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Speciation of Pulp Mill Derived Resin Acids in the Tarawera River, New Zealand

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We have previously reported the levels of resin acids and degraded resin neutrals in Tarawera River water and sediment samples, collected downstream of the discharge points of two pulp and paper mills (Wilkins, et al 1996a, 1996b, Wilkins & Panadam, 1987). While much is known about the levels of resin acids, cations, anion, and absorbance of Tarawera River water samples, and adjacent ground waters (Wilkins et al 1996b, 1998), no account of resin acid speciation in this natural receiving water has appeared. Previous work in our laboratory has shown that ultra filtration significantly reduces the recovery of resin acids from Tarawera River water samples (Osborne 1991).

In this paper we report an assessment of the level of extractable resin acids recoverable from Whatman No 1, glass fiber, and 3, 0.8, 0.45, 0.2, 0.05 and 0.025 µm filtered SH30 Tarawera River water samples. The results presented here show that in natural Tarawera River water (pH 7.3-7.6) resin acids are predominantly surface adsorbed (bound) to suspended solid material with particle sizes in the range 0.02-15 microns.

MATERIALS AND METHODS

Water samples, in screw capped 2.5 L glass Winchesters, were collected from the Tarawera River at the SH30 bridge on 16/6/98 and 14/12/98, and transported to our laboratory on the day of collection. Unless otherwise specified, water samples were stored at 5°C until required for extraction. Cation and color levels were determined using filtered (Whatman No 1) solutions. Na, K (diluted 5 fold), and Ca levels were determined at 422.7, 766.5 and 589.0 nm respectively, using a GBC 909 AA spectrometer and an air-acetylene flame. Fe levels were determined at 386 nm using a GBC 905 furnace AA spectrometer. Absorbances at 270, 340 and 440 nm were determined using a 1 cm quartz cell and a Hitachi 15-20 spectrometer. The pH of water samples was determined using an EPM-120 pH meter, calibrated against pH 6.86 and 4.00 buffer solutions. Conductivity was determined at 25°C using a Philip PR 9501 conductivity meter, calibrated against 0.01 mol/L KCl. Turbidity was determined using a Hach 2100 Turbidimeter. Total and free resin acid levels were determined for well mixed 1 L sub-samples of river water, typically prepared by combining 3 x 2.5 L of river water in a 10 L vessel. After vacuum assisted filtration through Whatman No 1, glass fiber (Whatman), or 3, 0.8, 0.45, 0.2, 0.05 or 0.025 µm (Millipore) filter papers, water samples were liquid/liquid extracted with CH_2Cl_2 for 16 h. *O*-Methylpodocarpic acid ethyl ester as internal standard was added to the extractive solutions which were

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concentrated using a rotary evaporator, derivatised with CH_2N_2, and analysed using selected ion mode (SIM) GUMS detection, as reported previously (Wilkins et al. 1996b). Bound resin acid levels were determined by Soxhlet extraction of Whatman No 1, glass fiber, or 3 to 0.025 µm (Millipore) filter papers with CH_2Cl_2 *O*-Methylpodocarpic acid ethyl ester, as internal standard, was added to extractive solutions, which were concentrated using a rotary evaporator, derivatised with CH2N2, and analysed using selected ion mode (SIM) GC/MS detection, as reported previously (Wilkins et al. 1996b). Bound resin acid levels are reported as µg/L of filtered river water. Recovery of *O*-methylpodocarpic acid spiked directly into water samples or onto filter papers, prior to liquid-liquid extraction or Soxhlet extraction, respectively, was typically in the range 75-115%. Replicate data (n = 4, 5 or 6), standard deviation and % CVs are reported for SH30, Whatman No 1 and glass fiber filtered river water samples (Table 2). Summary data for other river water samples are given in Table 3. All calculations were performed using purpose written Excel spreadsheets. Resin acid concentrations (Tables 1, 2, 3, 5 and 7) are rounded to ± 0.1, or 0.01 µg/L for concentrations in the range 0.02-0.99, or 1.0-65.0 µg/L, respectively.

