Replicate Effluent Samples Analyses for AXYS and PESC**

| | PESC (i) Feb-19 | PESC (ii) Feb-19 | mean | sd | CV (%) | **PESC (i) Mar-18** | **PESC (ii) Mar-18** | **mean** | **sd** | **CV (%)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Pimaric** | 15 | 12 | 14 | 2 | 16 | **13** | **11** | **12** | **1** | **12** |
| **Sandaracopimaric** | 5 | 5 | - | - | - | **5** | **5** | **-** | **-** | **-** |
| **Isopimaric** | 11 | 9 | 10 | 1 | 14 | **22** | **19** | **21** | **2** | **10** |
| **Dehydroabietic** | 21 | 16 | 19 | 4 | 19 | **18** | **16** | **17** | **1** | **8** |
| **Abietic** | 33 | 23 | 28 | 7 | 25 | **28** | **22** | **25** | **4** | **17** |
| **Palustric** | 5 | 5 | - | - | - | **6** | **5** | **5.5** | **0.7** | **13** |
| **Neoabietic** | 5 | 5 | - | - | - | **5** | **5** | **-** | **-** | **-** |

**Shaded values are < detection limit.**

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (a)

Compound: Chlorovanillins and Monochloroguaiacols (ng/L)

| | | MCV | MCV | DCV | MCG | MCG | MCG | (chloride) |
|---|---|---|---|---|---|---|---|---|
| | | 6- | 5- | 5,6- | 4- | 5- | 6- | (mg/L) |
| 1994 | Dec-28 | - | - | - | 72 | 210 | <0.63 | 157 |
| 1995 | Jan-11 | - | - | - | **72** | **8.8** | <0.47 | - |
| | Jan-16 | - | - | - | 110 | 22 | <0.65 | 224 |
| | Jan-22 | - | - | - | **77** | 8.8 | <0.46 | 251 |
| | Jan-30 | - | - | - | **120** | 26 | <1.8 | 258 |
| Mean | | | | | 90 | 55 | | |
| 1996 | Jan-15 | 3200 | <19 | <12 | **190** | 31 | **7.7** | 220 |
| | Jan-22 | 2000 | <16 | <6.4 | **170** | 34 | <2.0 | 220 |
| | Jan-24 | 1700 | **18** | <16 | **130** | 22 | 9.5 | 218 |
| | Jan-29 | 3000 | 16 | <25 | 200 | 44 | <2.0 | 209 |
| | Feb-05 | 2900 | <17 | <34 | 160 | 22 | **4.4** | 173 |
| | Feb-19 | 10000 | 18 | 27 | 180 | 38 | **4.5** | 183 |
| | Feb-26 | 3900 | 13 | **7** | 160 | 32 | **4.9** | 226 |
| | Mar-04 | 2600 | 8.4 | <0.77 | 170 | 41 | **5.8** | 238 |
| | Mar-11 | 2300 | 18 | **6** | 130 | 22 | **3.2** | 214 |
| | Mar-18 | 3100 | 13 | **2.2** | 150 | 24 | **2.7** | 156 |
| Mean | | 3470 | 15 | | 164 | 31 | | |

**NR = Not Reported** ***Shaded values are NDRs (not detected - incorrect ratio)***

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Servizi et al., pre-$ClO_2$ | Min | | | | | | |
| | Mean | NR | NR | NR | NR | NR | NR |
| | Max | | | | | | |
| Hall, $ClO_2$ transition | Sep-92 | | | | | | |
| | Oct-92 | NR | NR | NR | NR | NR | NR |
| | Mar-93 | | | | | | |
| NCASI;Chronic Effect | VERSAR | 107000 | - | 87500 | - | - | - |
| | TERRA | 650000 | - | 376000 | - | - | - |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (b)

Compound: Dichloroguaiacols, Trichloroguaiacols and Tetrachloroguaiacol (ng/L)

| | | DCG | DCG | DCG | TCG | TCG | TCG | TeCG | (chloride) |
|---|---|---|---|---|---|---|---|---|---|
| | | 4,6- | 4,5- | 3,4 | 3,4,6- | 3,4,5- | 4,5,6- | 3,4,5,6- | (mg/L) |
| 1994 | Dec-28 | **1.2** | **23** | **2.7** | <0.58 | **4.8** | **3** | - | 157 |
| 1995 | Jan-11 | <0.75 | **26** | <0.97 | <0.56 | **5.8** | **2.3** | - | - |
| | Jan-16 | **1.5** | **26** | **3.9** | <0.68 | **13** | **2.1** | <5.4 | 224 |
| | Jan-22 | <0.64 | **26** | **12** | <0.49 | **11** | **2.6** | - | 251 |
| | Jan-30 | **4.5** | **31** | **15** | <3.1 | <3.8 | **2.6** | - | 258 |
| Mean | | | | | | | | | |
| 1996 | Jan-15 | <2.2 | **46** | **8.7** | <5.8 | <6.8 | **6.5** | <12 | 220 |
| | Jan-22 | <2.2 | **26** | **4.4** | <5.6 | <6.6 | **8.8** | <11 | 220 |
| | Jan-24 | <2.0 | **19** | **3.9** | <4.7 | <5.5 | **9.7** | <7.8 | 218 |
| | Jan-29 | <5.2 | **84** | <6.7 | <5.7 | <7.3 | <5.0 | <14 | 209 |
| | Feb-05 | <19 | **67** | <24 | <6.0 | <7.7 | <5.3 | <12 | 173 |
| | Feb-19 | **4.9** | **38** | **9** | <2.4 | <2.8 | 9.5 | <3.0 | 183 |
| | Feb-26 | **5.9** | **37** | **5.1** | <1.4 | **2.9** | 2.3 | **2.5** | 226 |
| | Mar-04 | **2.3** | **29** | **3.8** | <1.4 | <1.5 | **4.4** | **1.8** | 238 |
| | Mar-11 | **4.8** | **29** | **7.6** | <2.6 | **4.8** | **20** | <3.6 | 214 |
| | Mar-18 | **4.2** | 23 | **6.6** | <0.98 | <0.77 | 9.5 | <0.77 | 156 |
| Mean | | | | | | | | | |
| Servizi et al., pre-$ClO_2$ | Min | | | | 2300 | 18700 | 3700 | 8700 | |
| | Mean | NR | NR | NR | 8100 | 41000 | 8500 | 44300 | |
| | Max | | | | 12900 | 81300 | 14900 | 92700 | |
| Hall, $ClO_2$ transition | Sep-92 | | 360 | | | 6450 | 1530 | 1490 | |
| | Oct-92 | NR | 320 | NR | NR | 1970 | 160 | 380 | |
| | Mar-93 | | 370 | | | 1900 | 630 | 320 | |
| NCASI;Chronic Effect | VERSAR | - | - | - | 30200 | 7500 | 3100 | 3200 | |
| | TERRA | - | - | - | 240000 | 240000 | 240000 | 240000 | |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (C)

