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Speciation of Particle-Associated Resin Acids and Chromophoric Compounds in Water Samples from the Biological Treatment System of Two New Zealand Pulp Mills

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Previous investigations of Tarawera River samples collected downstream of the discharge point of two New Zealand pulp and paper mills have shown that > 50% of the recoverable resin acids present in river water samples are bound to particles greater than 0.02 μm (Ali Kanber et al. 2000, 2005). Little however is known about the speciation of resin acids during primary and secondary treatment of the pulp and paper mill effluents, prior to their discharge to the Tarawera River.

This paper reports the changes in the levels of soluble and particle associated resin acids and chromophoric (colored) species in sodium azide stabilised water samples taken from the clarifier and four treatment ponds along with the size distributions of particles in these water samples.

MATERIALS AND METHODS

Water samples in screw capped 2.5 L glass winchesters or 20 L plastic containers were collected from the outflow of the clarifier and treatment ponds 1-4 (sites A-E respectively, Figure 1) and the Tarawera River at the SH30 bridge. Water samples were stabilized at the time of collection by the addition 0.1% of sodium azide (Ali Kanber et al, 2005) and stored at 4-8°C until required for analyses. Soluble and bound resin acid levels were determined for well mixed (sodium azide stabilized) clarifier, treatment pond 1-4 and Tarawera River water samples using the liquid-liquid or Soxhlet extraction and selected ion mode GC-MS methodologies reported previously (Ali Kanber et al. 2005). Clarifier and pond 1-4 samples were derived from sequential filtration of 600 mL (glass fibre), 500 mL (3 μm), 400 mL (0.8 μm), 300 mL (0.45 μm) and 200 mL (0.2 μm) and liquid/liquid extraction of 100 mL subsamples of the sodium stabilized water samples. Quantification was performed using *O*-methylpodocarpic acid as internal standard (Ali Kanber et al. 2005). The recovery of *O*-methylpodocarpic ethyl ester was typically 82-105%. Absorbances of azide stabilized water samples before and after sequential-filtration at 270, 340 and 440 nm were determined using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. Turbidity was determined using a Hatch 2100 turbidimeter. ICP-OES analyses were performed using a GBC Integra instrument. The total freeze dried solids (total S) contents of treatment system or river water samples (200-1000 mL depending on the site of sampling), were determined gravimetrically by pre-freezing the water sample in a beaker using a liquid nitrogen bath and freeze-drying the frozen sample for 2-4 days. Inorganic freeze-dried solids (inorg S) were determined after heating freeze-dried residue at 550°C

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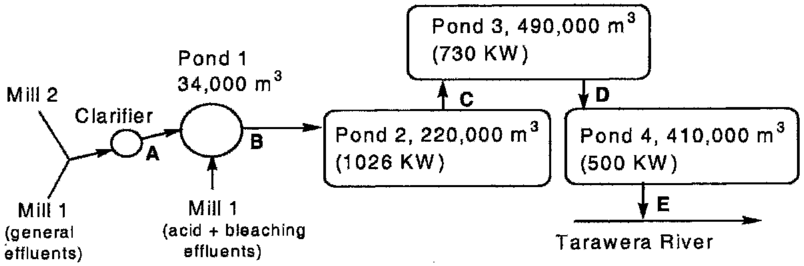

Figure 1. Treatment system characteristics. A-E designate sampling points.

overnight. Organic freeze-dried solids (org S), and % weight loss on ignition of freeze dried solids (% loi) were calculated as org S = total S-inorg S, and % loi = 100 x (total S-inorg S)/total S), respectively. Particle size analyses were performed using a Malvern Instruments (UK) Mastersizer-S particle analyser.

RESULTS AND DISCUSSION

After primary treatment (clarification) effluent waters from two New Zealand pulp and paper mills (mills 1 and 2) situated on the banks of the Tarawera River, are combined with bleaching effluent from mill 1 and subsequently treated in an aeration basin with (at the time of sampling) an average retention time of 5.5 days. Treatment system characteristics are presented in Figure 1. Soluble and bound resin acid levels identified in water samples from the clarifier, treatment ponds 1-4 and a SH30 Tarawera River sample are presented in Tables 1-3. Resin acid levels in pond 1 are higher than in the clarifier due to the impact of the bleach effluent from mill 1. The levels of resin acids in pond 2 and pond 3 were similar (5260 and 4690 µg/L respectively; Table 2) indicating at the time of sampling, pond 3 was contributing little to treatment.