River water collected on 14/12/98 was sequentially filtered through glass fiber (7.5 L), and 3 µm (6.4 L), 0.8 µm (5.3 L), 0.45 µm (4.2 L), 0.2 µm (3.1 L), 0.05 µm (2 L) and 0.025 µm (0.8 L) filter papers. After each filtration step, 1 L (or 0.7 L for 0.025 µm) of filtered water and the corresponding filter paper were liquid-liquid extracted, or Soxhlet extracted, respectively. Filtered water samples were prepared and liquid/liquid, or Soxhlet extracted (filter papers), on the same day. Cation, color, conductivity and turbidity levels were also determined for each of the filtered river water samples.

RESULTS AND DISCUSSION

In recent years pHs ranging from 2 to 12 have been used in liquid-liquid extraction of resin acid from pulp mill effluents. Some workers have advocated the use of an acidic extraction medium to minimise dissociation of resin acids, while other worker have recommended an alkaline extraction media in order to minimise resin acid isomerisation (Li et al, 1996; Morales et al, 1992; Voss & Rapsomatiotis, 1985, Richardson & Bloom, 1982).

Resin acid levels identified in replicate pH 4, pH 7.6 (natural river pH) and pH 10 liquid/liquid extractions of Tarawera River water samples collected at the SH30 bridge, ca 4 km downstream of the discharge points of two pulp and paper mills are presented in Table 1. These results show that for highly colored Tarawera River water samples, extraction at pH 10, offers no advantage over extraction at pH 7.6, while extraction at pH 4 results in a lesser recover of resin acids (ca 80% of that recoverable at pH 7.6).

The decreased recovery obtained after 0.45 µm filtration of pH 4, 7.6 and 10 river water samples (Table 1) suggested that some of the recoverable resin acids were bound to suspended solid materials (sediment particles, macromolecular aggregates of lignans, etc). While some information is available in respect of cation speciation in natural waterways (for example Shkinev et al (1996) have recently reported an assessment of Na, K, Mg, Ca, Mn, Ni, Al, Zn and Fe speciation in two German rivers, no information is available in respect of resin acid speciation in New Zealand recipient waters.

Table 1. SIM GC/MS determined resin acid levels (µg/L, mean of duplicate analyses) identified in pH adjusted SH30 Tarawera River water samples, collected 16/6/1998.

	seco1/2	pim	18-Ab	DHAA	abiet	13-ene	Cl's	TRA	%
pH 7.6 (as collected)	11.6	3.8	23.4	8.5	2.4	16.1	3.6	69.4	
pH 4	9.6	3.1	17.8	8.4	1.7	12.0	2.2	54.8	79%
pH 10	10.8	3.6	22.0	8.5	2.2	15.6	2.7	65.4	94%
pH 7.6 0.45 µm filtered	3.7	1.7	10.6	4.2	0.5	7.1	1.1	28.9	42%
pH 4 0.45 µm filtered	4.5	1.8	8.9	5.4	0.5	6.7	1.0	28.8	41%
pH 10 0.45 µm filtered	3.4	1.5	9.3	4.0	0.5	6.4	1.0	26.1	38%

Abbreviations: seco 1/2 = secodehydroabietic acids-1 and 2; pim = pimaric acid, 18-Ab = abietan-18-oic acid; DHAA = dehydroabietic acid; abiet = abietic acid; 13-ene = abiet-13-en-18-oic acid; Cl's = 12-Cl, 14-Cl and 12,14-dichlorodehydroabietic acids; TRA = total resin acids; % = % resin acids relative to unfiltered SH30 water, pH 7.6.

Replicate extractions of 0.45 µm filtered river water samples, collected 16/6/98, resulted in resin acid recoveries of 38-42% of that obtained for unfiltered pH 7.6 (natural) river water, irrespective of the extraction pH. Subsequently, multiple extractions (n = 3 to 6) of Whatman No 1, glass fiber, 0.8 and 0.45 µm filtered river water (collected 12/12/98) at its natural pH, verified the presence of appreciable levels of particle bound resin acids (Tables 2 and 3). Reproducibility and standard deviation data established the reliability and significance of the results. Color, conductivity and Na K, Ca and Fe) levels were also determined in replicate (n = 3 to 6) for the filtered river water samples (Table 4).