Compound: Monochlorocatechols and Dichlorocatechols (ng/L)

| | | MCC | MCC | DCC | DCC | DCC | DCC | (chloride) |
|---|---|---|---|---|---|---|---|---|
| | | 4- | 3- | 3,5 | 3,4- | 4,5 | 3,6- | (mg/L) |
| 1994 | Dec-28 | 12 | 30 | <2.2 | **16** | 77 | **18** | 157 |
| 1995 | Jan-11 | **11** | 67 | **26** | 110 | 190 | **26** | - |
| | Jan-16 | 16 | **43** | <2.4 | **47** | 190 | 29 | 224 |
| | Jan-22 | **9.9** | **72** | <1.8 | 110 | 310 | <1.2 | 251 |
| | Jan-30 | **17** | **40** | <10 | <6.2 | 160 | **9.3** | 258 |
| Mean | | 13 | | | | 185 | | |
| 1996 | Jan-15 | 18 | **6.2** | 9.7 | <11 | 33 | <12 | 220 |
| | Jan-22 | **16** | **6.1** | <3.4 | <3.9 | 56 | <4.1 | 220 |
| | Jan-24 | 20 | **7.9** | <3.0 | <3.4 | 34 | <3.6 | 218 |
| | Jan-29 | 38 | <22 | <8.0 | <10 | <11 | <9.9 | 209 |
| | Feb-05 | 35 | <27 | <23 | <29 | <32 | <28 | 173 |
| | Feb-19 | **4.6** | 7.2 | <2.5 | **30** | **15** | 15 | 183 |
| | Feb-26 | 36 | 10 | **4** | 13 | 47 | **21** | 226 |
| | Mar-04 | 43 | **8** | **2.8** | **24** | **43** | **33** | 238 |
| | Mar-11 | 40 | **11** | <2.0 | **23** | **30** | **26** | 214 |
| | Mar-18 | 13 | 8.2 | <0.86 | **2.3** | **25** | **22** | 156 |
| Mean | | 26 | | | | 35 | | |
| Servizi et al., pre-$ClO_2$ | Min | | | | | | | |
| | Mean | NR | NR | NR | NR | NR | NR | |
| | Max | | | | | | | |
| Hall, $ClO_2$ transition | Sep-92 | | | | | | | |
| | Oct-92 | NR | NR | NR | NR | NR | NR | |
| | Mar-93 | | | | | | | |
| NCASI;Chronic Effect | VERSAR | 79000 | - | - | - | 44500 | - | |
| | TERRA | 650000 | - | - | - | 376000 | - | |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (d)

Compound: Trichlorocatechols, Tetrachlorocatechol, Chlorosyringols and Chlorosyringaldehydes

| | | TCC | TCC | TeCC | DCSy | TCSy | MCShyd | DCShyd | (chloride) |
|---|---|---|---|---|---|---|---|---|---|
| | | 3,4,6- | 3,4,5- | 3,4,5,6- | 3,5- | 3,4,5- | 2- | 2,6- | (mg/L) |
| 1994 | Dec-28 | <4.3 | 6.6 | <3.7 | - | <3.3 | - | - | 157 |
| 1995 | Jan-11 | 4.6 | 7.4 | 2.2 | - | <4.9 | - | - | - |
| | Jan-16 | <1.1 | 8.5 | 3 | - | - | - | - | 224 |
| | Jan-22 | 5.3 | 9.7 | <5.8 | - | <6.2 | - | - | 251 |
| | Jan-30 | <3.8 | <4.0 | <2.9 | - | <7.4 | - | - | 258 |
| Mean | | | | | | | | | |
| 1996 | Jan-15 | <12 | <12 | 32 | <8.6 | <5.3 | <4.9 | <11 | 220 |
| | Jan-22 | <9.0 | **9.5** | 14 | <7.0 | <5.0 | <4.8 | <8.7 | 220 |
| | Jan-24 | **6.1** | **5** | 21 | <7.3 | <4.3 | <5.4 | <9.1 | 218 |
| | Jan-29 | <12 | <12 | **17** | <16 | <16 | <14 | <16 | 209 |
| | Feb-05 | <17 | <18 | **10** | <19 | <11 | <14 | <1 | 173 |
| | Feb-19 | <2.6 | **3.7** | 14 | <3.3 | <1.6 | **6.2** | 4.2 | 183 |
| | Feb-26 | **2.1** | **4.5** | 15 | <1.9 | <1.0 | **5.7** | **1.8** | 226 |
| | Mar-04 | **2.5** | **2.7** | 25 | <1.8 | <0.88 | **4.8** | 4.1 | 238 |
| | Mar-11 | **7.2** | **4.7** | 22 | <3.3 | <1.8 | 4.9 | <4.2 | 214 |
| | Mar-18 | **0.89** | <0.78 | 20 | <1.3 | <2.5 | **4.8** | 3.7 | 156 |
| Mean | | | | | | | | | |
| Servizi et al., pre-$ClO_2$ | Min | | | 1900 | | | | | |
| | Mean | NR | NR | 24800 | NR | NR | NR | NR | |
| | Max | | | 61200 | | | | | |
| Hall, $ClO_2$ transition | Sep-92 | | 4370 | 240 | | | | | |
| | Oct-92 | NR | <100 | <30 | NR | NR | NR | NR | |
| | Mar-93 | | 1370 | 50 | | | | | |
| NCASI;Chronic Effect | VERSAR | 38200 | 18000 | 7300 | - | 52800 | - | 14500 | |
| | TERRA | 200000 | 200000 | 200000 | - | 200000 | - | 376000 | |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (e)

