FRASER RIVER ACTION PLAN

The Effects Of Bleached Kraft Pulp-Mill Effluent On Periphyton Tissue

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Environment Canada Environnement Canada

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1.0 INTRODUCTION

1.1 BACKGROUND

The Fraser River Action Plan (FRAP) calls for research on environmental quality within the Fraser River Basin. An important component of the FRAP is the investigation of potential impacts of pulp mill effluents (PME) and treated sewage discharged to the river. To this end, a research team, headed by Dr. Joseph Culp and based within the Federal Department of the Environment, National Hydrology Research Institute (NHRI) in Saskatoon, is coordinating a FRAP research program designed to assess the environmental effects of these effluents on benthic communities through analysis of long-term data sets, field measurements, and controlled experiments. The specific objectives assigned to the NHRI research group are: (1) to identify those components of the benthic community most exposed to effluents, (2) to quantify the effects of effluents on the aquatic food web, and (3) to establish effective criteria/indicators for assessing cumulative effects of effluent exposure.

This report addresses the first two of these general objectives by assessing the response of periphyton (benthic algae) exposed to varying concentrations of PME. The endpoints used to assess this response include measurements of total biomass, changes in periphyton community structure and concentrations of PME contaminants in periphyton tissue. The results presented here form one component of a larger research project using artificial streams to investigate the effects of PME on the aquatic ecosystem (Culp *et al*. 1996). The results of this larger research project, in combination with studies in the Fraser River itself, will be used to develop criteria and biological indicators that can be used in assessing the cumulative effects of effluent exposure (i.e., objective 3, above).

1.2 RATIONAL AND OBJECTIVES

The periphyton community forms the base of the aquatic food web and not only constitutes a key ecosystem component but also represents a major pathway by which energy, and in some cases contaminants, are transmitted to other trophic levels within the system. Because of its ecological role and its sensitivity to pollution, periphyton has been proposed as a useful measurement parameter in assessing and monitoring the state of the aquatic ecosystem (Sgro and Johansen 1995; Culp *et al*. 1996). Several studies have documented changes in periphyton community structure in response to PME exposure and various environmental stresses (Carrick *et al*. 1988; Amblard *et al*. 1990; Snoeijs 1991; ten Cate *et al*. 1993; Sudhakar *et al*. 1994; Culp and Podemski 1996; Podemski and Culp 1996), but there is a lack of information on the concentration of specific contaminants in periphyton tissue exposed to PME and the effects of these contaminants on the survival, composition and growth of periphyton communities. The purpose of this experiment was to use an artificial stream system to quantify the effect of PME on periphyton biomass and community structure and to compare contaminant concentrations measured in periphyton tissue exposed to a variety of PME concentrations.

As discussed elsewhere (Culp *et al*. 1996), the use of artificial streams allows for direct and statistically rigorous comparisons of PME effects under environmentally realistic conditions (i.e. ambient light, temperature, etc.). The ability to test specific hypotheses regarding contaminant concentrations and ecological effects in biota will contribute to our understanding of the ecological consequence of PME exposure and will compliment basin-wide surveys of contaminants in other media including, suspended sediments, bed sediments and water (e.g., Sekela *et al*. 1995).

It is important to note that this experiment focused on contaminant concentrations and ecological response in primary producers (chiefly diatoms). Contaminant concentrations in biota from higher trophic levels (e.g., macroinvertebrates, fish) could be higher as a consequence of food web biomagnification. Furthermore, these experiments involved a relatively short exposure (42 days)

of organisms with a short life cycle (days-weeks). Although tissue concentrations of contaminants in some macroinvertebrates such as mayflies (Drouillard *et al*. 1996) and mussels (Burggraaf *et al*. 1996) reached equilibrium levels within 35 days, larger and longer lived organisms (e.g., large fish, aquatic mammals) exposed to environmentally persistent contaminants may experience greater bioaccumulation.

The value of this experimental approach lies in its ability to quantitatively demonstrate the effects of PME on periphyton as measured by growth response, community composition and contaminant levels. This approach could also be used to determine the consequence of changes in the quality or quantity of PME discharged to the river and, in conjunction with similar data from water and suspended sediment samples, will provide insight into the distribution and fate of contaminants within the ecosystem. Most importantly, these experiments explore a major pathway by which contaminants enter the aquatic food web.

2.0 METHODS

2.1 ARTIFICIAL STREAM FACILITY

The artificial stream system consisted of 16 circular tanks placed on two flat deck trailers. The trailers were located beside the Fraser River at the Northwood Pulp and Timber Ltd. site, immediately upstream of Prince George, British Columbia. River water was collected upstream of the mill discharge and was pumped into a head tank reservoir and then gravity-fed to the stream tanks through a system of pipes. Water flow to individual streams was controlled to provide a volume of 250 l and a water depth of approximately 50 cm. Water levels in the streams were maintained by an overflow drain. Current velocity was provided by a belt-driven propeller that could produce mid-water velocities exceeding 20 cm/sec. Pulp mill effluent was pumped from a common reservoir and through a set of peristaltic pumps allowing for precise control over the amounts of PME delivered to each tank.

Large stones were collected from the river, upstream of the pulp-mill discharge and ten such stones, complete with their periphyton community, were randomly assigned to each stream. The periphyton community was allowed to develop in the absence of PME for the next ten days, after which, macroinvertebrates and PME were added to the streams. Results discussed here constitute one part of a larger, 42-day, artificial stream experiment conducted in the fall of 1994. This experiment was designed to examine the effects of various dilutions of PME (0%, 1%, and 3%) on benthic food webs. The PME dilutions were chosen so as to represent the range of variation apparent in the Fraser River, upstream and downstream of Prince George. The experimental design and setup is described in more detail in Culp and Cash (1995).

2.2 PERIPHYTON BIOMASS, COMMUNITY STRUCTURE, AND CONTAMINANT CONCENTRATION

Benthic biofilm growing on unglazed porcelain tiles placed in each stream, were sampled every five days by using a scalpel to remove periphyton from the tile surface within a 9.6 cm^2 template. Periphyton samples were placed in vials and held on ice until they could be frozen later the same day. All samples were analyzed for chlorophyll a (CHL*a*) and ash free dry mass (AFDM) content. One rock from each stream was sampled in this manner at the end of the experiment in order to measure periphyton community structure. These samples were preserved in Lugol's solution and the periphyton community was later identified and enumerated under a microscope.

To assess PME contaminant concentrations in periphyton tissue, periphyton growing on the sides of the streams were sampled at the end of the experiment. In all, samples were collected from ten of the artificial streams (n = 3 for 0% and 1% streams; n = 4 for 3% streams); each of these samples was then analyzed for a variety of contaminants including (1) resin and fatty acids, (2) chlorinated phenolics, (3) polycyclic aromatic hydrocarbons (PAHs), and (4) polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF).

Sampling equipment was made of glass, stainless steel, or teflon. All sampling equipment was first washed with tap water and detergent and then rinsed in deionized water, acetone and finally hexane, before being air dried. The sampling equipment was wrapped in heat treated aluminum foil until used. Once collected, all periphyton samples were stored on dry ice until they could be transferred to a -40^{0}C freezer. All contaminant analyses were performed by AXYS Analytical Services Ltd. of Sidney, British Columbia. Details of all analytical methods used are given in Appendix 1.

The results of contaminant analyses are summarized throughout the text and provided in detail in Appendix 2. Differences among treatment levels were analyzed using a one-way ANOVA. Multiple comparisons of means were performed using Tukey's pairwise comparisons. In all analyses, a value equal to one half the detection limit was used when a contaminant concentration was below the detection limit.

3.0 RESULTS

3.1 BIOMASS

The results of the fall, 1994 CHL *a* analyses are presented in Figure 1. There was a general tendency for CHL *a* levels to increase over the course of the experiment regardless of treatment level. By the end of the experiment CHL *a* levels differed significantly among treatment levels ($F_{2,12} = 4.59$, $P < 0.05$) and were significantly lower in the control streams than in either of the PME additions. Chlorophyll *a* levels within the two levels of PME addition did not differ significantly by the end of the experiment (Figure 1).

