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Sodium, Calcium, and Resin Acid Levels in Ground Water and Sediments from Two Sites Adjacent to the Tarawera River, New Zealand

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We have previously reported the levels of sodium and a variety of pulp mill sourced organic compounds in water samples from the Tarawera River (Wilkins et al. 1996). This river, which receives effluents from two pulp mills, is located in the Bay of Plenty region of the North Island of New Zealand. During the two synoptic surveys, conducted in December 1991 and January-February 1992, the mean levels of sodium and total resin acids detected in downstream water samples were 65 and 74 ppm and, 34 and 121 ppb, respectively (Wilkins et al. 1996). An unusual aspect of this investigation was the detection of an appreciable level of abietan-18-oic acid.

At several points during its passage across the Western Rangitaiki Plains the Tarawera River is constrained behind a stop bank and perched 1-2 m above surrounding farmland. A series of drains and canals collect water from the surrounding farmland and discharge it to the Tarawera River 200 m prior to its entry into the sea, near the township of Matata. At two points the Western Drain traverses farmland in close proximity to the Tarawera River. Water samples from one of these sites (Otakiri Road) are typically characterised by an elevated sodium level (McIntosh, 1995). Leakage of river water, via ground water seepage has been hypothesised as the source of the additional sodium burden. Other than for the observation that seepage is periodically visible on adjacent farmland, much of which is drained by shallow surface drains linked to the Western Drain, little is known about the ground water hydrology and aquifer characteristics, or the sites at which seepage occurs and the conditions under which it is significant. A better understanding of the conditions and processes involved would assist in identifying attenuation and other effects experienced by inorganic and organic species in ground water and aquifers systems adjacent to the Tarawera River.

MATERIALS AND METHODS

River water, drain water, ground water and sediment samples were collected on 28th September 1995 (site A), or on 30th October 1995 (site B), from locations adjacent to the Tarawera River. Sample details are given in Table 1. The approximate topography of the sample stations are depicted in Figure 1.

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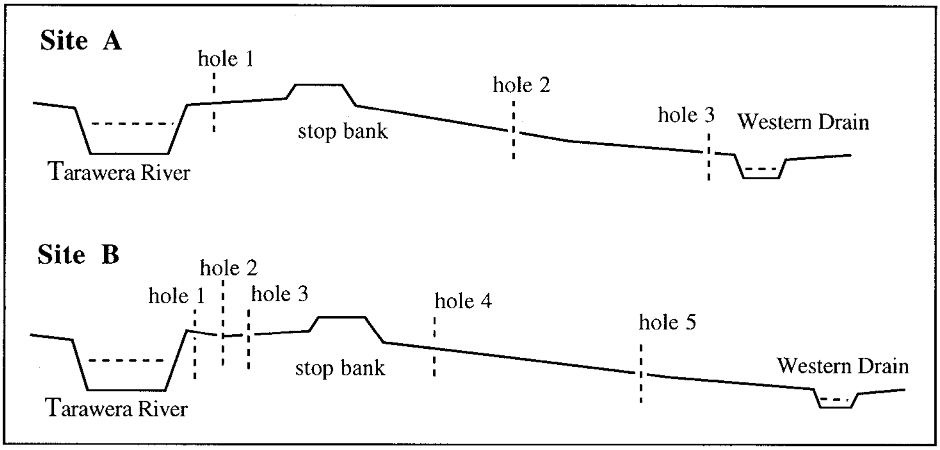

Figure 1. Schematic representation of the topography of the site A and B sample stations, adjacent to the Tarawera River.

Table 1. Sample station locations, sample dates and bore hole parameters.

	site code	distance from sea[a] (km)	distance from river (m)	distance from drain (m)	ground water depth[b] (m)	depth below river[c] (m)
28/9/95 samples						
drain (Johnsons Road)		16.0				
drain (Otakiri Road)	A	13.0	92			1.25
river (Otakiri Road)	A	13.0		92		
bore hole 1	A		2.1	89.9	2.5	-0.02
bore hole 2	A		44	48	1.0	0.20
bore hole 3	A		87	5	2.5	1.25
30/10/95 samples						
drain (Johnsons Road)		16.0				
drain (Otakiri Road)		13.0				
drain (E-M Road)		6.3				
drain (Waikamihi Stream)	B	9.1	122			
river (Waikamihi Stream)	B	9.1		122		
bore hole 1	B		0.7	121.3	1.2	0.02
bore hole 2	B		2.5	119.5	1.0	0.02
bore hole 3	B		4	118	1.0	0.04
bore hole 4	B		27	95	1.1	0.15
bore hole 5	B		50	72	0.6	0.02

drain = Western Drain, river = Tarawera River, E-M Road = Edgecumbe-Matata Road
[a] relative to the course of the Tarawera River, [b] depth below ground level, [c] depth of ground water below river water level.