Compound: Monochlorophenol and Dichlorophenols (ng/L)

| | | MCP | DCP | DCP | DCP | DCP | DCP | (chloride) |
|---|---|---|---|---|---|---|---|---|
| | | 4- | 2,6- | 2,4/2,5- | 3,5- | 2,3- | 3,4- | (mg/L) |
| 1994 | Dec-28 | <1.0 | **2.6** | **22** | **4.8** | **17** | <0.63 | 157 |
| 1995 | Jan-11 | **2.8** | **7** | **46** | **12** | 66 | <0.61 | - |
| | Jan-16 | **2.5** | **2.6** | **33** | 9.4 | **64** | <0.8 | 224 |
| | Jan-22 | **5.1** | **7.6** | **57** | <0.88 | <23 | <0.57 | 251 |
| | Jan-30 | **5.5** | **6.6** | **44** | <4.2 | **27** | <2.7 | 258 |
| Mean | | 4 | | | | | | |
| 1996 | Jan-15 | 16 | **26** | **72** | **6.8** | **24** | <1.8 | 220 |
| | Jan-22 | **16** | **37** | **80** | **16** | 27 | <1.3 | 220 |
| | Jan-24 | **13** | **50** | **110** | **18** | **24** | <1.4 | 218 |
| | Jan-29 | **18** | **55** | **53** | <6.5 | <6.2 | <4.5 | 209 |
| | Feb-05 | **9.4** | **33** | **20** | <5.2 | <4.9 | <3.7 | 173 |
| | Feb-19 | 23 | **3.3** | 21 | <1.9 | 8.6 | <1.2 | 183 |
| | Feb-26 | 22 | **13** | 42 | **3.1** | **10** | <0.82 | 226 |
| | Mar-04 | 20 | 3.3 | 27 | **3.2** | **24** | <1.3 | 238 |
| | Mar-11 | 16 | **6.5** | **21** | **3.2** | **24** | <1.3 | 214 |
| | Mar-18 | 13 | **6.3** | 32 | <1.6 | **32** | <1.5 | 156 |
| Mean | | 17 | | | | | | |
| Servizi et al., pre-$ClO_2$ | Min | | | | | | | |
| | Mean | NR | NR | NR | NR | NR | NR | |
| | Max | | | | | | | |
| Hall, $ClO_2$ transition | Sep-92 | | | | | | | |
| | Oct-92 | NR | NR | NR | NR | NR | NR | |
| | Mar-93 | | | | | | | |
| NCASI;Chronic Effect | VERSAR | 1100000 | 162000 | 70000 | - | - | - | |
| | TERRA | 650000 | 376000 | 376000 | - | - | - | |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (f)

Compound: Trichlorophenols (ng/L)

| | | TCP | TCP | TCP | TCP | TCP | TCP | (chloride) |
|---|---|---|---|---|---|---|---|---|
| | | 2,4,6- | 2,3,6- | 2,3,5- | 2,4,5- | 2,3,4- | 3,4,5- | (mg/L) |
| 1994 | Dec-28 | 5.3 | <2.4 | <2.3 | **3.1** | <1.8 | <1.8 | 157 |
| 1995 | Jan-11 | **5.6** | <0.74 | **8** | **14** | **2.7** | **2.8** | - |
| | Jan-16 | **4.9** | <3.4 | <3.4 | 16 | <2.6 | **4** | 224 |
| | Jan-22 | 6.4 | <0.63 | **5.6** | **13** | **4.6** | **2.7** | 251 |
| | Jan-30 | 5.7 | <5.9 | <6.0 | **4.7** | <5.4 | <5.4 | 258 |
| Mean | | 6 | | | | | | |
| 1996 | Jan-15 | 16 | <3.4 | <1.7 | <1.8 | **1.9** | **2** | 220 |
| | Jan-22 | 12 | <2.8 | <1.4 | <1.4 | <1.4 | <1.4 | 220 |
| | Jan-24 | 11 | <2.9 | <1.4 | <1.4 | <1.4 | <1.4 | 218 |
| | Jan-29 | 15 | <19 | <9.5 | <9.4 | <10 | <11 | 209 |
| | Feb-05 | 9.4 | <9.3 | <4.7 | <5.3 | <5.6 | <6.2 | 173 |
| | Feb-19 | 21 | **5.6** | **2.2** | **6.2** | <0.75 | <0.83 | 183 |
| | Feb-26 | 170 | **11** | 2.5 | **6.1** | <0.45 | 7.3 | 226 |
| | Mar-04 | 60 | <0.91 | **3.6** | <0.5 | <0.44 | <0.49 | 238 |
| | Mar-11 | 33 | <1.6 | **1.1** | **6.3** | <0.8 | <0.89 | 214 |
| | Mar-18 | 17 | <0.6 | <0.6 | <0.34 | <0.3 | <0.33 | 156 |
| Mean | | 36 | | | | | | |
| Servizi et al., pre-$ClO_2$ | Min | 2500 | | | | | | |
| | Mean | 6800 | NR | NR | NR | NR | NR | |
| | Max | 10500 | | | | | | |
| Hall, $ClO_2$ transition | Sep-92 | 1610 | | | | | | |
| | Oct-92 | 460 | NR | NR | NR | NR | NR | |
| | Mar-93 | 480 | | | | | | |
| NCASI;Chronic Effect | VERSAR | 3200 | - | - | 4500 | - | - | |
| | TERRA | 500000 | - | - | 150000 | - | - | |