The pattern resulting from the analysis of AFDM closely parallels that observed for CHL *a*. As was the case with CHL *a*, there was an overall tendency for AFDM levels to increase over the course of the experiment. In addition, values in control streams were significantly lower than that

observed in streams receiving 1% or 3% PME by the end of the experiment ($F_{2,12} = 17.59$, $P < 0.005$, Figure 2). Mean values of AFDM in the 1% and 3% treatment levels did not differ significantly at the end of the experiment.

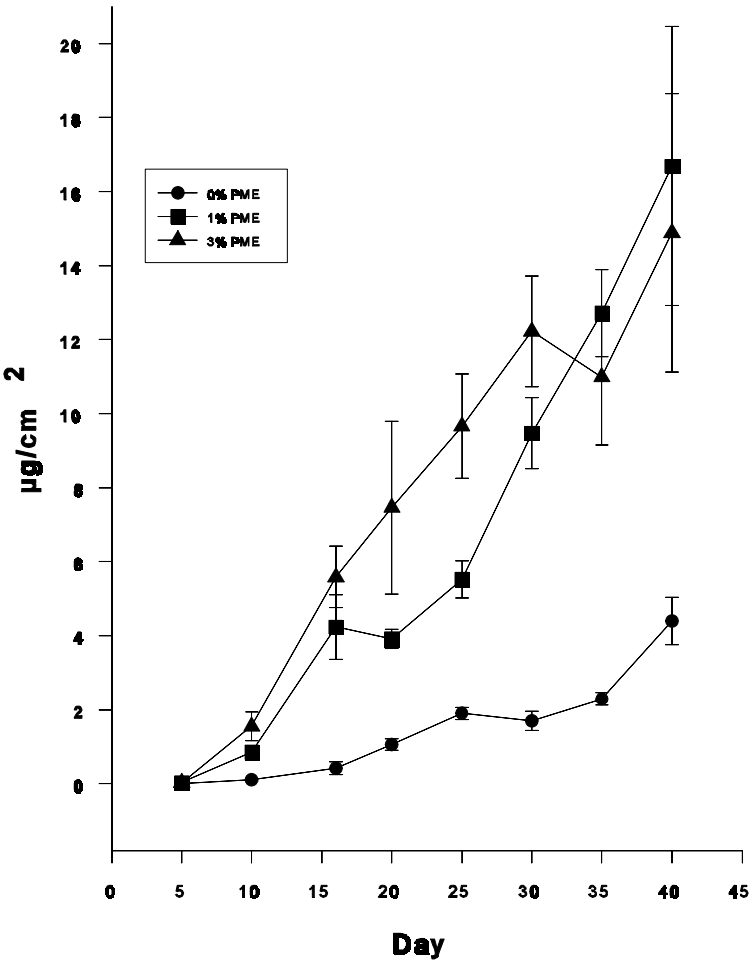

Figure 1. Mean chlorophyll *a* content (±SE) of algal samples collected from tiles within mesocosm tanks.

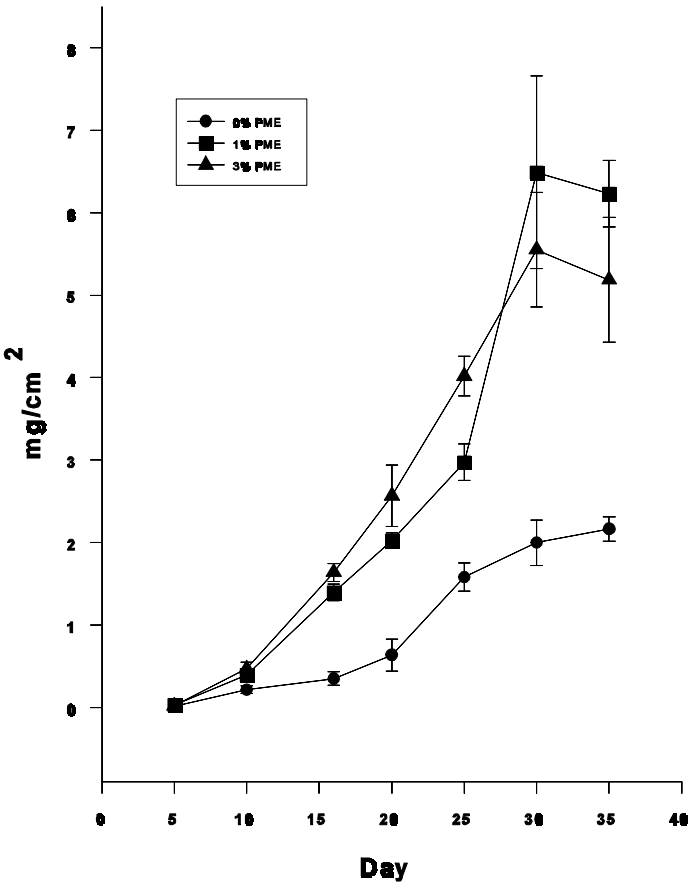

Figure 2. Mean ash free dry mass (±SE) of algal samples collected from tiles within mesocosm tanks.

3.2 COMMUNITY STRUCTURE

A total of 31 individual periphyton taxa were identified in samples collected from each tank at the end of the experiment (Table 1). Identified taxa included representatives from Cyanophyta (blue-

Table 1. Periphyton community collected from rocks in mesocosm facility, October, 1994.

Division	Species	0%	1%	3%
		Cells x $10^6/m^2$		
Cyanophyta	Oscillatoria sp. (mm)	0.0±0.0	1.5±0.8	0.0±0.0
Chlorophyta	Cladophora sp. (mm)	0.0±0.0	0.0±0.0	0.6±0.5
	Mougeotia sp. (mm)	0.0±0.0	0.7±0.6	1.6±0.6
	Scenedesmus sp.	1.5±1.3	0.0±0.0	0.0±0.0
	Spirogyra sp. (mm)	0.0±0.0	0.9±0.5	0.0±0.0
Chrysophyta	Achnanthes flexella	0.7±0.7	0.0±0.0	0.0±0.0
(Diatoms)	Achnanthes minutissima	93.4±16.9	126.8±27.9	60.5±16.3
	Achnanthes sp.	21.0±5.6	14.4±4.1	17.1±5.4
	Amphipleura pellucida	12.2±2.2	94.2±21.7	41.2±4.5
	Cocconeis placentula	0.4±0.3	0.0±0.0	0.0±0.0
	Cymatopleura solea	0.3±0.3	0.6±0.5	0.6±0.5
	Cymbella caespitosa	3.1±1.1	1.7±1.0	1.1±1.0
	Cymbella cistula	0.0±0.0	0.6±0.5	0.0±0.0
	Cymbella ventricosa	12.2±2.5	18.6±5.3	22.3±9.1
	Diatoma tenue	8.5±1.2	12.7±5.3	6.5±1.6
	Epithemia sorex	0.4±0.3	0.0±0.0	0.0±0.0
	Fragilaria capucina	2.2±2.0	7.4±4.1	0.0±0.0
	Fragilaria crotonensis	21.1±8.5	6.7±6.0	11.7±9.7
	Fragilaria sp.	200.1±15.9	239.0±38.4	174.3±19.0
	Fragilaria vaucheriae	21.2±9.6	427.1±241.1	305.1±154.6
	Frustulia rhomboides	0.3±0.3	0.0±0.0	0.0±0.0
	Gomphonema intricatum	0.0±0.0	1.1±1.0	2.0±0.9
	Gomphonema olivaceum	14.6±4.2	20.1±3.1	23.4±4.1
	Hannaea arcus	7.2±2.0	13.7±2.3	9.0±4.1
	Melosira varians	0.0±0.0	232.2±38.6	539.8±61.4
	Navicula sp.	3.2±1.0	1.7±1.0	4.7±1.7
	Nitzschia acicularis	0.7±0.7	4.9±2.0	0.0±0.0
	Nitzschia palea	24.8±2.9	75.3±14.4	65.7±15.6
	Stauroneis phoenicenton	0.4±0.3	0.6±0.5	0.0±0.0
	Synedra ulna	19.2±2.9	41.3±8.4	37.9±8.
	Tabellaria flocculosa	0.5±0.4	0.0±0.0	0.0 ±0.0

