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Pulp Mill Sourced Organic Compounds and Sodium Levels in Water and Sediments from the Tarawera River, New Zealand

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Two pulp mills, located downstream of the township of Kawerau, in the Eastern Bay of Plenty region, New Zealand, have for more than thirty five years, discharged effluent waters to the Tarawera River. We have reported (Wilkins and Panadam 1987) the presence in water samples taken from the lower reaches of the Tarawera River of a variety of pulp mill sourced compounds including, fatty acids, resin acids, and some chlorophenolic compounds. A unique aspect of the effluents was the presence of appreciable quantities of abietan-18-oic acid (a saturated resin acid) and four degraded resin hydrocarbons (fichtelite, dehydroabietin, tetrahydroretene and retene).

In connection with the studies directed towards an updating of the Tarawera River Management Plan (BOPCC 1985) we investigated the levels of sodium, fatty acids, resin acids, degraded resin hydrocarbons and chlorophenolic substances, at points above and below the final discharges of the two pulp mills. A substantial part of the toxicity associated with bleach kraft mill effluents can be attributed to the presence of resin acids and chlorophenols (Suntio et al 1988). Upstream of the mill discharges, river water has a high quality, while downstream water is highly coloured and has a diminished dissolved oxygen level (Macintosh 1995). The principle objectives of the two three week synoptic surveys were to (i) identify the mean levels of pulp mill sourced compounds in effluents discharged to the Tarawera River, (ii) assess the extent to which these compounds were persistent in downstream water samples, and (iii) determine sediment loading characteristics.

During the survey period Mill 1 produced 75 000 tonnes annually of pulp, mainly utilised for tissue paper production, using a bleached sulphonated chemi-thermomechanical process in combination with hydrogen peroxide bleaching, while Mill 2 produced 270 000 tonnes annually of kraft pulp (from two kraft mills), and 310 000 tonnes annually of mechanical pulp (from a stone ground mill and a refiner mill). A part of this mill's production was bleached using the following sequences: (i) chlorine, caustic extraction, hypochlorite (100 000 tonnes anually) and (ii) oxygen, sequential chlorine dioxide and Chlorine, caustic and oxygen extraction, chlorine dioxide (140 000 tonnes annually).

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METHODS AND MATERIALS

Mill discharges and river water samples were investigated during the periods Nov 18th - Dec 7th, 1991 and Jan 20th - Feb 6th 1992. Ten 24 hour composite water samples were collected at 48 hour intervals from eight sampling points (Table 1). During the two survey periods Mill 2 operated on a continuous basis, whereas Mill 1 operated on an intermittent basis; typically 4-5 days per week. Grab water samples were also collected on 8th May, 1992.

Table 1. Sampling stations

site	location	code	distance from sea (km)
1	Kawerau bridge	KB	28.5
2	Mill 1 discharge	Mill 1	27.2
3	Upstream Ruruanga	UR	26.9
4	Pipe bridge	PB	21.5
5	Mill 2 discharge	Mill 2	21.4
6	State highway 30 bridge	SH30	18.4
7	Awakaponga flow gauge	A W	6.5
8	Upstream Awakaponga canal	UAC	1.1

Water samples, collected and transported in 2.5 L glass Winchesters, were extracted within 24-48 hr of collection. Resin acid and fatty acid levels were determined using a previously reported protocol (Wilkins and Panadam, 1987) involving liquid-liquid extraction, followed by methylation with diazomethane and GC-FID analyses on a 20 m x 0.22 m HP-l (Hewlett Packard) capillary column installed in a HP5890 GC. Behenic acid (100 µL of a 0.5 mg/mL solution in chloroform) was added as a surrogate standard, to monitor recovery efficiency (typically >85%). Peak identifications were verified by GCMS analyses on a HP-1 capillary column installed in a HP5890 GC interfaced to a HP5970B mass selective detector. GC-FID and GCMS data was processed using purpose written EXCEL spreadsheets. Typical reproducibility data for eight replicate extractions of a Mill 1 effluent, collected prior to the 1st survey period, is given in Table 2. Sodium levels were determined by AA analyses, using a Pye Unicam spectrophotometer. Water flow data was supplied by Environment Bay of Plenty.