Apendix 5: Chlorophenolic Compounds - Northwood Pulp Mill (g)

Compound: Tetrachlorophenols, Pentachlorophenol and Chlorodehydroabietic (ng/L)

| | | TeCP | TeCP | TeCP | PCP | CDHA | DCDHA | (chloride) |
|---|---|---|---|---|---|---|---|---|
| | | 2,3,5,6- | 2,3,4,6- | 2,3,4,5- | 2,4,5- | 12/14 | 12,14 | (mg/L) |
| 1994 | Dec-28 | <4.5 | <2.5 | <3.1 | 14 | 860 | 160 | 157 |
| 1995 | Jan-11 | <5.0 | <2.7 | <3.4 | 3.9 | 2700 | 350 | - |
| | Jan-16 | <5.0 | <2.8 | <3.5 | 5.4 | 710 | 90 | 224 |
| | Jan-22 | <4.4 | <2.4 | <3.0 | 7 | 1200 | 68 | 251 |
| | Jan-30 | <13 | <7.1 | <8.9 | <4.2 | - | - | 258 |
| Mean | | | | | | 1368 | 167 | |
| 1996 | Jan-15 | <4.9 | <4.2 | <4.6 | 8.2 | 480 | <16 | 220 |
| | Jan-22 | <5.4 | <4.6 | <4.5 | <4.9 | 1300 | <27 | 220 |
| | Jan-24 | <4.0 | <3.4 | <3.4 | <4.3 | 760 | 43 | 218 |
| | Jan-29 | <13 | <11 | <11 | <11 | 860 | <46 | 209 |
| | Feb-05 | <11 | <9.4 | <9.4 | <10 | 690 | <40 | 173 |
| | Feb-19 | <4.0 | <3.4 | <3.0 | 7 | 160 | <30 | 183 |
| | Feb-26 | <1.2 | 10 | <0.93 | 4 | 650 | <31 | 226 |
| | Mar-04 | <2.0 | 3.4 | <1.4 | 5.5 | 760 | <31 | 238 |
| | Mar-11 | <5.2 | <4.4 | <3.5 | 7.1 | 190 | <22 | 214 |
| | Mar-18 | <1.8 | **1.7** | <1.3 | 7.9 | 190 | <25 | 156 |
| Mean | | | | | | 604 | | |
| Servizi et al., pre-$ClO_2$ | Min | | 300 | | 600 | | | |
| | Mean | NR | 2500 | NR | 1100 | NR | NR | |
| | Max | | 3900 | | 1800 | | | |
| Hall, $ClO_2$ transition | Sep-92 | <50 | <50 | <50 | <20 | | | |
| | Oct-92 | <50 | <50 | <50 | <50 | NR | NR | |
| | Mar-93 | <50 | <50 | <50 | <30 | | | |
| NCASI;Chronic Effect | VERSAR | - | 10000 | - | 13000 | - | - | |
| | TERRA | - | - | - | - | - | - | |

**APPENDIX 6: Chlorophenolic* Compounds Laboratory Quality Assurance** (a)

AXYS Chlorophenolics Quality Check : Spiked Water Matrix Samples

| | 1994/95 Survey | | | 1996 Survey | | | 1996 Survey | | | 1996 Survey | | | Control Limits | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Set 1 | expected | | Set 2 | expected | | Set 3 | expected | | Set 4 | expected | | LCL** | UCL** |
| | ng/L | ng/L | difference | ng/L | ng/L | difference | ng/L | ng/L | difference | ng/L | ng/L | difference | | |
| 6MCV | **-** | - | - | **100** | 95 | 1.05 | **120** | 130 | 0.92 | **120** | 140 | 0.86 | 0.88 | 1.29 |
| 56DCV | **-** | - | - | **180** | 140 | 1.29 | **310** | 290 | 1.07 | **310** | 320 | 0.97 | 0.78 | 1.31 |
| 4MCG | **100** | 100 | 1.00 | **56** | 52 | 1.08 | **150** | 140 | 1.07 | **150** | 150 | 1.00 | 0.81 | 1.13 |
| 46DCG | **62** | 50 | 1.24 | **120** | 56 | 2.14 | **95** | 100 | 0.95 | **95** | 130 | 0.73 | 0.26 | 1.59 |
| 45DCG | **70** | 60 | 1.17 | **120** | 88 | 1.36 | **120** | 120 | 1.00 | **120** | 150 | 0.80 | 0.52 | 1.39 |
| 346TCG | **91** | 84 | 1.08 | **100** | 91 | 1.10 | **110** | 130 | 0.85 | **110** | 110 | 1.00 | 0.73 | 1.28 |
| 345TCG | **190** | 180 | 1.06 | **98** | 130 | 0.75 | **230** | 240 | 0.96 | **230** | 210 | 1.10 | 0.6 | 1.32 |
| 456TCG | **113** | 110 | 1.03 | **94** | 93 | 1.01 | **140** | 150 | 0.93 | **140** | 150 | 0.93 | 0.91 | 1.16 |
| 3456TCG | **333** | 330 | 1.01 | **180** | 180 | 1.00 | **410** | 420 | 0.98 | **410** | 410 | 1.00 | 0.88 | 1.15 |
| 4MCC | **60** | 61 | 0.98 | **55** | 25 | 2.20 | **110** | 99 | 1.11 | **110** | 91 | 1.21 | 0.45 | 1.55 |
| 36DCC | **100** | 110 | - | **110** | 100 | 1.10 | **120** | 130 | 0.92 | **120** | 150 | 0.80 | 0.82 | 1.53 |
| 34DCC | **83** | 100 | 0.83 | **110** | 96 | 1.15 | **110** | 120 | 0.92 | **110** | 120 | 0.92 | 0.73 | 1.61 |
| 45DCC | **67** | 88 | 0.76 | **110** | 100 | 1.10 | **100** | 100 | 1.00 | **100** | 100 | 1.00 | 0.69 | 1.79 |
| 346TCC | **101** | 150 | 0.67 | **200** | 190 | 1.05 | **160** | 160 | 1.00 | **160** | 140 | 1.14 | 0.35 | 2.16 |
| 345TCC | **157** | 240 | 0.65 | **200** | 200 | 1.00 | **240** | 250 | 0.96 | **240** | 260 | 0.92 | 0.51 | 2.1 |
| 3456TCC | **49** | 59 | 0.83 | **190** | 190 | 1.00 | **120** | 130 | 0.92 | **120** | 130 | 0.92 | 0.84 | 1.44 |
| 345TCS | **-** | - | - | **-** | - | - | **-** | - | - | | - | - | 0.4 | 1.6 |
| | Samples | | | Samples | | | Samples | | | Samples | | | | |
| Relevent Samples | Dec28/94<br>Jan11/95<br>Jan16/95<br>Jan22/95<br>Jan30/95 | | | Jan15/96<br>Jan22/96<br>Jan24/96 | | | Jan29/96<br>Feb05/96 | | | Feb19/96<br>Feb26/96<br>Mar04/96<br>Mar11/96<br>Mar16/96 | | | | |