The analyses of organic substances in recipient water samples is compounded by the continuing bio-degradation of organic substances after sample collection. Degradation can (for example) be arrested by the addition of sodium azide or mercuric salts, however these species interfere with cation analyses and may function as resin acid focculation agents (eg by formation of mercuric resin acid salts). Application of curve fitting techniques to resin acid levels determined for river water samples stored at 5°C in screw capped glass Winchesters for 1, 6 and 22 days (see Tables 2 and 3) were consistent with the conclusions that total resin acid levels decayed exponentially with a half-life of 19 days, and that over a 3 day period resin acid levels typically decayed by 5-7%. This decrease is of the order of, or in most cases less than, the standard deviation established for replicate extractions (see Table 2). Equipment limitations necessitated that groups of filtration and extraction experiments were typically carried out over 2-3 day periods. The results presented in Tables 2 and 3 should be interpreted accordingly. On two occasions unfiltered river water samples, sample F (Table 2) and samples E and F (Table 3), were allowed to stand in open beakers, at 5°C for 24 hr, before liquid/liquid extraction. These samples exhibited resin acid levels 79-83% of those determined for replicate samples (ex fully filled, capped, Winchesters) extracted the preceding day.

Filtration through glass fiber and Whatman No 1 filter paper reduced total resin acid levels to 64 and 68% respectively of the average level determined for SH30 water samples extracted 24-48 hours previously. The bulk of resin acids removed by filtration were recovered by Soxhlet extraction of the filter papers. The standard deviation and % coefficient of variation (% CV) determined for the Soxhlet extractions were higher than those determined for liquid/liquid extraction of filtered river water samples (see Table 2). Filtration through 0.45 µm and 0.8 µm filter papers (performed 6 and 22 days after collection respectively), resulted in resin acid reductions of 34-35% relative to similarly aged river water samples.

Table 2. SIM GC/MS determined resin acid levels (µg/L, mean of replicate analyses) identified in Tarawera River SH30 water samples, collected 14/12/98.