Table 2. *Concentrations* (ppb) and standard deviation parameters determined for some fatty acids and resin acids in eight replicate extractions of a Mill 1 effluent.

	extraction number										
compound	1	2	3	4	5	6	7	8	mean	σ	CV[a]
palmitic acid	438	442	443	432	433	398	449	450	436	17	4
stearic acid	110	106	107	107	104	103	105	110	106	3	2
pimaric acid	1870	1806	1933	1974	1937	1471	1573	1680	1780	186	10
dehydroabietic acid	7675	7313	7896	8116	8004	6473	6522	6978	7372	655	9
abietic acid	1400	1376	1405	1411	1361	1077	1066	1159	1282	153	12

[a] coefficient of variation (%)

The levels of chlorophenolic substances in the methylated liquid/liquid extracts were determined using selected ion mode (SIM) GCMS analyses (two analyses per extract: one for chlorophenols methyl ethers and one for guaiacol methyl ethers). Recoveries of spiked chlorophenols were typically 67-91%. Ions monitored were

m/z 210+212, 244+246, 278+280, 206+208, 240+242 and 274+276, for the methyl ethers of 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, 4,5-dichloroguaicaol, 3,4,5-trichloroguaicaol and tetrachloroguaiacol respectively. SIM GCMS response factors were determined for these ions, using a standard solution of the six chlorophenol methyl ethers. Detection limits for fatty acids, resin acids and chlorophenols, detected as the corresponding methyl esters or ethers were, 2-3 ppb (CG-FID for fatty acids and resin acids) and 0.02-0.05 ppb (SIM GCMS for chlorophenols), depending on baseline and peak resolution characteristics.

Sediment samples, collected 10th September, 1992, were wet sieved through 1000 mesh and centrifuged to afford clay-like material which was freeze dried for 36 h and sieved through 200 mesh. Weighed portions (*c* 5 g) were extracted in a Soxhlet apparatus for 24 h with hexane-isopropanol (1:1). The resulting extractive solutions were evaporated to *c* 2 mL and derivatised with an ethereal diazomethane solution. Quantification was performed using a combination of GC-FID (for resin acids and fatty acids) and SIM GCMS procedures (for chlorodehydroabietic acid isomers). Ions of m/z 273+275 and m/z 307+309 were monitored for mono- and dichlorodehydroabietic acid isomers respectively, in a manner analogous to that reported elsewhere (Wilkins, Healey and Liepe 1995).

RESULTS AND DISCUSSION

Ten 24 hr composite samples, collected every 48 hr, were analysed for each of the sample sites (ie a total of 80 samples per survey period). The mean (n = 10) levels of fatty acids, resin acids, fichtelite, and chlorophenols identified in the Mill 1 and Mill 2 discharges during the two surveys are given in Table 3. Preliminary experiments indicated that the recovery of chlorophenols (typically 67-91%) from the methylated liquid/liquid extracts, were generally 2-15% less than those recovered using the methodolgy of Stark et al. (1985). However, this was considered satisfactory for the purpose of the two synoptic surveys, since this halved the number of extractions per water sample, and combined the contributions from equivalently chlorinated guaiacol, catechol and veratrole analogues into a single peak which was quantified as the veratrole analogue. The mean level of total resin acids, fatty acids, chlorophenols, and fichtelite, detected in water samples from the eight sites investigated are given in Table 4.

Mean water flows, and sodium levels are given in Table 5. Both mills take and discharge their process water into the Tarawera River, downstream of the township of Kawerau, typically at the rate of 0.15 m^3/sec (Mill 1) and 2.75 m^3/sec (Mill 2). Effluent from Mill 1 is combined with Kawerau town sewage and subjected to a two stage hybrid anaerobic treatment process, prior to its discharge to the Tarawera River approximately 100 m below the intake point. After primary clarification, effluent from Mill 2 is piped downstream to a 45 hectare lagoon system comprised of four ponds with volumes of 25 000, 200 000, 500 000 and 400 000 m^3(total 5-6 day retention time) for biological treatment prior to its discharge to the river about 6 km below the intake point. Pond 1 is anaerobic while the other three ponds are mechanically aerated (total 2256 kW). Effluent from Mill 1 typically represents less than 1% of river flow, while effluent from Mill 2 generally represents 8-12.5% of river flow (Pang 1993).