* results are surrogate recovery corrected

** mean +/- 3 x stdev

Appendix 6: Chlorophenolic Compounds Laboratory Quality Assurance

1994/95 and 1996 Survey Spiked Water Matrix Samples - Surrogate Recovery (%)

(b)

| CODE | SURROGATE-13C | Compound | LCL* (%) | UCL* (%) | Spiked Matrix Set 1 | Spiked Matrix Set 2 | Spiked Matrix Set 3 | Spiked Matrix Set 4 |
|---|---|---|---|---|---|---|---|---|
| A | 4-CHLOROPHENOL | 4-Chlorophenol | 34 | 155 | 87 | 99 | 94 | 110 |
| B | 2,4-DICHLOROPHENOL | 2,6-Dichlorophenol | 27 | 142 | 85 | 81 | 79 | 110 |
| | | 2,4/2,5-Dichlorophenol | | | | | | |
| | | 3,5-Dichlorophenol | | | | | | |
| | | 2,3-Dichlorophenol | | | | | | |
| | | 3,4-Dichlorophenol | | | | | | |
| C | 4-CHLOROGUAIACOL | 6-Chloroguaiacol | 47 | 148 | 93 | 73 | 97 | 110 |
| | | 4-Chloroguaiacol | | | | | | |
| | | 5-Chloroguaiacol | | | | | | |
| D | 2,4,6-TRICHLOROPHENOL | 2,4,6-Trichlorophenol | 29 | 136 | 86 | 89 | 80 | 110 |
| | | 2,3,6-Trichlorophenol | | | | | | |
| | | 2,3,5-Trichlorophenol | | | | | | |
| E | 2,4,5-TRICHLOROPHENOL | 2,4,5-Trichlorophenol | 44 | 136 | 90 | 100 | 92 | 110 |
| | | 2,3,4-Trichlorophenol | | | | | | |
| | | 3,4,5-Trichlorophenol | | | | | | |
| | | 3-Chlorocatechol | | | | | | |
| | | 4-Chlorocatechol | | | | | | |
| F | 5-CHLOROVANILLIN | 5-Chlorovanillin | 49 | 136 | - | 47 | 98 | 92 |
| | | 6-Chlorovanillin | | | | | | |
| G | 2,3,4,5-TETRACHLOROPHENOL | 4,6-Dichloroguaiacol | 51 | 149 | 110 | 110 | 110 | 100 |
| | | 3,4-Dichloroguaiacol | | | | | | |
| | | 4,5-Dichloroguaiacol | | | | | | |
| | | 2,3,5,6-Tetrachlorophenol | | | | | | |
| | | 2,3,4,5-Tetrachlorophenol | | | | | | |
| | | 2,3,4,6-Tetrachlorophenol | | | | | | |
| | | 3,5-Dichlorosyringol | | | | | | |
| H | 4,5-DICHLOROCATECHOL | 3,6-Dichlorocatechol | 36 | 96 | 74 | 65 | 65 | 60 |
| | | 3,5-Dichlorocatechol | | | | | | |
| | | 3,4-Dichlorocatechol | | | | | | |
| | | 4,5-Dichlorocatechol | | | | | | |
| | | 3,4,6-Trichlorocatechol | | | | | | |
| | | 3,4,5-Trichlorocatechol | | | | | | |
| I | 4,5,6-TRICHLOROGUAIACOL | 3,4,6-Trichloroguaiacol | 53 | 126 | 92 | 58 | 89 | 100 |
| | | 3,4,5-Trichloroguaiacol | | | | | | |
| | | 4,5,6-Trichloroguaiacol | | | | | | |
| J | PENTACHLOROPHENOL | 5,6-Dichlorovanillin | 53 | 139 | 98 | 67 | 96 | 110 |
| | | Pentachlorophenol | | | | | | |
| | | 2-Chlorosyringaldehyde | | | | | | |
| | | 2,6-Dichlorosyringaldehyde | | | | | | |
| K | 3,4,5,6-TETRACHLOROGUAIACOL | 3,4,5,6-Tetrachloroguaiacol | 41 | 144 | 94 | 45 | 88 | 120 |
| | | 3,4,5-Trichlorosyringol | | | | | | |
| L | 3,4,5,6-TETRACHLOROCATECHOL | 3,4,5,6-Tetrachlorocatechol | 28 | 111 | 75 | 64 | 76 | 47 |