green algae), Chlorophyta (green algae) and Chrysophyta (diatoms). Of these three groups, diatoms were clearly the most important and dominated the periphyton community at all treatment levels. Diatoms were not only the most numerically abundant group within the periphyton community, but also accounted for 26 of the 3 1 identified taxa (i.e., 83.9%). Consistent with the CHL *a* and AFDM analyses described above, total cell densities at the end of the experiment were significantly higher in the 1% treatment level ($\bar{x}$ = 1341 ± 243 cells x$10^6/m^2$) and 3% PME ($\bar{x}$ = 1323 ± 255 cells x $10^6/m^2$) additions than in the 0% treatment level ($\bar{x}$ = 469 ± 45 cells x $10^6/m^2$, one-way ANOVA, $F_{2,12}$ = 5.88, $P < 0.05$). Total cell densities did not differ signifkantly between the 1% and 3% treatment levels.

In addition to changes in the amount of periphyton present, periphyton community structure also changed following the addition of PME. More specifically, the dominant taxa tended to change as a function of PME concentration (Figure 3). Changes in community structure were also

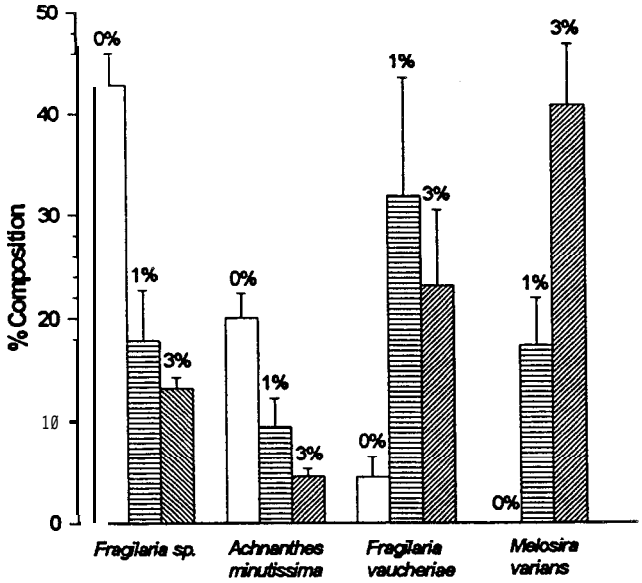

Figure 3. Mean percent composition (±SE) of periphyton taxa in artificial streams. Values above bars indicate PME dilution.

investigated using multivariate techniques (i.e., Principal Component Analysis, or PCA). The results of PCA are given in Figures 3 and 4 and indicate that PME effects, not only the amount of periphyton present, but also the nature of the community itself.

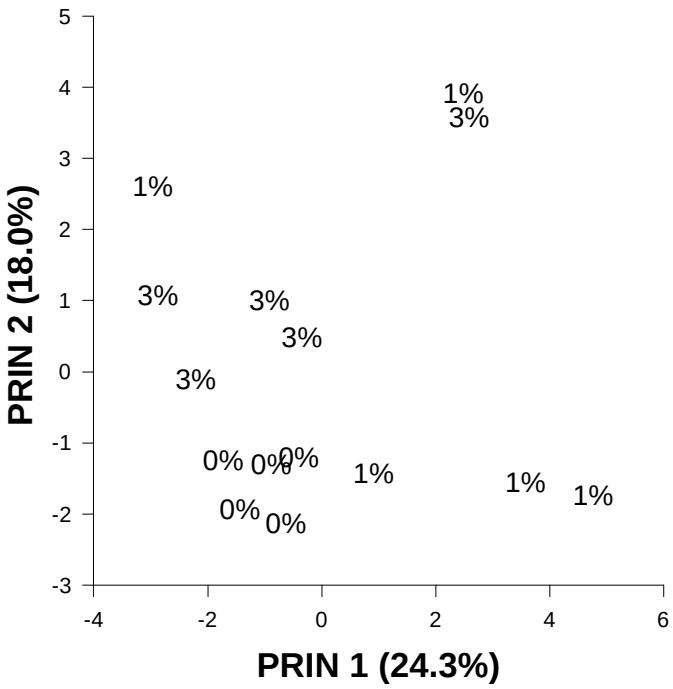

Figure 4. PCA results on periphyton community structure within artificial streams (0% = 0%PME, 1% = 1%PME, 3% = 3% PME).

Taken together, the first three principal component axes account for 57.3% of the total variation observed in periphyton community structure within the mesocosm facility. Each of the three axes represent a shift in the relative importance of certain taxa within the community. For example, the first principal component axis accounts for 24.3% of the total variation and largely represents a shift from a community with relatively lower levels of such taxa as *Achnathes minutissima, Nitzchia palea* and *Spirogyra sp.* and higher levels of *Comphonema intricatum, Cymbella*

caespitosa and *Mougeotia sp.* along the lower end of the axis, toward the reverse situation along the opposite end of the axis. Those communities positioned close to one another along this axis are considered to be similar to one another, at least with respect to the taxa represented by this axis. Those communities that are positioned further from one another are considered to be more different**.**

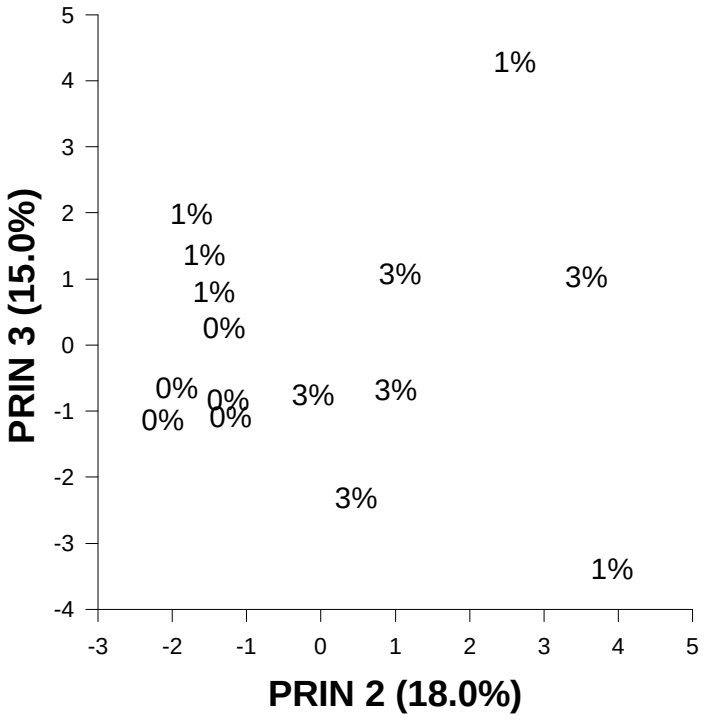

Figure 5. PCA results on periphyton community structure within artificial streams (0% = 0%PME, 1% = 1%PME, 3% = 3% PME).

Thus, results of the PCA indicate that while control communities do not differ greatly from one another, they do differ from those communities exposed to PME treatment (Figures 3,4). It is important to note that the observed shifts within the periphyton community represents shifts among different types of diatoms rather than shifts from a diatom dominated community toward

one dominated by other taxa such as green algae. The ecological consequences of these observed shifts in community structure await further investigation.