	seco 1/2	pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30 A [a]	8.3	6.7	17.8	10.0	15.8	2.4	61.0	
SH30 B	8.2	6.5	18.0	10.1	15.2	2.7	60.7	
SH30 C	9.0	7.0	17.0	10.1	15.5	2.5	61.1	
SH30 D	9.2	7.1	17.9	10.6	16.0	2.3	63.0	
SH30 E	8.1	6.8	17.7	10.5	15.7	2.5	61.2	
average	8.6	6.8	17.7	10.3	15.6	2.5	61.4	
stdev	0.49	0.23	0.39	0.29	0.31	0.14	0.94	
% CV	5.8%	3.3%	2.2%	2.8%	2.0%	5.7%	1.5%	
SH30 F (+24 hr)[b]	5.8	5.7	14.0	8.5	12.0	2.0	48.0	78%
Whatman No 1 filt. A[c]	5.8	5.9	12.3	7.7	10.8	2.0	44.3	
Whatman No 1 filt. B	5.9	6.3	13.3	7.8	11.7	2.2	47.1	
Whatman No 1 filt. C	5.9	6.1	12.6	8.0	11.2	1.9	45.7	
Whatman No 1 filt. D	4.3	4.6	9.9	6.5	8.9	1.5	35.7	
Whatman No 1 filt. E	5.3	5.7	12.1	7.4	10.7	1.9	43.2	
Whatman No 1 filt. F	4.0	4.2	9.1	8.3	8.3	1.4	35.2	
average (n = 6)	5.2	5.5	11.6	7.6	10.3	1.8	41.9	68%
stdev	0.85	0.84	1.67	0.62	1.36	0.29	5.15	
% CV	16%	15%	14%	8.2%	13%	16%	12%	
Whatman No 1 Sox. A[c]	0.73	0.80	2.4	1.33	2.2	0.24	7.7	
Whatman No 1 Sox. B	0.49	0.53	1.4	0.85	1.3	0.27	4.8	
Whatman No 1 Sox. C	0.43	0.47	1.2	0.68	1.0	0.23	4.0	
Whatman No 1 Sox. D	0.37	0.40	1.1	0.62	0.8	0.12	3.4	
Whatman No 1 Sox. E	0.42	0.32	0.9	0.55	0.7	0.28	3.2	
Whatman No 1 Sox. F	0.54	0.60	1.4	0.83	1.2	0.04	4.3	
average (n = 6)	0.45	0.52	1.4	0.81	1.2	0.20	4.6	7.5%
stdev	0.13	0.17	0.53	0.28	0.54	0.09	1.7	
% CV	26%	32%	39%	35%	46%	48%	36%	
glass fiber filtered A[b]	6.5	5.2	11.5	11.5	8.8	1.8	45.2	
glass fiber filtered B	6.2	4.9	10.8	8.6	8.1	1.6	40.1	
glass fiber filtered C	6.1	4.9	10.8	6.8	8.4	1.7	38.5	
glass fiber filtered D	5.5	4.5	10.1	7.1	7.9	1.7	36.7	
glass fiber filtered E	6.0	4.8	10.7	7.0	8.1	1.6	38.3	
glass fiber filtered F	5.8	4.6	9.6	6.6	7.1	1.6	35.3	
average (n = 6)	5.9	4.7	10.46	7.2	7.9	1.6	39.0	64%
stdev	0.34	0.24	0.65	1.91	0.56	0.09	3.5	
% CV	5.8%	5.0%	6.2%	27%	7.1%	5.8%	8.9%	
glass fiber Soxhlet A[b]	1.5	1.3	4.5	2.8	3.4	0.51	14.0	
glass fiber Soxhlet B	1.6	1.4	4.3	3.1	3.0	0.52	13.9	
glass fiber Soxhlet C	1.8	1.9	5.5	3.1	4.8	0.66	17.8	
glass fiber Soxhlet D	1.5	1.4	4.1	2.6	3.5	0.52	13.6	
glass fiber Soxhlet E	1.7	1.7	5.1	2.7	4.4	0.56	16.2	
glass fiber Soxhlet F	1.4	1.1	3.8	1.9	2.7	0.42	11.3	
average (n = 6)	1.6	1.5	4.6	2.7	3.7	0.54	14.4	24%
stdev	0.15	0.28	0.63	0.45	0.82	0.08	2.2	
% CV	9.5%	19%	14%	17%	22%	15%	15%	

Abbreviations are as in Table 1, [a] extracted 15/12/98, [b] extracted 16/12/98, [c] extracted 17/12/98.

Table 3. SIM GC/MS determined resin acid levels (µg/L,) (mean of replicate analyses) identified in SH30 Tarawera River, and 0.45 and 0.8 µm filtered, water samples, collected 14/12/1998.

	seco 1/2	pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30[a] (n = 4)	6.0	4.2	17.1	9.7	12.8	1.9	51.6	
stdev	0.34	0.10	0.34	0.50	0.32	0.10	1.1	
% CV	5.7%	2.4%	2.0%	5.2%	2.5%	5.0%	2.2%	
SH30 (+24 hr)[b] (n = 2)	4.5	3.6	13.9	8.0	10.9	2.2	42.9	83%
0.45 mm filtered (n = 4)	2.5	1.5	5.5	5.0	3.1	0.71	17.5	34%
stdev	0.33	0.21	1.36	0.53	0.58	0.10	3.2	
% CV	13%	14%	25%	11%	19%	14%	18%	
0.45 mm Soxhlet (n = 6)	2.5	1.7	8.2	5.3	6.0	0.81	24.6	47%
stdev	0.53	0.47	1.64	1.36	1.70	0.25	5.7	
% CV	21%	27%	20%	26%	28%	31%	23%	
SH30[c] (n = 3)	1.8	0.95	9.2	9.0	5.7	2.2	28.9	
stdev	0.12	0.09	0.35	0.35	0.75	0.0	1.6	
% CV	6.5%	9.5%	3.8%	3.8%	13%	-	5.5%	
0.8 µm filtered (n = 3)	0.93	0.29	2.5	4.1	1.6	0.67	10.0	35%
stdev	0.09	0.06	0.32	0.67	0.12	0.20	1.0	
% CV	9.9%	19%	13%	16%	7.4%	29%	10%	
0.8 µm Soxhlet (n = 3)	0.68	0.43	4.2	3.4	3.3	1.2	13.2	47%
stdev	0.09	0.04	0.44	0.42	0.46	0.19	0.9	
% CV	14%	8.4%	10%	12%	14%	8.3%	6.8%	