Our results show that virtually none of the resin acids exciting from the clarifier are particle bound (Table 1) whereas 66-75% of the resin acids exiting from pond 4 are associated with 0.45 µm or greater particles (Table 2). While the total level of resin acids falls, the particle associated component reaches a maximum in pond 2 and declines more slowly than soluble resin acid becoming the larger fraction of the total resin acid present (Figure 2). During passage through the treatment system, soluble pimaric and dehydroabietic acid levels fall substantially while the bound levels of these acids stay approximately constant (Figure 3). Abietic acid was almost completely degraded, being either aromatised to afford dehydroabietic acid or hydrogenated to afford abiet-13-enoic acid according to Figure 4 (Tavendale, 1994). Consistent with this scheme, abiet-13-enoic acid was subsequently transformed to abietan-18-oic acid in both the soluble and bound forms (Figure 3).

Absorbance and turbidity data for sequentially filtered clarifier, treatment pond and river water samples are presented in Table 4. Filtration generally reduced color and turbidity levels. For example, filtration by 0.45 µm produced similar reductions in absorbance at 270, 340 and 440 nm for all ponds of the treatment system but had very much less effect on the Tarawera River water.

Table 1. Resin acid levels (µg/L) determined for clarifier and pond 1 water samples, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
Clarifier (n = 2)[a]	305	1290	tr	3485	487	1901	-	7470	
glass fibre (liq/liq)	301	1270	-	3320	462	1470	-	6820	91%
3 µm (liq/liq)	292	1230	-	3440	451	1650	-	7060	95%
0.8 µm (liq/liq)	285	1250	-	3720	437	706	-	6390	86%
0.45 µm (liq/liq)	257	1080	-	3150	394	1270	-	6150	82%
0.2 µm (liq/liq)	270	1140	-	3160	419	1450	-	6440	86%
glass fibre (Sox)	5	2	-	40	14	-	-	61	1%
3 µm (Sox)	1	4	-	7	tr	-	-	12	.>1%
0.8 µm (Sox)	1	4	-	5	1	-	-	11	>1%
0.45 µm (Sox)	tr	1	-	2	tr	-	-	3	>1%
0.2 µm (Sox)	1	3	-	5	1	-	-	9	>1%
Pond 1 (n = 2)[a]	472	1480	25	3270	2890	750	22	8900	
glass fibre (liq/liq)	456	1390	15	3320	2670	749	14	8600	97%
3 µm (liq/liq)	454	1410	10	3420	2840	801	16	8950	101%
0.8 µm (liq/liq))	435	1320	8	3120	2500	659	13	8050	91%
0.45 µm (liq/liq)	378	1230	6	3310	2530	627	19	8100	91%
0.2 µm (liq/liq)	408	1230	5	3160	2450	342	12	7600	86%
glass fibre (Sox)	13	101	5	77	321	-	tr	517	6%
3 µm (Sox)	1	8	tr	6	23	-	3	41	>1%
0.8 µm (Sox)	1	4	-	5	12	-	tr	22	>1%
0.45 µm (Sox)	1	4	-	4	9	-	tr	18	>1%
0.2 µm (Sox)	17	81	-	90	3	-	tr	191	2%

[a] Average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered water.

Similarly, filtration by 0.45 µm reduced turbidities to 2-4% of the unfiltered pond water but Tarawera River water retained 15% of its turbidity after such filtration. Apparently, river water contains particles contributing to color and turbidity that are less filterable (smaller) than treatment pond water. Removals of color, turbidty and bound resin acids by filtration do not appear to be correlated. The levels of selected elements (Na K, Ca, Si, Al, Fe, S and B) total, organic and inorganic freeze-dried solids and loss on ignition (loi) determined for treatment system and river water are presented in Table 5. In general, cation levels in ponds 2, 3 and 4 were conservative and levels in the SH30 Tarawera River water sample were comparable with those reported in other investigations (Wilkins and Panadam 1987; Wilkins et al 1996a, 1996b; McIntosh 1995).