3.3 CONTAMINANT CONCENTRATIONS

3.3.1 Resin Acids

Resin acids are naturally occurring breakdown products of wood that may be found in relatively high concentrations in PME and are known to be toxic to biota (McLeay *et al*. 1986). Recent improvements in pulp-mill technologies are believed to have resulted in decreased levels of resin acids in PME, particularly chlorinated resin acids. However, these compounds are still detected in water and suspended sediments downstream of Prince George (Sekela *et al*. 1995).

Although eleven different resin acids were identified in the periphyton samples (Table 2), dehydroabietic and abietic acids dominated in all samples. Pimaric acid was also common at the 1% and 3% treatment levels. Total concentrations of resin acids in periphyton were significantly affected by effluent level ($F_{2,7} = 26.8$, $P < 0.001$) and ranged from a low of 92.4 ng/g in 0% streams to a high of 5045.7 ng/g in 3% streams. Resin acid concentrations in the 3% streams were significantly higher than that observed in the 0% or 1% streams. Concentrations did not differ significantly between 0% and 1% treatment levels (Table 2).

The general pattern observed for total resin acids was reflected in measured levels of dehydroabietic, abietic and pimaric acids. In each case, acid concentrations rose from 200 to 1000 fold with increasing effluent addition; and while contaminant levels in 0% and 1% PME dilutions did not differ, both were significantly lower than that observed in the 3% PME dilution. Resin acid concentrations in periphyton exposed to PME were one to two orders of magnitude lower than that observed in suspended sediment samples collected downstream of Prince George at Marguerite (Sekela *et al*. 1995).

Table 2: Mean (± SE) concentrations of resin acids (ng/g) in periphyton exposed to different dilutions of PME (for each compound, means with the same superscript are not significantly different from one another).

	PME Dilution		
	0%	**1%**	**3%**
Pimaric	$1.2^{a} \pm 0.6$	$236.7^{a} \pm 19.1$	$1067.5^{b} \pm 131.9$
Sandraracopimaric	$11.67^{a} \pm 2.23$	$13^{a} \pm 1.4$	$60.8^{b} \pm 5.0$
Isopimaric	$5.2^{a} \pm 0.6$	$210^{a} \pm 17.0$	$847.5^{b} \pm 110.5$
Palustric	$3.7^{a} \pm 1.0$	$7.7^{a} \pm 2.4$	$31^{b} \pm 3.2$
Dehydroisopimaric	$1.9^{a} \pm 0.3$	$27.3^{a} \pm 1.4$	$119.8^{b} \pm 18.2$
Dehydroabietic	$56.3^{a} \pm 30.1$	$283.3^{a} \pm 22.3$	$1092.5^{b} \pm 142.4$
Abietic	$5.9^{a} \pm 1.3$	$423.3^{a} \pm 29.9$	$1700^{b} \pm 196.9$
Neoabietic	$5.0^{a} \pm 1.2$	$8.2^{a} \pm 0.9$	$33.8^{b} \pm 4.3$
12/14 Chlorodehydroabietic	$0.4^{a} \pm 0.0$	$16.3^{a} \pm 1.8$	$73.5^{b} \pm 11.8$
12, 14 Dichlorodehydroabietic	$1.2^{a} \pm 0.2$	$3.5^{a} \pm 0.3$	$19.5^{b} \pm 3.3$
Total Resin Acids	$92.5^{a} \pm 27.2$	$1229.4^{a} \pm 91.7$	$5045.8^{b} \pm 622.9$

Neither the British Columbia Ministry of Environment Lands and Parks (BCMELP), nor the Canadian Council of Resource and Environment Ministers (CCREM) have developed guidelines or criteria for resin acid concentrations in the tissue of freshwater biota (CCREM 1987, BCMELP 1994). However concentrations of dehydroabietic and total resin acids measured in the water column downstream of Prince George were well below BCMELP guidelines (Sekela *et al.* 1995). In addition, dehydroabietic, abietic, pimaric, isopimaric and total resin acids in periphyton exposed to the 3% dilution of PME were similar to that measured in freshwater mussels exposed to PME for 28 days (Burggraaf *et al*. 1996). In that experiment, measured levels of resin acids did not cause mussel mortality, either in the 28 day exposure period or in the 21 day post-exposure period. These findings suggest that tissue concentrations of resin acids measured in this experiment do not pose a direct mortality risk to periphyton or other aquatic biota.

3.3.2 Fatty Acids

Like resin acids, fatty acids are naturally occurring breakdown products of wood and are a common component of PME. Although concentrations of fatty acids in PME are high, relative to resin acids, these compounds tend to be less toxic (Poole *et al*. 1978; McLeary 1987). As with resin acids, neither the BCMELP nor the CCREM have developed guidelines or criteria for fatty acids in the tissues of freshwater biota (CCREM 1987, BCMELP 1994).

Eleven different fatty acids were identified in the periphyton samples (Table 3). In all periphyton samples, the fatty acids were composed primarily of myristic, palmitic and linolenic acids.

Table 3: Mean (± SE) concentrations of fatty acids (ng/g) in periphyton exposed to different dilutions of PME (for each compound, means with the same superscript are not significantly different from one another).

	PME Dilution		
	0%	**1%**	**3%**
Capric	$53^{a} \pm 3$	$51^{a} \pm 6$	$66^{a} \pm 6$
Lauric	$128^{a} \pm 14$	$133^{a} \pm 7$	$218^{b} \pm 17$
Myristic	$13633^{a} \pm 1680$	$19333^{a,b} \pm 272$	$25250^{b} \pm 2678$
Palmitic	$32333^{a} \pm 4722$	$38000^{a} \pm 943$	$44750^{a} \pm 4628$
Linolenic	$25333^{a} \pm 2842$	$46333^{a} \pm 5423$	$33000^{a} \pm 3373$
Linoleic	$7966^{a} \pm 844$	$9767^{a} \pm 546$	$7725^{a} \pm 715$
Oleic	$10566^{a} \pm 2350$	$6333^{a} \pm 357$	$6775^{a} \pm 422$
Stearic	$953^{a} \pm 148$	$1340^{a} \pm 93$	$5575^{a} \pm 3590$
Arachidic	$223^{a,b} \pm 14$	$190^{a} \pm 5$	$332^{b} \pm 32$
Behenic	$407^{a} \pm 17$	$907^{b} \pm 55$	$1575^{c} \pm 129$
Lignoceric	$750^{a} \pm 61$	$983^{a} \pm 49$	$1575^{b} \pm 114$
Total Fatty Acids	$92348^{a} \pm 12508$	$123370^{a} \pm 6873$	$126841^{a} \pm 13960$

Observed concentrations of palmitic and linolenic acids and of total fatty acids did not vary significantly as a function of PME addition. Concentrations of myristic acid did rise significantly with increasing PME concentration ($F_{2,7} = 5.8$, $P < 0.05$), however, mean concentrations differed significantly only between the 0% ($\bar{x}$ = 13633 ± 1680 ng/g) and 3% ($\bar{x}$ = 25250 ± 2678 ng/g) treatment levels.

Although relevant guidelines for fatty acids in biota do not exist, results of this experiment indicate that (with the possible exception of myristic acid) concentrations of fatty acids in periphyton do not change significantly as a result of PME addition. Fatty acid levels in periphyton exposed to PME were about half that measured in suspended sediments collected downstream of Prince George (Sekela *et al*. 1995). Fatty acid concentrations in water collected downstream of Prince George were considerably lower than that required to produce either mortality or sub-lethal effects in rainbow trout (Sekela *et al.* 1995).

3.3.3 Chlorinated Phenolics

Chlorinated phenolics are a family of compounds comprised of three main classes, phenols, guaiacols and catechols. These compounds are commonly associated with a variety of industrial activities and while recent changes in pulp mill technology (i.e., progress toward chlorine substitution) have dramatically reduced their levels in PME, they continue to be detected in benthos and sediment downstream of pulp mills. In addition to their potential toxicological effects, chlorinated phenolics have also been associated with tainting (taste and odour problems) in fish and drinking water downstream of bleached kraft pulp-mills (Cash *et al* 1996).