Abbreviations are as in Table 1; [a] extracted 20/12/98; [b] extracted 21/12/98 after overnight storage in a beaker at room temperature; [c] extracted 5/1/99.

Table 4. Color (absorbance), conductivity and cation levels (ppm) determined for SH30 Tarawera River water samples, collected 14/12/98.

	270 nm	340 nm	440 nm	cond x 10^{-3}	Na ppm	K ppm	Ca ppm	Fe ppm
SH30 (15/12/98)[a]	0.186	0.074	0.027	0.410	67.6	8.2	0.80	0.18
stdev (n = 6)	0.002	0.000	0.001	0.000	1.7	0.1	0.10	0.05
Whatman No1	0.179	0.071	0.023	0.410	66.5	8.0	0.84	0.18
stdev (n = 6)	0.002	0.001	0.002	0.000	1.8	0.1	0.07	0.01
Glass fiber	0.169	0.061	0.019	0.410	66.4	7.9	0.62	0.21
stdev (n = 6)	0.003	0.002	0.002	0.000	0.9	0.2	0.07	0.05
SH30 (20/12/98)[a]	0.163	0.060	0.019	0.410	61.8	8.5	0.82	0.12
stdev (n = 6)	0.002	0.001	0.001	0.000	2.5	0.4	0.02	0.01
0.45 µm filtered	0.137	0.047	0.013	0.406	56.9	8.5	0.86	0.11
stdev (n = 6)	0.003	0.001	0.001	0.000	0.9	0.3	0.05	0.02
SH30 (7/1/98)[a]	0.161	0.060	0.019	0.410	65.3	8.1	0.80	0.13
stdev (n = 4)	0.001	0.001	0.001	0.000	2.0	0.3	0.08	0.02
0.80 µm filtered	0.130	0.046	0.011	0.406	64.9	8.3	0.84	0.11
stdev (n = 4	0.003	0.001	0.001	0.000	2.5	0.1	0.07	0.06

[a] extraction date

Greater levels of resin acids were recovered by Soxhlet extraction of the respective filter papers (c 47% of the levels in unfiltered river water samples). Filtration through Whatman No 1, glass fiber, 0.45 and 0.8 µm filter papers did not alter cation or conductivity levels (Table 4). Color levels were however attenuated, especially so at 340 and 440 nm. The downward trend in color levels exhibited by unfiltered SH30 Tarawera River water samples (eg absorbances of 0.186, 0.074 and 0.027 at 270, 340 and 440 nm respectively when first collected compared to absorbances of 0.163, 0.060 and 0.019 respectively after 6 days) can be attributed to the gradual flocculation (precipitation) of lignans and other chromophoric polyphenols during storage at 5°C.

The results obtained for river water sequentially filtered through glass fiber, 3, 0.8, 0.45, 0.2, 0.05 and 0.025 µm filtered papers are presented in Tables 5 and 6. Resin acid removal was consistent with results reported in Tables 3 and 4. The design of the multi-filtration experiment is such that for a particular pore size, the sum of the liquid/liquid and Soxhlet extracted resin acid levels should equal the liquid/liquid determined level of resin acids in the preceding filtered water sample (Figure 1).