* +/- 3 x stdev

Appendix 6: Chlorophenolic Compounds Laboratory Quality Assurance
1994/95 Survey Effluent Samples - Surrogate Recovery (%)

| CODE | SURROGATE-13C | Compound | LCL* (%) | UCL* (%) | (C) Dec28/94 | Jan11/95 | Jan16/95 | Jan22/95 | Jan30/95 |
|---|---|---|---|---|---|---|---|---|---|
| A | 4-CHLOROPHENOL | 4-Chlorophenol | 34 | 155 | 92 | 60 | 81 | 69 | 77 |
| B | 2,4-DICHLOROPHENOL | 2,6-Dichlorophenol | 27 | 142 | 100 | 78 | 85 | 78 | 96 |
| | | 2,4/2,5-Dichlorophenol | | | | | | | |
| | | 3,5-Dichlorophenol | | | | | | | |
| | | 2,3-Dichlorophenol | | | | | | | |
| | | 3,4-Dichlorophenol | | | | | | | |
| C | 4-CHLOROGUAIACOL | 6-Chloroguaiacol | 47 | 148 | 99 | 97 | 99 | 91 | 90 |
| | | 4-Chloroguaiacol | | | | | | | |
| | | 5-Chloroguaiacol | | | | | | | |
| D | 2,4,6-TRICHLOROPHENOL | 2,4,6-Trichlorophenol | 29 | 136 | 100 | 85 | 97 | 93 | 89 |
| | | 2,3,6-Trichlorophenol | | | | | | | |
| | | 2,3,5-Trichlorophenol | | | | | | | |
| E | 2,4,5-TRICHLOROPHENOL | 2,4,5-Trichlorophenol | 44 | 136 | 120 | 85 | 110 | 86 | 87 |
| | | 2,3,4-Trichlorophenol | | | | | | | |
| | | 3,4,5-Trichlorophenol | | | | | | | |
| | | 3-Chlorocatechol | | | | | | | |
| | | 4-Chlorocatechol | | | | | | | |
| F | 5-CHLOROVANILLIN | 5-Chlorovanillin | 49 | 136 | - | - | - | - | - |
| | | 6-Chlorovanillin | | | | | | | |
| G | 2,3,4,5-TETRACHLOROPHENOL | 4,6-Dichloroguaiacol | 51 | 149 | 110 | 86 | 100 | 93 | 90 |
| | | 3,4-Dichloroguaiacol | | | | | | | |
| | | 4,5-Dichloroguaiacol | | | | | | | |
| | | 2,3,5,6-Tetrachlorophenol | | | | | | | |
| | | 2,3,4,5-Tetrachlorophenol | | | | | | | |
| | | 2,3,4,6-Tetrachlorophenol | | | | | | | |
| | | 3,5-Dichlorosyringol | | | | | | | |
| H | 4,5-DICHLOROCATECHOL | 3,6-Dichlorocatechol | 36 | 96 | 73 | 53 | 69 | 59 | 56 |
| | | 3,5-Dichlorocatechol | | | | | | | |
| | | 3,4-Dichlorocatechol | | | | | | | |
| | | 4,5-Dichlorocatechol | | | | | | | |
| | | 3,4,6-Trichlorocatechol | | | | | | | |
| | | 3,4,5-Trichlorocatechol | | | | | | | |
| I | 4,5,6-TRICHLOROGUAIACOL | 3,4,6-Trichloroguaiacol | 53 | 126 | 110 | 80 | 95 | 85 | 79 |
| | | 3,4,5-Trichloroguaiacol | | | | | | | |
| | | 4,5,6-Trichloroguaiacol | | | | | | | |
| J | PENTACHLOROPHENOL | 5,6-Dichlorovanillin | 53 | 139 | 100 | 84 | 91 | 77 | 81 |
| | | Pentachlorophenol | | | | | | | |
| | | 2-Chlorosyringaldehyde | | | | | | | |
| | | 2,6-Dichlorosyringaldehyde | | | | | | | |
| K | 3,4,5,6-TETRACHLOROGUAIACOL | 3,4,5,6-Tetrachloroguaiacol | 41 | 144 | 98 | 79 | 85 | 71 | 77 |
| | | 3,4,5-Trichlorosyringol | | | | | | | |
| L | 3,4,5,6-TETRACHLOROCATECHOL | 3,4,5,6-Tetrachlorocatechol | 28 | 111 | 56 | 46 | 48 | 49 | 56 |

* +/- 3 x stdev

Appendix 6: Chlorophenolic Compounds Laboratory Quality Assurance

1996 Survey Effluent Samples - Surrogate Recovery (%)

(d)