Table 3. Mean (n = 10) concentrations (ppb) of fatty acids, resin acids, fichtelite and chlorophenols in Mill 1 and 2 discharges. Standard deviations are given brackets.

compound	Mill 1		Mill 2	
	1st survey	2nd survey	1st survey	2nd survey
myristic acid	54 (25)	28 (28)	tr	tr
palmitic acid	429 (266)	193 (217)	26 (5)	15 (3)
oleic acid group[b]	243 (131)	157 (198)	7 (4)	7 (3)
stearic acid	253 (180)	139 (175)	10 (3)	7 (2)
other fatty acids	270 (89)	137 (82)	43 (7)	23 (12)
secodehydroabietic acid-1	112 (53)	127 (47)	27 (11)	15 (6)
secodehydroabietic acid-2	83 (43)	77 (27)	13 (5)	8 (3)
pimaric acid	494 (234)	567 (208)	10 (13)	9 (3)
sandaracopimaric acid	98 (46)	96 (29)	a	a
isopimaric acid group[c]	469 (188)	1042 (551)	15 (13)	a
dehydroabietic acid	1808 (789)	3310 (1695)	186 (65)	80 (39)
abietan-18-oic acid	-	-	480 (221)	169 (81)
abietic acid	726 (691)	330 (134)	29 (13)	a
kinleithic acid	-	955 (396)	-	-
other resin acids	798 (430)	1725 (1985)	263 (110)	102 (64)
fichtelite	-	-	32 (15)	20 (5)
2,4,6-trichlorophenol	0.06 (0.03)	0.2 (0.1)	1.8 (0.6)	2.8 (0.8)
2,3,4,6-tetrachlorophenol	-	-	0.05 (0.05)	0.1 (0.1)
pentachlorophenol	-	-	tr	0.1 (0.1)
4,4-dichloroguaiacol	-	-	1.4 (0.7)	0.6 (0.3)
3,4,5-trichloroguaiacol	0.05 (0.03)	0.03 (0.03)	1.2 (0.3)	1.6 (1.3)
tetrachloroguaiacol	tr	-	0.8 (0.3)	1.6 (0.9)

[a]included in other resin acids total, [b]sum of 18:1 and 18:2 isomers, [c]may include minor levopimaric and palustric acid contributions, tr = trace.

Table 4. Mean (n = 10) concentrations (ppb) determined for fatty acids, resins acids, fichtelite and chlorophenols in water samples. Standard derivations are given in brackets.

site (code)	Σ fatty acids[a]	Σ resin acids[a]	fichtelite	Σ chlorophenols[a]
1st survey				
site 1 (KB)	31 (22)	-	-	-
site 2 (Mill 1)	182 (55)	4588 (2210)	-	0.1 (0.1)
site 3 (UR)	33 (33)	tr	-	-
site 4 (PB)	36 (22)	tr	-	-
site 5 (Mill 2)	86 (11)	1023 (437)	32 (15)	5.2 (1.0)
site 6 (SH30)	45 (32)	121 (59)	8 (4)	0.3 (0.2)
site 7 (AW)	27 (14)	108 (44)	7 (3)	0.3 (0.1)
site 8 (UAC)	50 (41)	92 (33)	6 (3)	0.2 (0.1)
2nd survey				
site 1 (KB)	12 (2)	-	-	-
site 2 (Mill 1)	654 (648)	7204 (3359)	-	0.2 (0.1)
site 3 (UR)	16 (4)	tr	-	-
site 4 (PB)	16 (7)	tr	-	-
site 5 (Mill 2)	52 (13)	382 (190)	20 (5)	8.0 (2.8)
site 6 (SH30)	45 (32)	34 (6)	4 (1)	0.8 (0.3)
site 7 (AW)	11 (3)	29 (7)	4 (1)	0.8 (0.3)
site 8 (UAC)	15 (8)	23 (5)	3 (1)	0.4 (0.2)

[a] sum of compounds named in Table 3; tr = trace.