The toxicity of chlorinated phenolics varies considerably but is generally a function of the degree of chlorine substitution (Crosley 1995). For this reason the 43 diierent chlorinated phenolics identified in the periphyton (see Appendix 2) were summarized and analyzed as a function of the degree of chlorine substitution and by general class (Table 4).

Table 4: Mean (± SE) concentrations of chlorinated phenolics (ng/g) in periphyton exposed to different dilutions of PME (for each compound, means with the same superscript are not significantly different from one another).

	PME Dilution		
	0%	**1%**	**3%**
Total Chloro - Phenols	$0.68^{a} \pm 0.04$	$0.98^{a} \pm 0.14$	$0.91^{a} \pm 0.10$
Total Chloro - Guaiacols	$0.25^{a} \pm 0.05$	$0.64^{a} \pm 0.14$	$0.54^{a} \pm 0.03$
Total Chloro - Catechols	$0.51^{a} \pm 0.10$	$1.11^{a} \pm 0.03$	$2.45^{b} \pm 0.21$
Total Mono - Chlorinated Phenolics	$0.68^{a} \pm 0.12$	$3.22^{b} \pm 0.11$	$4.34^{c} \pm 0.23$
Total Di - Chlorinated Phenolics	$0.78^{a} \pm 0.10$	$1.43^{a,b} \pm 0.13$	$1.87^{b} \pm 0.20$
Total Tri-- - Chlorinated Phenolics	$0.20^{a} \pm 0.01$	$0.32^{a} \pm 0.01$	$0.66^{b} \pm 0.05$
Total Tetra - Chlorinated Phenolics	$0.10^{a} \pm 0.00$	$0.24^{b} \pm 0.04$	$0.33^{b} \pm 0.02$
Pentachlorophenol	$0.02^{a} \pm 0.00$	$0.02^{a} \pm 0.00$	$0.02^{a} \pm 0.00$
Total Chlorinated Phenolics	$1.79^{a} \pm 0.16$	$5.25^{b} \pm 0.26$	$7.23^{c} \pm 0.44$

In general, concentrations of chlorinated phenolics tended to increase with increasing levels of PME, however, statistical analyses were complicated by the large number of non-detection values (see Appendix 2). As discussed above, a value equal to 50% of the detection limit was used in those cases where the contaminant could not be detected. A technique such as this is unlikely to bias the analysis if the number of non-detects is low but the risk of bias increases with increasing frequency of non-detects. The analyses of chlorinated phenolics given below should thus be viewed with caution and in light of the fact that all concentrations, regardless of treatment level were low.

The concentration of total chlorinated phenolics was significantly affected by the addition of PME ($F_{2,7} = 62$, $P < 0.001$) and ranged from a low of 1.8 ng/g in 0% streams to a high of 7.2 ng/g in 3% streams. Mean concentrations of total chlorinated phenolics varied significantly among all

treatment levels. This pattern of increasing concentrations of chlorinated phenolics in periphyton with increasing concentrations of PME was also apparent when mono-, di-, tri-- and tetra-chlorinated phenolics and total catechols were considered separately. However, measured concentrations of total phenols and total guaiacols were not significantly affected by the addition of PME (Table 4). Concentrations of pentachlorophenol were below the detection limit in all ten samples.

Current BCMELP guidelines for chlorophenols in biota are limited to flavour impairment criteria for fish muscle tissue (BCMELP 1994). However, observed concentrations of chlorinated phenolics in periphyton samples are generally three to four orders of magnitude below these guidelines and one order of magnitude below that measured in suspended sediments downstream of Prince George (Sekela *et al*. 1995). Similarly, measured levels of pentachlorophenol and 2,3,4,6-tetrachlorophenol were below detection in all samples (Appendix 2) and at least four orders of magnitude below the pentachlorophenol concentration in fish tissue that is thought to pose a cancer risk to piscivorous (fish-eating) wildlife (Haines *et al*. 1994). These findings suggest that current levels of these contaminants in PME do not represent a direct toxicological threat to periphyton. Extrapolation from measured levels in periphyton to predicted levels in fish tissue is beyond the scope of this study.

3.3.4 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are produced by both natural (forest fires, biosynthesis) and industrial (pulp mill) processes. Higher molecular weight (4-7 rings) PAHs such as chrysene, benzo(*a*)pyrene, benzofluoranthene, and ideno(1,2,3-cd)pyrene are known to be carcinogenic, while lower molecular weight (2-3 ring) PAHs such as naphthalene, fluorene, phenanthrene and anthracene can be acutely toxic to aquatic organisms (Canadian Environmental Protection ACT (CEPA) 1994).

Measures of total PAHs in periphyton samples indicated that levels in the 1% ($\bar{x}$ = 17.1 ± 0.7 ng/g) treatment level were significantly lower ($F_{2,7}$= 7.8, $P < 0.05$) than that observed in the 3% treatment level ($\bar{x}$ = 26.6 ± 1.5 ng/g). Interestingly, observed levels in the 0% treatment level ($\bar{x}$ = 20.1 ± 1.9 ng/g) did not differ significantly from that in the 1% or 3% other treatment levels (Table 5).

Among the lower weight PAHs, contaminant concentrations did not differ as a function of PME for naphthalene, acenaphthylene, or acenapthene. However, in the case of fluorene, phenanthrene, anthracene, fluoranthene and pyrene concentrations in the 3% treatment level were significantly higher than that in either of the other levels. Measured concentrations did not differ significantly between streams supplied with 0% and 1% PME.

Of the higher weight PAHs only chrysene concentrations differed as a result of PME addition. This effect was limited to the 3% treatment level, which resulted in concentrations significantly higher ($F_{2,7}$ = 8.9, $P < 0.05$) than that in the 0% or 1% treatment levels

In summary, only six of 17 PAHs measured in periphyton tissues varied significantly with PME addition. Of those that did respond to PME, significant differences were confined to higher concentrations at the 3% dilution. PAH concentrations at the 0% and 1% levels did not differ significantly for any of the compounds tested. Although guidelines do not exist for PAH concentrations in the tissues of aquatic biota, periphyton concentrations of all PAHs measured at all PME dilutions were below those measured in suspended sediments collected downstream of Prince George (Sekela *et al.* 1995). None of the suspended sediment samples (corrected for carbon content) exceeded the BCMELP interim bed sediment quality criteria (Sekela *et al.* 1995).

Table 5: Mean (± SE) concentrations of polycyclic aromatic hydrocarbons (PAHs) (ng/g) in periphyton exposed to different dilutions of PME (for each compound, means with the same superscript are not significantly different from one another).