Table 2. Resin acid levels (µg/L) determined for pond 2, 3 and 4 water samples, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
Pond 2 (n=2)	267	462	702	2960	721	103	44	5261	
glass fibre (liq/liq)	249	364	321	2920	433	32	26	4340	82%
3 µm (liq/liq)	220	333	303	2770	437	16	24	4100	78%
0.8 µm (liq/liq)	235	314	186	2780	378	8	21	3920	74%
0.45 µm (liq/liq)	196	289	197	2700	336	tr	23	3740	71%
0.2 µm (liq/liq)	205	300	138	2770	329	tr	17	3760	71%
glass fibre (Sox)	33	130	304	47	290		tr	805	15%
3 µm (Sox)	3	14	36	23	21	-	1	97	2%
0.8 µm (Sox)	5	19	49	36	12	-	1	122	2%
0.45 µm (Sox)	3	10	17	27	18	-	2	76	1%
0.2 µm (Sox)	3	14	22	24	24	-	1	87	2%
Pond 3 (n = 2)	270	366	732	2770	451	69	34	4690	
glass fibre (liq-liq)	220	261	313	2430	245	38	30	3540	75%
3 µm (liq-liq)	229	249	219	2540	212	23	20	3490	74%
0.8 µm (liq-liq)	254	254	173	2580	188	19	17	3480	74%
0.45 µm (liq-liq)	235	251	171	2630	208	24	18	3540	75%
0.2 µm (liq-liq)	226	220	124	2470	176	14	16	3250	69%
glass fibre (Sox)	22	65	284	98	193	-	8	670	14%
3 µm (Sox)	8	28	97	42	72	-	3	250	5%
0.8 µm (Sox)	2	5	19	11	13	-	1	52	1%
0.45 µm (Sox)	1	2	6	5	4	-	tr	18	>1%
0.2 µm (Sox)	2	5	10	10	8	-	tr	35	>1%
Pond 4 (n = 4)[a]	61	93	591	150	14		13	923	
glass fibre (liq-liq)	54	24	236	119	2		14	449	49%
3 µm (liq-liq)	36	34	145	69	4		7	293	32%
0.8 µm (liq-liq)	35	32	109	62	3		5	247	27%
0.45 µm (liq-liq)	34	25	98	66	2		4	230	25%
0.2 µm (liq-liq)	41	28	65	80	3		4	220	24%
glass fibre (Sox)	17	43	366	64	8	-	2	500	54%
3 µm (Sox)	2	3	20	4	tr	-	7	36	4%
0.8 µm (Sox)	1	4	24	5	tr	-	tr	34	4%
0.45 µm (Sox)	2	4	22	4	tr	-	1	33	4%
0.2 µm (Sox)	1	3	13	3	tr	-	1	20	2%

[a] Average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abiet = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered pond 2, 3 or 4 water

Table 3 Resin acid levels (µg/L) determined for a SH30 Tarawera River water sample, collected 1/11/99.

	seco	pim	18-Ab	DHAA	13-ene	abiet	Cls	total	%
SH30 (n = 2)[a]	4.8	5.8	22.6	9.1	20.0	tr	0.2	62.5	
glass fibre(liq/liq)	4.7	4.7	17.0	7.4	13.3	tr	0.2	42.5	68%
3 µm (liq/liq)	3.9	3.1	9.3	5.4	7.9	-	tr	29.7	48%
0.8 µm (liq/liq)	3.3	2.7	7.8	4.3	6.3	-	0.2	24.6	39%
0.45 µm (liq/liq)	3.3	2.3	6.8	5.1	5.4	-	0.1	23.0	37%
0.2 µm (liq/liq)	3.6	1.8	3.7	4.6	3.3	-	0.1	17.0	27%
glass fibre (Sox)	0.9	1.6	8.6	3.0	6.6	-	0.1	20.7	33%
3 µm (Sox)	0.4	0.8	3.5	1.3	2.9	-	tr	8.8	14%
0.8 µm (Sox)	tr	0.3	1.3	0.5	-	-	tr	2.2	3%
0.45 µm (Sox)	tr	-	1.1	0.5	-	-	tr	1.7	3%
0.2 µm (Sox)	0.1	-	0.7	0.2	-	-	tr	1.1	2%

[a]Average of duplicate analyses. Abbreviations: tr = trace, seco = secodehydroabietic acids 1 and 2, pim = pimaric acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, 13-ene = abiet-13-enoic acid, abietic = abietic acid, Cls = 12-chloro, 14-chloro and 12,14-dichlorodehydroabietic acids, total = total resin acids, % = recovery relative to unfiltered SH30 water.

The levels of organic solids peaked at 656 mg/L in pond 1 reflecting the organic load added with the bleach effluent from mill 1. Subsequently organic solids decreased down the treatment system.