Table 5. Mean (n = 10) water flows (m^3/sec) and sodium concentrations (ppm. Standard deviations are given in brackets.

site (code)	water flow (m^3/sec) 1st survey	2nd survey	Na concentration (ppm) 1st survey	2nd survey
site 1 (KB)	19.93 (1.10)	19.12 (1.15)	52 (2)	52 (4)
site 2 (Mill 1)	0.15 (0.01)	0.15 (0.02)	120 (19)	180 (62)
site 3 (UR)			53 (2)	53 (2)
site 4 (PB)	20.13 (0.61)	19.21 (0.86)	61 (3)	61 (2)
site 5 (Mill 2)	2.74 (0.18)	2.51 (0.25)	176 (9)	171 (6)
site 6 (SH30)			72 (3)	74 (5)
site 7 (AW)	24.31 (0.74)	23.19 (1.05)	65 (5)	65 (4)
site 8 (UAC)			65 (5)	65 (2)[a]

[a] for n = 9 samples

An intriguing aspect of our investigations was the apparent rapid attenuation (removal) of resin acids in the 5.8 km section of the Tarawera River between the Mill 1 and Mill 2 discharge points. Barely detectable levels of resin acids were identified in the GC-FID profiles of water samples collected from sites 3 and 4, intermediate between the Mill 1 and Mill 2 discharge points. The rapid attenuation of resin acids observed during the two survey periods was further investigated (Table 6) using a set of water samples collected on 8th May 1992. SIM GCMS analysis revealed 184:1 to 1152:1 fold attenuations, rather than the expected c 100:1 to 150:1 fold attenuations of resin acids in this region of the river. On the other hand values close to the anticipated 10:1 attenuation, attributable only to a dilution effect, were observed for resin acids in a site 6 (SH30) water sample, collected 3 km downstream of Mill 2's discharge point.

Table 6. Attenuation factors determined using selected ion GCMS for some resin acids detected in water samples collected 8th May, 1992.

compound	ion (m/z)	attenuation factor Mill 1/US[a]	Mill 1/PB[b]	Mill 2/SH30[c]
secodehydroabietic acid-1	146	184:1	471:1	7.6:1
secodehydroabietic acid-2	146	215:1	505:1	8.0:1
abietan-18-oic acid	163			9.5:1
dehydroabietic acid	239	1152:1	980:1	6.5:1
14-chlorodehydroabietic acid	273+275			10.0:1
12,14-dichlorodehydroabietic acid	307+309			10.8:1

[a] site 3, [b] site 4, [c] site 6

Between the Mill 1 and Mill 2 discharge points, the Tarawera River flows through a geothermal area and receives a number of other effluents (Pang 1993, 1994). Geothermal steam condensate and filter backwash from the Mill 2 intake is discharged at a rate of 0.04 m^3/sec 200 m downstream of the Mill 1 discharge. Effluent for a geothermal bore field is discharged at a rate of 0.118 m^3/sec 1900 m downstream of the Mill 1 discharge. In addition there are a number of natural geothermal seepages into the river in this region.

It is possible that interactions between species in the geothermal discharges and Mill 1 effluents occur in this region of the river, leading to flocculated and/or complexed resin acid species, which are not recovered by the liquid/liquid extraction protocol. The nature of the process (or processes) whereby removal is apparently achieved in this section of the Tarawera River is the subject of continuing investigations in our, and other laboratories.

During the 2nd survey period Mill 1 fatty acid levels fell into two distinct subsets; three samples collected on 20th January, 5th February and 7th February had total fatty acid levels of 1382, 1193 and 2041 ppb respectively, while the other seven samples had levels of 187 to 381 ppb. It subsequently emerged that an anaerobic digester which was first commissioned in January 1992 (ie it was not operational during the first survey period) was only in use on the former three days. Apparently, the anaerobic digester is capable of degrading most of the fatty acids. Conversely the anaerobic digester appears to be responsible for the formation of kinleithic acid, a compound believed to be an anaerobic degradation product of abietic acid (Wilkins et al. 1989), since this compound was only a significant constituent of the latter set of seven samples (levels in the range 968-1351 ppb).