Table 5. SIM GC/MS determined resin acid levels (µg/L) identified in multi-filtered Tarawera River SH30 water samples

	seco	1/2 pim	18-Ab	DHAA	13-ene	Cl's	TRA	%
SH30 A (24/12/98)[a]	3.1	3.8	12.9	8.3	11.0	1.8	40.9	
SH30 B (24/12/98)	3.0	2.9	11.4	8.2	10.5	1.8	37.8	
average	3.1	3.4	12.2	8.3	10.8	1.8	39.6	100%
glass fiber (liq/liq)	1.7	1.9	6.6	5.5	5.4	1.1	22.20	56%
3 µm (liq/liq)	1.4	1.4	5.1	4.9	3.8	0.9	17.5	44%
0.8 µm (liq/liq)	1.3	0.9	2.8	4.8	2.2	0.5	12.5	32%
0.45 µm (liq/liq)	1.2	1.0	3.4	4.0	2.5	0.6	12.7	32%
0.2 µm (liq/liq)	1.0	0.7	2.5	1.8	2.1	0.6	8.7	22%
0.05 µm (liq/liq)	0.9	0.5	1.1	3.2	-	0.3	6.0	15%
0.025 µm (liq/liq)	0.5	0.4	0.2	2.4	-	-	3.5	9%
glass fiber (Soxhlet)	0.5	0.6	2.6	1.8	3.2	0.4	9.1	23%
3 µm (Soxhlet)	0.23	0.4	1.3	1.1	1.7	0.2	4.9	13%
0.8 µm (Soxhlet)	0.08	0.1	0.5	0.4	0.6	0.1	1.8	5%
0.45 µm (Soxhlet)	0.06	0.1	0.2	0.3	0.3	tr	1.0	3%
0.2 µm (Soxhlet)	0.1	0.2	0.6	0.6	0.7	0.1	2.3	6%
0.05 µm (Soxhlet)	0.3	0.6	1.5	1.7	1.3	0.2	5.6	14%
0.025 µm (Soxhlet)	-	-	0.2	0.9	-	0.1	1.2	3%

Abbreviations are as in Table 1, [a] extraction date.

There appears to be a logarithmic relationship between filter pore size and resin acid level (Figure 2). A downward trend was apparent in color levels with the greatest change (% reduction) in color occurring at 440 nm. A similar downward trend was apparent in turbidity levels. Conductivity, Na, K and Ca levels were not affected by filtration. On the other hand, Fe levels were substantially attenuated by 0.05 µm filtration, as was also the case in the conventional filtration experiment. This suggests the presence in Tarawera River water samples of fine Fe colloidal particles < 0.1 µm in size. Resin acid levels did not correlate with Fe levels.

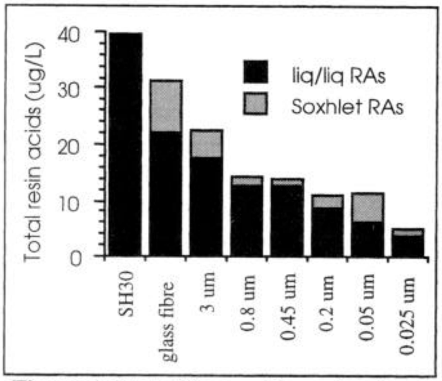

Figure 1. Plot of free and bound resin acid levels determined for multi-filtered Tarawera River water samples.

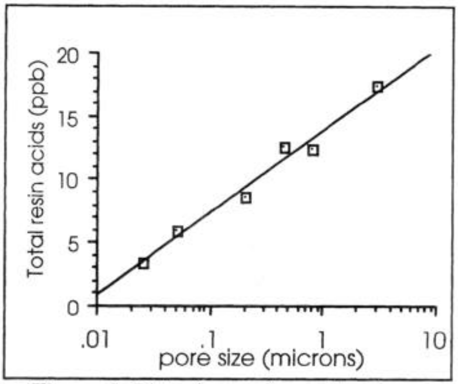

Figure 2. Plot of pore size and resin acid levels determined for multi-filtered Tarawera River water samples.