	PME Dilution		
	0%	**1%**	**3%**
Naphthalene	$2.07^{a} \pm 0.10$	$1.90^{a} \pm 0.05$	$2.37^{a} \pm 0.19$
Acenaphthylene	$0.16^{a} \pm 0.02$	$0.13^{a} \pm 0.01$	$0.17^{a} \pm 0.02$
Acenaphthene	$0.31^{a} \pm 0.05$	$0.22^{a} \pm 0.05$	$0.38^{a} \pm 0.02$
Fluorene	$0.40^{a,b} \pm 0.01$	$0.33^{b} \pm 0.03$	$0.56^{a} \pm 0.05$
Phenanthrene	$3.83^{a} \pm 0.31$	$3.50^{a} \pm 0.05$	$5.65^{b} \pm 0.38$
Anthracene	$0.22^{a} \pm 0.03$	$0.39^{a} \pm 0.06$	$0.91^{b} \pm 0.12$
Fluoranthene	$2.4^{a} \pm 0.17$	$2.57^{a} \pm 0.07$	$4.82^{b} \pm 0.24$
Pyrene	$1.4^{a} \pm 0.08$	$1.27^{a} \pm 0.14$	$2.70^{b} \pm 0.30$
Benz(a)anthracene	$0.23^{a} \pm 0.09$	$0.37^{a} \pm 0.01$	$0.73^{b} \pm 0.07$
Chrysene	$0.84^{a} \pm 0.07$	$0.95^{a} \pm 0.06$	$1.35^{b} \pm 0.09$
Benzofluoranthenes	$1.05^{a} \pm 0.36$	$0.60^{a} \pm 0.05$	$0.98^{a} \pm 0.05$
Benzo(e)pyrene	$0.63^{a} \pm 0.18$	$0.38^{a} \pm 0.05$	$0.61^{a} \pm 0.04$
Benzo(a)pyrene	$0.24^{a} \pm 0.18$	$0.12^{a} \pm 0.06$	$0.27^{a} \pm 0.07$
Perylene	$4.83^{a} \pm 0.27$	$3.80^{a} \pm 0.19$	$4.05^{a} \pm 0.30$
Dibenz(ah)anthracene	$0.60^{a} \pm 0.29$	$0.14^{a} \pm 0.00$	$0.24^{a} \pm 0.04$
Indeno(1,2,3-cd)pyrene	$0.32^{a} \pm 0.22$	$0.12^{a} \pm 0.00$	$0.16^{a} \pm 0.02$
Benzo(ghi)perylene	$0.59^{a} \pm 0.17$	$0.30^{a} \pm 0.09$	$0.63^{a} \pm 0.04$
Total PAHs	$20.13^{a,b} \pm 1.90$	$17.08^{b} \pm 0.70$	$26.59^{a} \pm 1.54$

3.3.5 Dioxins and Furans

Dioxins and furans are produced by a variety of industrial processes and historically, have been closely identified with pulp and paper production. These compounds are known to be environmentally persistent, have a high potential for bio-accumulation and are highly toxic. In recent years, changes in pulp-mill technology (i.e., progress towards complete chlorine substitution in kraft bleach pulp-mills) have reduced greatly environmental concentrations of these contaminants in both sediments and biota (Muir and Pastershank 1996). However, primary dioxin/furan congeners including 2,3,7,8-T_4CDD and 2,3,7,8-T_4CDF continue to be detected in measurable quantities in biota and sediments collected downstream of pulp-mills in British Columbia (Sekela *et al*. 1995) and in other regions of Canada (Carey *et al*. 1996; Wrona *et al*. 1996).

Analysis of dioxin/furan concentrations in periphyton samples indicated extremely low levels of these contaminants. Concentrations of 2,3,7,8-T_4CDD fell below the detection limit in all ten samples while concentrations of 2,3,7,8-T_4CDF exceeded the detection limit only in the four 3% streams and in one of the 1% streams. For these reasons, periphyton concentrations of these contaminants could not be analyzed statistically.

Although statistical analyses were not performed it should be noted that 2,3,7,8 - TCDD Toxic Equivilants (TEQs) did not change as a result of PME addition and varied between 0.1 and 0.3 pg/g, depending on the treatment of values below the detection limit. The draft Canadian Environmental Quality Guidelines for TCDD TEQs in tissues of freshwater biota is 1.1 pg/g (Environment Canada 1995), well above any of the values measured in this experiment, indicating that the concentrations of dioxins/furans in this experiment did not pose a significant toxicological risk to the periphyton community.

4.0 DISCUSSION

This study is the first to examine biomass and community responses of periphyton exposed to PME while simultaneously quantifying concentrations of common PME contaminants in the periphyton tissue. Such an experiment was made possible through the use of an artificial stream system in which exposure to PME can be accurately and precisely controlled. The results of the artificial stream experiments clearly indicate that the most pronounced impact of PME on the periphyton community was that of nutrient enrichment and subsequent increases in primary production. There was little evidence of any direct contaminant effects of PME on the periphyton community.

Total periphyton biomass, as measured by chlorophyll *a* (CHL *a*) and periphyton ash free dry mass (AFDM), increased over the course of the experiment regardless of treatment level and by the end of the experiment was four to six fold higher in the 1% and 3% streams, relative to the 0% streams. Diatoms clearly dominated the periphyton community at all treatment levels. Diatoms were not only the most numerically abundant group within the periphyton community, but also accounted for 84% of identified taxa (i.e., 83.9%). Observed shifts within the periphyton community represented changes in relative densities among different types of diatoms rather than shifts from a diatom dominated community toward one dominated by other taxa such as green algae.

As illustrated in the previous section of this report, measured concentrations of PME contaminants were generally low in periphyton tissue. Dioxin and furan levels in periphyton were below detection levels in all samples and tissue concentrations of fatty acids did not vary significantly with PME addition. Concentrations of total resin acids and total chlorinated phenolics did vary with treatment level but the differences were only apparent in a minority of individual compounds within each contaminant group and were largely restricted to mean differences between the 0% and 3% treatment levels. Concentrations of total PAHs also varied significantly across treatment levels but mean concentrations differed only between the 1% and

3% treatment levels; mean values for the 0% treatment level were intermediate between the two effluent additions and did not differ significantly from either.

Unfortunately, there is a paucity of data and regulations/guidelines relating tissue concentrations of the contaminants examined in this experiment to direct toxic effects, particularly in periphyton. Guidelines relating to the contaminant concentrations in water (and to a lesser extent sediments) required to protect biota are much better developed and are reflective of the relative ease of standard acute toxicology tests (e.g., 48-hour, acute lethality tests). Measuring tissue concentrations of contaminants is often more difficult and more expensive than standard toxicological testing but can also provide greater insight into the pathways by which contaminants move through the food web as well as their chronic toxicological effects at the level of the individual.

Despite a lack of regulatory guidelines regarding the direct toxic effects of PME contaminants on periphyton, the results of this experiment indicate that contaminant concentrations are generally low and their toxic effects on periphyton probably minimal, at least at the PME dilutions tested here. This finding is in agreement with the work of McCubbin and Folke (1993) who evaluated the toxicity of PME in mills located on the Peace and Athabasca rivers in Alberta. The mills tested employ a technology similar to that used by Northwood Pulp and Timber Ltd and, while periphyton was not assessed directly, the authors concluded that PME of this type was "weakly toxic" to the ecosystem.

The extent to which the observed shifts in periphyton community structure are a response to nutrient addition rather than contaminant exposure is unclear and cannot be tested using this experimental design. However, in a similar set of experiments, performed on the Athabasca River at the Weldwood of Canada Ltd pulp mill and designed to distinguish between nutrient and contaminant effects of PME, results suggest that the observed shift in periphyton community structure was a consequence of nutrient addition rather than contaminant exposure (C. L. Podemski, personal communication). These same experiments also demonstrated that exposure

to PME produced increases in periphyton biomass and macroinvertebrate numbers and size but no measurable contaminant effects on either periphyton or macroinvertebrates (Culp and Podemski 1996; Podemski and Culp 1996; Culp *et al*. 1996).

In addition to the possible enrichment and contaminant effects of PME on periphyton, the colour of PME can affect primary productivity by reducing the amount of available light and hence the rate of photosynthesis. Light attenuation, caused by the addition of PME, has been shown to impact phytoplankton communities in marine and lake environments (reviewed in Tana and Lehtinen 1996) and has the potential to reduce the light available to riverine periphyton communities as well. In the current study, the effect of PME on light attenuation and photosynthetic activity was not assessed directly. While the addition of effluent clearly changed water colour in both 1% and 3% streams (personal observation) it is not clear if this change significantly altered light penetration, particularly at water depths employed in this experiment and typical of river riffles (approximately 50 cm). More importantly, any effects of PME on light attenuation were probably masked by the effects of nutrients (nitrogen and phosphorous) contained in the PME.