Abietan-18-oic acid and dehydroabietic acid were the dominant resin acids identified in Mill 2 effluents and subsequent downstream samples (Table 7). The mean dilution factors calculated for these resin acids at sites downstream of the Mill 2 discharge (values in the range 8.9-14.1) are in accord with flow data (Table 5) and are comparable with the *c* 10:1 attenuation factors subsequently determined using SIM GCMS for the set of water samples collected 8th May, 1992 (Table 6). Clearly little removal of these resin acids, and other pulp mill sourced compounds (see Table 4), occurs in the 21 km region of the Tarawera River below the Mill 2 discharge point.

Table 7. Mean (n = 10) concentrations (ppb) with standard deviations in brackets, and dilution factors (relative to the Mill 2 discharge), determined for dehydroabietic acid (DHAA) and abietan-18-oic acid (18-Ab).

	1st survey				2nd survey			
	conc. (ppb)		dilution factor		conc. (ppb)		dilution factor	
site (code)	DHAA	18-Ab	DHAA	18-Ab	DHAA	18-Ab	DHAA	18-Ab
site 5 (Mill 2)	186 (85)	480 (221)			80 (39)	169 (81)		
site 6 (SH30)	20 (11)	47 (30)	9.3	10.2	8 (2)	18 (3)	10.0	9.4
site 7 (AW)	21 (10)	48 (23)	8.9	10.0	8 (2)	16 (4)	10.0	10.6
site 8 (UAC)	16 (6)	39 (17)	11.6	12.3	6 (2)	12 (3)	13.3	14.1

The levels of fatty acids, resin acids, and degraded resin neutrals (fichtelite and dehydroabietin) identified in sieved (< 200 mesh) sediment samples collected on 18th September, 1992, are given in Table 8. The sediment results generally parallel the water results given in Table 4, other than that the sediment levels were typically 10 000 fold greater than was the case for the water samples. In keeping with the apparent absence of resin acids in site 3 and 4 water samples (see Table 4), only low levels of resin acids were detected in the site 3 and 4 sediment samples. However, generally similar levels of fatty acids were detected in all of the sediment samples, including those collected from sites 3 and 4.

Abietan-18-oic acid and chlorodehydroabietic acid isomers are diagnostic marker compounds for a Mill 2 contribution to the sediments, since these compounds are not constituents of the effluents discharged by Mill 1. The level of abietan-18-oic acid detected in sediments downstream of Mill 2's discharge point (sites 4, 5 and 6) exceeded that of dehydroabietic acid by a least a factor of 1.5, as is also the case for the corresponding water samples.

Table 8. Concentrations (ppm) of fatty acids, resin acids, fichtelite and dehydroabietin detected in some Tarawera River sediment samples.

compound	site 1 (KB)	site 2 (UR)	site 3 (PB)	site 4 (SH30)	site 5 (AW)	site 6[a] (UAC)
palmitoleic acid	-	4	5	7	8	5
palmitic acid	48	48	56	42	46	32
oleic acid group[b]	108	100	97	82	136	88
stearic acid	15	19	25	18	17	13
arachidonic acid	9	-	-	8	9	17
behenic acid	12	15	10	18	19	19
lignoceric acid	16	11	14	16	15	17
secodehydroabietic acid-1	-	-	-	52	39	40
secodehydroabietic acid-2	-	-	-	62	66	43
pimaric acid	13	14	15	98	88	123
sandaracopimaric acid	-	-	-	18	16	22
abiet-13-en-oic acid	-	-	-	55	53	50
pimaran-18-oic acid	-	-	-	40	46	49
isopimaric acid	-	12	17	132	107	141
abietan-18-oic acid	-	-	-	470	400	503
dehydroabietic acid	28	36	37	270	203	291
abietic acid	13	10	18	107	80	138
12-chlorodehydroabietic acid	-	-	-	4	4	4
14-chlorodehydroabietic acid	-	-	-	18	20	20
12,14-dichlorodehydroabietic acid	-	-	-	13	13	12
fichtelite	-	-	-	30	64	22
dehydroabietin	-	-	-	9	18	8

[a] collected 300 m downstream of the water sampling point, [b] sum of 18:1 and 18:2 isomers.

The levels of pulp mill sourced compounds identified in this investigation can be compared with those identified in sediments and water samples collected from the biological treatment systems and receiving waters of another New Zealand kraft mill. (Stuthridge et al. 1991, Zender et al. 1994, Tavendale et al. 1995).

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