Table 6. Color, turbidity, conductivity and cation levels (ppm) determined for SH30 Tarawera River water, collected 14/12/98.

	270 nm	340 nm	440 nm	turbidity	cond x 10^{-3}	Na ppm	K ppm	Ca ppm	Fe ppm
SH30	0.147	0.051	0.016	2.94	0.410	65.2	9.0	0.86	0.24
glass fiber filtered	0.145	0.048	0.013	1.50	0.406	66.3	7.9	0.70	0.22
3 µm filtered	0.136	0.044	0.011	1.14	0.406	69.1	8.2	0.84	0.21
0.8 µm filtered	0.132	0.042	0.007	1.20	0.406	63.9	8.0	0.72	0.26
0.45 µm filtered	0.126	0.037	0.006	1.20	0.406	68.0	8.3	0.77	0.20
0.2 µm filtered	0.117	0.034	0.006	0.97	0.404	66.3	8.3	0.68	0.22
0.05 µm filtered	0.117	0.033	0.005	0.87	0.404	66.3	8.7	0.71	0.02
0.025 µm filtered	0.111	0.030	0.004	0.80	0.404	68.9	8.0	0.74	0.02

Generally, low levels of degraded resin neutrals (principally fichtelite) are also present in Tarawera River water samples (Wilkins & Panadam, 1987), however on some occasions elevated levels of resin neutrals may be present (released, for example, during periodic dredging of effluent treatment ponds). Water samples collected on 16/6/98 contained greater than normal levels of resin neutrals (Table 1). Resin neutrals were more efficiently recovered from unfiltered water samples, without pH adjustment, than was the case at pH 4 and pH 10. 0.045 µm filtration prior to liquid extraction substantially reduced the recoverability of resin neutrals.

Table 7. SIM GC/MS determined resin neutral levels (µg/L) identified in SH30 Tarawera River water samples collected 16/6/98. % recoveries relative to natural, unfiltered river water are given in brackets.

	fichtelite	dehydro-abietin	tetrahydro-retene	retene	total resin neutrals
SH30	5.7	0.70	4.2	11.0	21.6
SH30 pH 4	4.8 (84%)	0.42 (61%)	2.9 (68%)	7.1 (64%)	15.2 (70%)
SH30 pH 10	4.5 (79%)	0.50 (71%)	3.0 (72%)	7.7 (70%)	15.8 (73%)
SH30 0.45 µm	2.2 (38%)	0.16 (23%)	0.44 (10%)	0.8 (7%)	3.6 (17%)
SH30 pH 4 0.45 µm	2.6 (45%)	0.17 (25%)	0.66 (15%)	1.1 (10%)	4.5 (21%)
SH30 pH10 0.45 µm	2.1 (36%)	0.10 (14%)	0.41 (10%)	0.8 (7%)	3.3 (15%)

The greater the aromaticity of the substrate (3, 2, 1 and 0 aromatic rings are present in retene, tetrahydroretene, dehydroabietin and fichtelite respectively), the greater the removal by 0.45 µm filtration. It is apparent that resin neutrals, which because of their hydrocarbon nature and absence of a carboxyl group are less hydrophilic than resin acids, are more extensively surface absorbed to suspended solid particles than are resin acids (Table 1).

This work shows that liquid/liquid extraction can be used to reliably recover free and adsorbed resin acids in Tarawera River (but not necessarily other) water samples. Our results have implications in respect of the ability of some extraction protocols to recover both free and particle bound resin acids and resin neutrals. In particular, there appears to be a need to critically assess if solid phase methods (eg those using Bond-elut type C8 or Cl8 cartridges) recover resin acids and resin neutrals by a combination of absorption (from the aqueous phase to the C8 or Cl8 phase), and by filtration (trapping of particulates, which may or may not release absorbed resin acids when flushed with methanol or other eluents). We also anticipate that a knowledge of resin acid speciation effects and associations with particulate matter and chromophoric macromolecules, will contribute to the development of improved treatment technologies for pulp mill and other effluent waters.

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