| CODE | SURROGATE-13C | Compound | LCL* (%) | UCL* (%) | Jan15/96 | Jan22/96 | Jan24/96 | Jan29/96 | Feb05/96 | Feb19/96 | Feb26/96 | Mar04/96 | Mar11/96 | Mar16/96 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 4-CHLOROPHENOL | 4-Chlorophenol | 34 | 155 | 38 | 64 | 52 | 84 | 130 | 100 | 110 | 110 | 120 | 130 |
| B | 2,4-DICHLOROPHENOL | 2,6-Dichlorophenol<br>2,4/2,5-Dichlorophenol<br>3,5-Dichlorophenol<br>2,3-Dichlorophenol<br>3,4-Dichlorophenol | 27 | 142 | 51 | 69 | 62 | 77 | 100 | 100 | 100 | 99 | 98 | 98 |
| C | 4-CHLOROGUAIACOL | 6-Chloroguaiacol<br>4-Chloroguaiacol<br>5-Chloroguaiacol | 47 | 148 | 30 | 33 | 33 | 93 | 110 | 100 | 110 | 97 | 110 | 82 |
| D | 2,4,6-TRICHLOROPHENOL | 2,4,6-Trichlorophenol<br>2,3,6-Trichlorophenol<br>2,3,5-Trichlorophenol | 29 | 136 | 63 | 78 | 69 | 80 | 96 | 82 | 91 | 88 | 86 | 97 |
| E | 2,4,5-TRICHLOROPHENOL | 2,4,5-Trichlorophenol<br>2,3,4-Trichlorophenol<br>3,4,5-Trichlorophenol<br>3-Chlorocatechol<br>4-Chlorocatechol | 44 | 136 | 74 | 82 | 76 | 87 | 92 | 84 | 97 | 87 | 84 | 94 |
| F | 5-CHLOROVANILLIN | 5-Chlorovanillin<br>6-Chlorovanillin | 49 | 136 | 36 | 41 | 41 | 120 | 120 | 87 | 88 | 79 | 83 | 64 |
| G | 2,3,4,5-TETRACHLOROPHENOL | 4,6-Dichloroguaiacol<br>3,4-Dichloroguaiacol<br>4,5-Dichloroguaiacol<br>2,3,5,6-Tetrachlorophenol<br>2,3,4,5-Tetrachlorophenol<br>2,3,4,6-Tetrachlorophenol<br>3,5-Dichlorosyringol | 51 | 149 | 84 | 85 | 88 | 110 | 110 | 98 | 120 | 110 | 100 | 110 |
| H | 4,5-DICHLOROCATECHOL | 3,6-Dichlorocatechol<br>3,5-Dichlorocatechol<br>3,4-Dichlorocatechol<br>4,5-Dichlorocatechol<br>3,4,6-Trichlorocatechol<br>3,4,5-Trichlorocatechol | 36 | 96 | 48 | 49 | 52 | 71 | 75 | 46 | 67 | 62 | 63 | 60 |
| I | 4,5,6-TRICHLOROGUAIACOL | 3,4,6-Trichloroguaiacol<br>3,4,5-Trichloroguaiacol<br>4,5,6-Trichloroguaiacol | 53 | 126 | 40 | 42 | 46 | 100 | 100 | 77 | 90 | 83 | 76 | 84 |
| J | PENTACHLOROPHENOL | 5,6-Dichlorovanillin<br>Pentachlorophenol<br>2-Chlorosyringaldehyde<br>2,6-Dichlorosyringaldehyde | 53 | 139 | 49 | 50 | 52 | 93 | 97 | 75 | 86 | 89 | 78 | 90 |
| K | 3,4,5,6-TETRACHLOROGUAIACOL | 3,4,5,6-Tetrachloroguaiacol<br>3,4,5-Trichlorosyringol | 41 | 144 | 34 | 36 | 39 | 92 | 94 | 76 | 84 | 85 | 74 | 84 |
| L | 3,4,5,6-TETRACHLOROCATECHOL | 3,4,5,6-Tetrachlorocatechol | 28 | 111 | 43 | 45 | 48 | 57 | 59 | 44 | 61 | 59 | 53 | 57 |

* +/- 3 x stdev

(e)