In summary, analysis of periphyton tissues exposed to PME in an artificial stream system revealed the presence of certain common PME contaminants but the absence of others. Dioxins and furans are closely associated with PME but were not detected in measurable quantities in any of the samples analyzed in this experiment. Similarly, levels of chlorinated phenolics were generally at or below detection limits in most samples. Concentrations of fatty acids (with the possible exception of myristic acid) did not vary significantly with PME addition and, while resin and PAHs were detected in all samples, their concentrations were generally low and significant differences among treatment levels were, for the most part, limited to differences in mean concentrations in 0% and 3% streams. The apparently low concentrations of contaminants in periphyton tissue is probably a reflection of changes in pulp-mill technology instituted in the early 1990s. These changes were a response to increased public concern over the environmental impacts of the pulp and paper industry and they served to dramatically reduce the effluent

concentrations of a variety of contaminants, particularly chlorinated contaminants (Sekela 1995; Wrona *et al*. 1996).

Given the current levels of contaminants in PME, and the dilution of this effluent in rivers such as the Fraser River, the primary effect of PME appears to be increased primary production as a result of nutrient addition. Any toxic effects of PME on the periphyton community appear to be minimal and are likely masked by the much greater enrichment effect.

It should also be noted that while nutrient enrichment may not result in the loss of periphyton, it nevertheless represents a major anthropogenic impact and a clear disturbance away from the nutrient-limited situation that was the historical norm in this part of the Fraser River. The long-term ecological implications of changes in primary productivity have not been investigated in this part of the basin but this is an area of research that clearly merits further investigation.

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APPENDIX 1

ANALYTICAL METHODS

As discussed in the text, all samples were analyzed by AXYS Analytical Services LTD of Sidney, British Columbia. What follows is a brief description of analytical methods as given by AXYS.

RESIN AND FATTY ACIDS

All samples were spiked with an aliquot of surrogate standard solution containing o-methylpodocarpic acid and perdeuterated lauric, myristic, palmitic, stearic and arachidic acids. Tissue samples were ground with sodium sulphate, packed in a glass chromatographic column and eluted with solvent. The extract was derivatized with diazomethane to produce methyl esters of the resin and fatty acids. The derivatized extract was cleaned up on a silica gel prior to analysis by GC/MS. GC/MS analysis was performed on a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler and a DG10 data system.

CHLORINATED PHENOLICS

Tissue samples were spiked with an aliquot of surrogate standard solution containing twelve ^{13}C-labelled chlorinated phenolic compounds and then ground with sodium sulphate and solvent-extracted by column elution. The extract was then converted to acetate derivatives of chlorophenolics by reaction with acetic anhydride. The derivatized compounds were extracted into hexane and the extract cleaned up using silica gel column chromatography. The final extract was concentrated and spiked with an aliquot of recovery standard solution prior to GC/MS analysis for the target chlorophenolics. GC/MS analysis was performed on a Finnigan INCOS 50 mass spectrometer with a Varian 3400 GC, a CTC autosampler and a DG10 data system.

POLYCYCLIC AROMATIC HYDROCARBONS

All samples were spiked with an aliquot of surrogate standard solution containing deuterated homologues of acenaphthene, chrysese, naphthalene, perylene, phenantherrene, dibenz[ah]anthracene, pyrene, benzo[ghi]perylene and benzo[a]pyrene. Tissue samples were base-digested, extracted with pentane, and the extract fractionated by column chromatography on silica into polar and non-polar fractions. The polar fraction was analyzed for PAH by gas chromatography with low resolution (quadrupole) mass spectrometric detection (GC/MS). GC/MS analysis was performed on a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler and a DG10 data system.

POLYCHLORINATED DIBENZODIOXIN/DIBENZOFURAN ANALYSIS

All samples were spiked with ^{13}C-labelled surrogates (tetrachlorodioxin, tetrachlorofuran, pentachlorodioxin, pentachlorofuran, hexachlorodioxin, hexachlorofuran, heptachlorodioxin, heptachlorofuran, and octachlorodioxin) prior to analysis. Tissue samples were ground with sodium sulphate, packed in glass chromatographic column and eluted with solvent. The extracts were subject to a series of clean-up steps prior to analysis by high resolution gas chromatography with high resolution mass spectrometric detection (HRGC/HRMS). HRGC/HRMS analysis was carried out on a VG Ultima AutoSpec mass spectrometer equipped with a Hewlett Packard 5890 GC, a CTC autosampler and a VAX workstation.

APPENDIX 2

CONTAMINANT CONCENTRATIONS

RESIN ACIDS*

	PME Dilution									
Resin Acids	0%	0%	0%	1%	1%	1%	3%	3%	3%	3%
Pimaric	**0.34**	2.6	0.57	260	260	100	1200	980	1400	690
Sandaracopimaric	17	10	8.0	16	13	10	70	67	62	44
Isopimaric	**6.5**	3.8	5.3	240	220	170	1000	760	1100	530
Palustric	**6**	**1.7**	3.4	12	**2.05**	9.1	32	32	39	21
Dehydroisopimaric	**2.55**	**1.9**	**1.3**	30	28	24	150	96	160	73
Dehydroabietic	23	16	130	320	300	230	1300	1000	1400	670
Abietic	9	**3.8**	**4.85**	460	460	350	2000	1600	2100	1100
Neoabietic	7.5	**5**	**2.5**	**6**	9.6	9.0	45	33	36	21
12/14 Chlorodehydroabietic	0.5	**0.38**	**0.305**	19	18	12	96	66	94	38
12,14 Dichlorodehydroabietic	1.55	**1.25**	**0.9**	**4**	**3.7**	**2.9**	28	18	22	10
Total Resin Acids	74	46	157	1367	1314	1007	5921	4652	6413	3197

* Concentrations are expressed as ng/g

Bolded values replace non-detections and are 50% of the detection limit for that sample.

FATTY ACIDS*

PME Dilution

Fatty Acids	0%	0%	0%	1%	1%	1%	3%	3%	3%	3%
Capric	61	51	48	64	40	48	76	62	77	49
Lauric	150	140	96	148	130	120	240	240	230	160
Myristic	17000	14000	9900	20000	19000	19000	30000	24000	30000	17000
Palmitic	42000	33000	22000	38000	36000	40000	51000	44000	54000	30000
Linolenic	31000	26000	19000	46000	35000	58000	42000	26000	37000	27000
Linoleic	9000	9000	5900	9600	8700	11000	9000	6400	9300	6200
Oleic	16000	9500	6200	7200	6000	5800	8000	6400	7000	5700
Stearic	1300	870	690	1120	1400	1500	18000	1300	1900	1100
Arachidic	250	190	230	200	190	180	370	310	410	240
Behenic	440	410	370	1040	860	820	1700	1500	1900	1200
Lignoceric	820	830	600	1100	950	900	1700	1600	1800	1200
Total Fatty Acids	118021	93991	65034	124472	108270	137368	162086	111812	143617	89849