Particle size analyses (Figure 5) confirms the effectiveness of the clarifier in removing particles larger than 100 µm. In pond 1 particle sizes are centred on 10-20 µm. Particle sizes for pond 2 show an anomalous peak centred on 500-600 µm. It is likely that agitation (mechanical aeration and/or on-going dredging operations) caused resuspension of bottom sediment to give this result. These particles had largely settled by the time the water exited from pond 3. However, apart from elevated Ca levels and somewhat higher absorbances, there is no indication of significantly increased suspended solids or resin acids in pond 2.

Our results show that resin acids become bound to particles as they pass down the treatment system and the total bound fraction degrades more slowly than the soluble fraction. This finding is consistent with those of previous workers have reported the presence of elevated levels of particles (Kasko, 1996) in pulp mill effluent after biological and physical treatment. Hall and Liver (1996) have observed that in a laboratory experiment resin acids were strongly absorbed onto biomass. Our results also have implications in respect of the development of strategies to reduce the toxicity of pulp mill effluents discharged from biological treatment systems since Hoel and Aarsand (1995) have shown that the toxicity of pulp mill effluents towards to *Daphne magna* is predominantly attributable to the presence of particle bound resin acids.

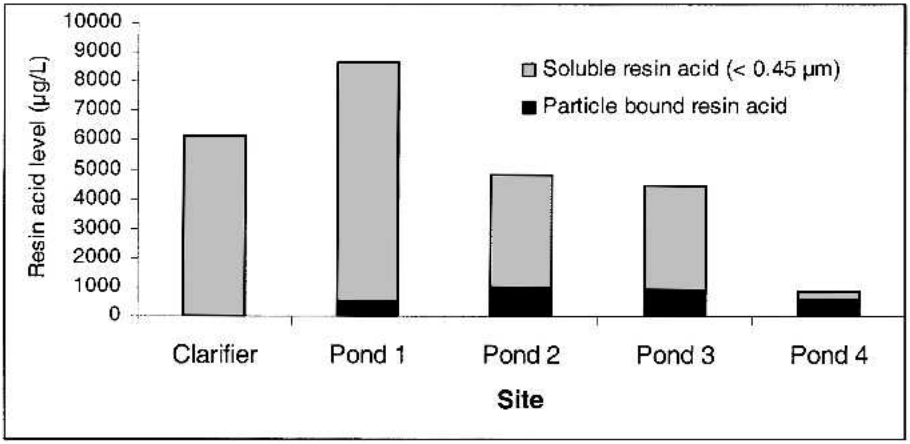

Figure 2. Levels of particle bound (> 0.45 µm) and soluble resin acids (< 0.45 µm) identified in clarifier and biological treatment pond water samples.

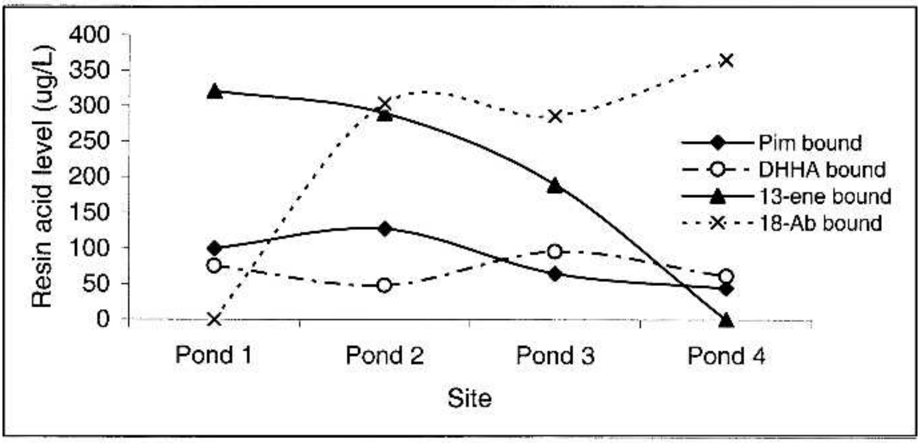

Figure 3. Levels of particle bound (> 0.45 µm) pimaric acid, dehydroabietic acid, abiet-13-enoic acid and abietan-18-oic acid identified in biological treatment pond water samples.

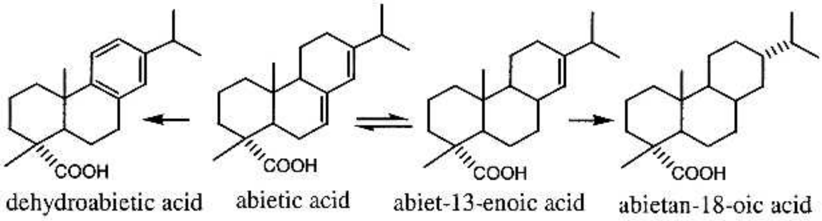

Figure 4. Chemical structures and interconversion pathways for some resin acids.