## AXYS Chlorophenolics Quality Check : Spiked Matrix Water Samples and Control Ranges

| | 1994/95 Survey | | | 1996 Survey | | | 1996 Survey | | | 1996 Survey | | | Control Limits | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Set 1 ng/L | expected ng/L | difference | Set 2 ng/L | expected ng/L | difference | Set 3 ng/L | expected ng/L | difference | Set 4 ng/L | expected ng/L | difference | LCL** | UCL** |
| 6-MCV | - | - | - | 95 | 100 | 0.95 | 130 | 120 | 1.08 | 140 | 120 | 1.17 | 0.88 | 1.29 |
| 5-MCV | - | - | - | 96 | 100 | 0.96 | 130 | 130 | 1.00 | 140 | 130 | 1.08 | 0.82 | 1.29 |
| 5,6-DCV | - | - | - | 140 | 180 | 0.78 | 290 | 310 | 0.94 | 320 | 310 | 1.03 | 0.78 | 1.31 |
| 4-MCG | 100 | 100 | 1.00 | 52 | 56 | 0.93 | 140 | 150 | 0.93 | 150 | 150 | 1.00 | 0.81 | 1.13 |
| 5-MCG | 100 | 110 | 0.91 | - | - | - | 110 | 110 | 1.00 | 100 | 110 | 0.91 | 0.78 | 1.08 |
| 6-MCG | 100 | 113 | 0.88 | - | - | - | 99 | 100 | 0.99 | 100 | 100 | 1.00 | 0.82 | 1.09 |
| 4,6-DCG | 50 | 62 | 0.81 | 56 | 120 | 0.47 | 100 | 95 | 1.05 | 130 | 95 | 1.37 | 0.26 | 1.59 |
| 4,5-DCG | 60 | 70 | 0.86 | 88 | 120 | 0.73 | 120 | 120 | 1.00 | 150 | 120 | 1.25 | 0.52 | 1.39 |
| 3,4-DCG | 65 | 85 | 0.76 | 58 | 110 | 0.53 | 130 | 120 | 1.08 | 160 | 120 | 1.33 | 0.39 | 1.53 |
| 3,4,6-TCG | 84 | 91 | 0.92 | 91 | 100 | 0.91 | 130 | 110 | 1.18 | 110 | 110 | 1.00 | 0.73 | 1.28 |
| 3,4,5-TCG | 180 | 190 | 0.95 | 130 | 96 | 1.35 | 240 | 230 | 1.04 | 210 | 230 | 0.91 | 0.6 | 1.32 |
| 4,5,6-TCG | 110 | 113 | 0.97 | 93 | 94 | 0.99 | 150 | 140 | 1.07 | 150 | 140 | 1.07 | 0.91 | 1.16 |
| 4-MCC | 61 | 60 | 1.02 | 25 | 55 | 0.45 | 99 | 110 | 0.90 | 91 | 110 | 0.83 | 0.45 | 1.55 |
| 3-MCC | 100 | 107 | 0.93 | - | - | - | 92 | 110 | 0.84 | 89 | 110 | 0.81 | 0.57 | 1.31 |
| 3,5-DCC | 190 | 150 | 1.27 | - | - | - | 110 | 100 | 1.10 | 110 | 100 | 1.10 | 0.69 | 1.73 |
| 3,4-DCC | 100 | 83 | 1.20 | 96 | 110 | 0.87 | 120 | 110 | 1.09 | 120 | 110 | 1.09 | 0.73 | 1.61 |
| 4,5-DCC | 88 | 67 | 1.31 | 100 | 110 | 0.91 | 100 | 100 | 1.00 | 100 | 100 | 1.00 | 0.69 | 1.79 |
| 3,6-DCC | 110 | 100 | 1.10 | 100 | 110 | 0.91 | 130 | 120 | 1.08 | 150 | 120 | 1.25 | 0.82 | 1.53 |
| 3,4,6-TCC | 150 | 101 | 1.49 | 190 | 200 | 0.95 | 160 | 160 | 1.00 | 140 | 160 | 0.88 | 0.35 | 2.16 |
| 3,4,5-TCC | 240 | 157 | 1.53 | 200 | 200 | 1.00 | 250 | 240 | 1.04 | 260 | 240 | 1.08 | 0.51 | 2.1 |
| TeCC | 59 | 49 | 1.20 | 190 | 190 | 1.00 | 130 | 120 | 1.08 | 130 | 120 | 1.08 | 0.84 | 1.44 |
| 3,5-DCSy | - | - | - | - | - | - | 450 | 430 | 1.05 | 470 | 430 | 1.09 | 0.69 | 1.27 |
| 3,4,5-TCSy | - | - | - | - | - | - | 350 | 340 | 1.03 | 340 | 340 | 1.00 | 0.4 | 1.6 |
| 2-MCShyd | - | - | - | 25 | 90 | 0.28 | 160 | 170 | 0.94 | 170 | 170 | 1.00 | 0.3 | 1.86 |
| 2,6-DCShyd | - | - | - | 69 | 200 | 0.35 | 410 | 430 | 0.95 | 400 | 430 | 0.93 | 0.37 | 1.27 |
| 4-MCp | 74 | 78 | 0.95 | 51 | 52 | 0.98 | 110 | 110 | 1.00 | 110 | 110 | 1.00 | 0.75 | 1.3 |
| 2,6-DCP | 74 | 72 | 1.03 | 86 | 110 | 0.78 | 100 | 96 | 1.04 | 110 | 96 | 1.15 | 0.87 | 1.28 |
| 2,4/2,5-DCP | 140 | 140 | 1.00 | 100 | 110 | 0.91 | 210 | 200 | 1.05 | 210 | 200 | 1.05 | 0.89 | 1.14 |
| 3,5-DCP | 110 | 110 | 1.00 | - | - | - | 110 | 110 | 1.00 | 120 | 110 | 1.09 | 0.84 | 1.27 |
| 2,3-DCP | 30 | 127 | 0.24 | - | - | - | 130 | 130 | 1.00 | 140 | 130 | 1.08 | 0.81 | 1.26 |
| 3,4-DCP | 100 | 97 | 1.03 | - | - | - | 110 | 110 | 1.00 | 100 | 110 | 0.91 | 0.42 | 1.85 |
| 2,4,6-TCP | 34 | 35 | 0.97 | 110 | 120 | 0.92 | 53 | 52 | 1.02 | 54 | 52 | 1.04 | 0.85 | 1.12 |
| 2,3,6-TCP | 79 | 81 | 0.98 | - | - | - | 150 | 150 | 1.00 | 140 | 150 | 0.93 | 0.78 | 1.26 |
| 2,3,5-TCP | 100 | 102 | 0.98 | - | - | - | 94 | 100 | 0.94 | 84 | 100 | 0.84 | 0.56 | 1.48 |
| 2,4,5-TCP | 120 | 127 | 0.94 | 91 | 100 | 0.91 | 160 | 150 | 1.07 | 160 | 150 | 1.07 | 0.79 | 1.18 |
| 2,3,4-TCP | 110 | 123 | 0.89 | - | - | - | 110 | 110 | 1.00 | 100 | 110 | 0.91 | 0.75 | 1.22 |
| 3,4,5-TCP | 79 | 75 | 1.05 | - | - | - | 74 | 80 | 0.93 | 69 | 80 | 0.86 | 0.71 | 1.27 |
| 2,3,5,6-TeCP | 320 | 380 | 0.84 | - | - | - | 370 | 310 | 1.19 | 400 | 310 | 1.29 | 0.42 | 1.54 |
| 2,3,4,6-TeCP | 150 | 170 | 0.88 | 97 | 110 | 0.88 | 260 | 230 | 1.13 | 290 | 230 | 1.26 | 0.57 | 1.42 |
| 2,3,4,5-TeCP | 190 | 190 | 1.00 | - | - | - | 190 | 190 | 1.00 | 190 | 190 | 1.00 | 0.84 | 1.16 |
| PCP | 340 | 357 | 0.95 | 170 | 170 | 1.00 | 470 | 450 | 1.04 | 460 | 450 | 1.02 | 0.84 | 1.12 |
| 12/14-CDHA | 860 | 790 | 1.09 | 420 | 400 | 1.05 | 360 | 400 | 0.90 | 4000 | 4000 | 1.00 | - | |
| 12,14-DCDHA | 1300 | 1200 | 1.08 | 480 | 580 | 0.83 | 330 | 580 | 0.57 | 3200 | 5800 | 0.55 | - | |

**Effluent Samples**

**Set 1**

| Samples |
|---|
| Dec28/94 |
| Jan11/95 |
| Jan16/95 |
| Jan22/95 |
| Jan30/95 |

**Set 2**

| Samples |
|---|
| Jan15/96 |
| Jan22/96 |
| Jan24/96 |

**Set 3**

| Samples |
|---|
| Jan29/96 |
| Feb05/96 |

**Set 4**

| Samples |
|---|
| Feb19/96 |
| Feb26/96 |
| Mar04/96 |
| Mar11/96 |
| Mar16/96 |