* Concentrations are expressed as ng/g

CHLORINATED PHENOLICS*

	PME Dilution									
Chlorophenolics	0%	0%	0%	1%	1%	1%	3%	3%	3%	3%
4-Chlorophenol	**0.02**	0.12	**0.04**	0.25	0.23	0.14	**0.02**	0.14	0.17	0.19
2,6-Dichorophenol	**0.02**	**0.02**	**0.02**	0.12	0.10	0.11	0.21	0.21	0.29	0.11
2,4/2,5-Dichlorophenol	0.12	0.10	0.11	0.10	0.11	0.12	0.13	**0.01**	0.10	0.13
3,5-Dichlorophenol	0.25	0.10	0.16	0.32	0.21	0.14	0.16	**0.02**	0.29	0.26
2,3-Dichloropenol	0.18	0.10	0.10	0.06	**0.02**	**0.02**	**0.02**	**0.02**	0.10	**0.03**
3,4-Dichlorophenol	**0.02**	**0.02**	**0.02**	0.21	**0.02**	**0.03**	0.06	0.08	0.10	0.06
6-Chloroguaiacol	**0.01**	**0.01**	**0.01**	**0.01**	**0.03**	**0.01**	**0.02**	**0.02**	**0.02**	**0.01**
4-Chloroguaiacol	**0.08**	**0.01**	0.07	0.17	0.19	0.20	0.24	0.26	0.33	0.32
5-Chloroguaiacol	**0.19**	**0.02**	0.08	0.63	**0.03**	0.28	0.16	**0.02**	0.12	0.07
2,4,6-Trichlorophenol	**0.01**	**0.02**	**0.01**	**0.02**	**0.02**	**0.01**	**0.02**	**0.02**	**0.01**	**0.02**
2,3,6-Trichlorophenol	**0.04**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.03**
2,3,5-Trichlorophenol	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.02**
2,4,5-Trichlorophenol	**0.01**	**0.01**	**0.01**	**0.01**	**0.02**	**0.01**	**0.02**	**0.02**	**0.01**	**0.01**
2,3,4-Trichlorophenol	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.02**
3,4,5-Trichlorophenol	**0.02**	**0.02**	**0.01**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
3-Chlorocatechol	0.43	**0.03**	**0.05**	**0.04**	**0.05**	**0.05**	0.41	0.18	0.39	0.18
4-Chlorocatechol	0.10	**0.02**	**0.02**	0.08	**0.09**	0.09	0.45	0.33	0.45	0.34
4,6-Dichloroguaiacol	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.02**	**0.01**	**0.01**
3,4-Dichloroguaiacol	**0.01**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.02**
4,5-Dichloroguaiacol	**0.01**	**0.01**	**0.01**	0.04	**0.03**	0.05	**0.01**	0.07	0.08	0.10
3-Chlorosyringol	**0.01**	**0.01**	**0.01**	**0.02**	**0.01**	**0.01**	**0.02**	**0.01**	**0.02**	**0.01**
3,6-Dichlorocatechol	**0.03**	**0.03**	**0.02**	**0.02**	**0.03**	**0.03**	**0.02**	**0.02**	**0.02**	**0.03**
3,5-Dichlorocatechol	**0.04**	**0.05**	**0.03**	**0.03**	**0.04**	**0.04**	**0.03**	**0.03**	0.11	0.10
3,4-Dichlorocatechol	**0.02**	0.03	0.39	0.38	0.42	0.50	0.48	0.28	0.59	0.41
4,5-Dichlorocatechol	**0.02**	**0.03**	**0.02**	0.23	0.15	0.18	0.52	0.46	0.64	0.55
2,3,5,6-Tetrachlorophenol	**0.03**	**0.03**	**0.04**	**0.03**	**0.04**	**0.03**	**0.02**	**0.03**	**0.03**	**0.02**
2,3,4,6-Tetrachlorophenol	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.01**	**0.02**	**0.02**	**0.01**
2,3,4,5-Tetrachlorophenol	**0.02**	**0.02**	**0.03**	0.08	**0.03**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
5-Chlorovanillin	**0.06**	**0.10**	**0.06**	**0.03**	**0.05**	**0.05**	**0.03**	**0.03**	**0.03**	**0.05**

CHLORINATED PHENOLICS (continued)*

	PME Dilution									
Chlorophenolics	0%	0%	0%	1%	1%	1%	3%	3%	3%	3%
6-Chlorovanillin	**0.07**	0.25	0.18	2.00	2.30	2.60	2.40	3.10	3.00	3.80
3,5-Dichlorosyringol	**0.03**	**0.04**	**0.05**	**0.05**	**0.04**	**0.04**	**0.04**	**0.04**	**0.05**	**0.05**
3,4,6-Trichloroguaiacol	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
3,4,5-Trichloroguaiacol	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
4,5,6-Trichloroguaiacol	**0.01**	**0.02**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	**0.02**	**0.01**
3,4,6-Trichlorocatechol	**0.03**	**0.04**	**0.03**	**0.03**	**0.05**	**0.04**	0.14	0.10	0.16	0.14
3,4,5-Trichlorocatechol	**0.03**	**0.04**	**0.03**	0.13	0.15	0.11	0.30	0.26	0.36	0.29
5,6-Dichlorovanillin	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.03**	**0.03**	**0.02**
Pentachlorophenol	**0.02**	**0.03**	**0.02**	**0.02**	**0.02**	**0.03**	**0.02**	**0.02**	**0.02**	**0.02**
2-Chlorosyringaldehyde	**0.01**	**0.02**	**0.01**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**
3,4,5,6-Tetrachloroguaiacol	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.02**	**0.01**	**0.02**
3,4,5-Trichlorostringol	**0.02**	**0.02**	**0.02**	**0.04**	**0.01**	**0.03**	0.23	**0.02**	**0.06**	**0.02**
3,4,5,6-Tetrachlorocatechol	**0.02**	**0.02**	**0.01**	0.21	0.08	0.11	0.25	0.22	0.31	0.27
2,6-Dichlorostringaldehyde	**0.02**	**0.03**	**0.02**	0.13	**0.02**	**0.04**	**0.04**	**0.05**	**0.07**	**0.03**
Total Chlorophenols	2.07	1.52	1.80	5.69	4.77	5.30	6.65	6.34	8.15	7.80

* Concentrations are expressed as ng/g

Bolded values replace non-detections and are 50% of the detection limit for that sample.

POLYCYCLIC AROMATIC HYDROCARBONS

	PME Dilution									
PAHs	0%	0%	0%	1%	1%	1%	3%	3%	3%	3%
Naphthalene	2.00	2.30	1.90	2.00	1.80	1.90	2.30	3.00	2.20	2.00
Acenaphthylene	0.17	0.20	0.12	0.13	0.11	0.16	0.16	0.16	**0.14**	0.13
Acenaphthene	0.42	0.32	0.20	0.32	0.23	**0.10**	0.35	0.40	0.44	0.32
Fluorene	0.40	0.42	0.37	0.34	0.26	0.39	0.52	0.48	0.72	0.52
Phenanthrene	3.80	4.50	3.20	3.50	3.40	3.60	5.40	5.50	6.90	4.80
Anthracene	0.25	0.27	0.15	0.44	0.24	0.48	1.10	0.70	1.20	0.65
Fluoranthene	2.50	2.70	2.00	2.70	2.40	2.60	4.80	4.60	5.60	4.30
Pyrene	1.50	1.50	1.20	1.60	1.00	1.20	2.80	2.70	3.50	1.80
Benz(a)anthracene	**0.02**	0.40	0.27	0.39	0.37	0.36	0.75	0.74	0.90	0.52
Chrysene	0.79	1.00	0.73	0.88	0.88	1.10	1.40	1.30	1.60	1.10
Benzofluoranthenes	1.90	0.85	0.41	0.71	0.60	0.48	1.00	1.10	1.00	0.80
Benzo(e)pyrene	1.00	0.66	0.24	0.49	0.35	0.29	0.72	0.62	0.60	0.50
Benzo(a)pyrene	0.68	**0.04**	**0.05**	0.27	**0.05**	**0.05**	0.46	0.29	**0.07**	0.25
Perylene	5.00	5.30	4.20	4.20	3.80	3.40	3.20	4.40	4.80	3.80
Dibenz(ah)anthracene	1.30	**0.34**	**0.17**	**0.15**	**0.15**	**0.14**	**0.38**	**0.21**	**0.23**	**0.16**
Indeno(1,2,3-cd)pyrene	**0.03**	**0.08**	**0.08**	**0.11**	**0.12**	**0.13**	0.18	**0.14**	**0.24**	**0.11**
Benzo(ghi)perylene	0.92	0.64	**0.20**	0.52	**0.19**	**0.19**	0.68	0.68	0.68	0.49
Total PAHs	22.67	22.25	15.49	18.75	15.94	16.56	26.20	27.01	30.91	22.25

* Concentrations are expressed as ng/g

Bolded values replace non-detections and are 50% of the detection limit for that sample.