Table 4. Absorbance at 270, 340 and 440 nm and turbidity (NTU) determined for unfiltered (UF) and filtered pond 1-4 and SH30 Tarawera River water samples collected 1/11/99.

	absorbance (nm)			% absorbance (nm)[a]			turbidity	
	270	340	440	270	340	440	NTU	%[a]
Pond 1 (UF)	1.794	0.744	0.283				53.0	
glass fibre	1.268	0.432	0.097	71%	58%	34%	19.8	37%
3 μm	1.134	0.369	0.068	63%	50%	24%	3.89	7%
0.45 μm	1.103	0.365	0.069	61%	49%	24%	1.67	3%
Pond 2 (UF)	2.036	0.755	0.289				43.5	
glass fibre	1.507	0.471	0.112	74%	62%	39%	16.5	38%
3 μm	1.397	0.427	0.097	69%	69%	34%	7.60	17%
0.45 μm	1.279	0.379	0.074	63%	50%	26%	1.93	4%
Pond 3 (UF)	1.895	0.717	0.262				44.3	
glass fibre	1.468	0.495	0.124	77%	69%	47%	17.2	39%
3 μm	1.251	0.402	0.093	66%	56%	35%	3.11	7%
0.45 μm	1.316	0.442	0.110	69%	62%	42%	0.99	2%
Pond 4 (UF)	1.587	0.618	0.224				43.5	
glass fibre	1.247	0.426	0.110	79%	69%	49%	17.6	40%
3 μm	1.224	0.429	0.121	77%	69%	54%	4.12	9%
0.45 μm	1.160	0.397	0.101	73%	64%	45%	0.93	2%
SH30 (UF)	0.349	0.074	0.018				7.78	
glass fibre	0.339	0.068	0.016	97%	92%	89%	3.83	49%
3 μm	0.329	0.064	0.013	94%	86%	72%	2.35	30%
0.45 μm	0.324	0.058	0.011	93%	78%	61%	1.15	15%

[a] % absorbance, or turbidity relative to unfiltered water

Table 5. Elements (mg/L), freeze-dried solid levels (mg/L) and loss on ignition determined for treatment system and Tarawera River water samples collected 1/11/99.

	clarifier	pond 1	pond 2	pond 3	pond 4	SH30
Na	209	243	223	223	221	70
Ca	25	42	63	52	45	11
K	3.0	3.1	2.7	2.6	2.5	2.1
Si	24	23	25	25	24	27
S	8.7	9.8	8.4	11	6.0	0.8
Al	0.77	0.91	0.75	0.82	0.66	0.72
Fe	0.02	0.14	0.21	0.24	0.12	0.03
B	0.26	0.27	0.27	0.25	0.26	0.54
total S	1074	1426	1256	1162	1087	394
% loi	41%	46%	33%	30%	0.26	0.22
org S	440	656	414	349	283	87
inorg S	634	770	842	813	804	307

total S = total freeze-dried solids, % loi = % weight loss on ignition of freeze-dried solids, org S = organic freeze dried solids, inorg S = inorganic freeze dried solids.

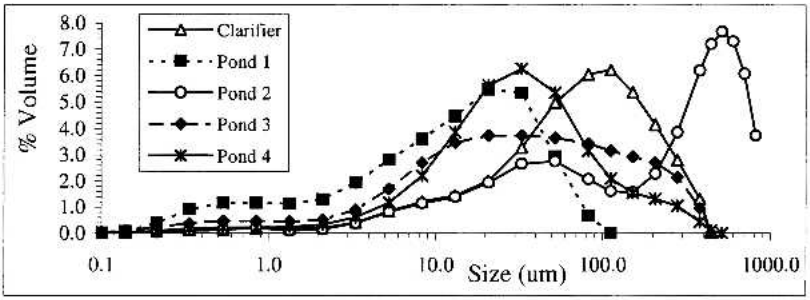

Figure 5. Particle size distributions (% volume) determined for clarifier and treatment pond samples.

While it is clear that filtration can substantially reduce resin acid levels and color, technical difficulties such as membrane fouling and the operating costs of large scale plants are such that removal of particle or biomass associated organic species by micro-filtration has not been adopted as a viable treatment option for pulp and paper mill effluents. However, methodologies for the removal of particles such as coagulation, flocculation and granular filtration can be expected to be effective in removing the bound resin acids as well as being effective in color removal.

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