The liquid-liquid or Soxhlet extraction, derivatisation, and gas chromatographic protocols applied to 1 L water samples, or to sieved (< 250 µm) sediments (typically 15 g samples) were as reported previously (Wilkins et al. 1996), other than the use of *O*-methylpodocarpic acid and ethyl *O*-methylpodocarpate as surrogate (recovery) and primary (quantification) standards respectively, and selected ion mode (SIM) GC-MS detection. SIM GC-MS response factors were determined relative to ethyl *O*-methylpodocarpate, for methylated specimens of *O*-methylpodocarpic acid, pimaric acid, dehydroabietic acid, chlorodehydroabietic acid isomers, and 12,14-dichlorodehydroabietic acid. SIM GC-MS response factors were also determined for the methyl esters of secodehydroabietic acid isomers and abietan-18-oic acid using a reference solution containing a known, GC-FID determined, amount of these compounds (Wilkins et al. 1996). Ions monitored were *m/z* 146, 121, 163, 239, 227, 273+275 and 307+309, arising from the methyl esters of secodehydroabietic acid isomers, pimaric acid, abietan-18-oic acid, dehydroabietic acid, *O*-methylpodocarpic acid (and its ethyl ester), chlorodehydro-abietic acid isomers and dichlordehydroabietic acid, respectively. Detection limits of 0.1 ppb and 0.01 ppm were applied to water and sediment analyses, respectively. The reproducibility and recovery characteristics of the analytical protocols was assessed in replicate extractions. Results for four replicate liquid-liquid extractions of a Tarawera River water sample are given in Table 2.

Table 2. SIM GC-MS determined concentrations (ppb) of resin acids for four replicate extractions of a Tarawera River water sample, collected 12th February 1995. at the SH30 bridge.

	1	2	3	4	mean	σ	CV
secodehydroabietic acid-1	4.5	5.7	4.2	4.8	4.8	0.7	15
secodehydroabietic acid-2	1.9	2.6	1.6	2.1	2.0	0.4	20
pimaric acid	10.4	10.1	9.1	8.2	9.4	1.0	11
abietan-18-oic acid	35.9	45.5	32.9	39.7	38.5	5.4	14
dehydroabietic acid	15.7	16.7	13.2	14.9	15.1	1.5	10
12-chlorodehydroabietic acid	0.3	0.3	0.3	0.2	0.3	-	-
14-chlorodehydroabietic acid	1.7	1.8	1.2	1.3	1.5	0.3	23
12,14-dichlorodehydroabietic acid	2.9	3.3	2.0	2.1	2.6	0.6	23
% recovery of PDA[a]	93.7	86.8	93.3	87.6	90.4	3.7	4

[a] PDA = *O*-methylpodocarpic acid

Sodium and calcium levels were determined using a GBC 909 atomic absorption (AA) spectrometer. Samples were filtered through Whatman No 1 filter paper prior to AA analyses. Sodium levels were determined using solutions which had been diluted 20 fold.

RESULTS AND DISCUSSION

Ground water was encountered in three bore holes drilled at site A (Otakiri Road) on 28th September 1995, but not 12th October 1995. Visual inspection of the river bank established that on 28th September 1995, the river level was c 600 mm higher than on 12th October 1995 when the river flow was considered to be ‘normal’. The sodium and calcium levels encountered in Tarawera River, Western Drain and ground water from three bore holes at site A are presented in Table 3, and can be compared with those reported in earlier investigations (McIntosh 1995). These investigations have shown that water from the lower reaches of the Tarawera River is characterised by a high sodium level, due to a combination of pulp mill and geothermal inputs, and by a low calcium level, due to its low availability in the rhyolitic rocks which make up the Western Rangitaiki Plains. Calcium is also low in geothermal waters, but may be enhanced in agricultural soils through the application of lime ($CaCO_3$) and superphosphate ($CaHPO_4$, $CaSO_4.2H_2O$). The Na/Ca ratio of the water samples is a useful indicator of the extent to which ground water is influenced by river water (see Table 3).

Table 3. Concentrations of sodium, calcium, Na/Ca ratio, and flow rates, determined for some Western Drain, Tarawera River and ground water samples.

	Flow (L/s)	Na (ppm)	Ca (ppm)	Na/Ca ratio
28/9/1995 samples				
Western Drain, Otakiri Road[a]		33	2.4	14
Tarawera River, Otakiri Road[a]		64	2.2	29
bore hole 1		57	1.9	30
bore hole 2		40	2.8	14
bore hole 3		26	8.8	3.0
17/3/1993 samples[b]				
Tarawera River, Awakaponga	18485	72	7.1	10
Western Drain, Johnsons Road	4	16	9.3	1.7
Western Drain, Otakiri Road[a]	10	52	9.6	5.4
Western Drain, Edgecumbe-Matata Road	73	42	5.3	7.9
Awakaponga Canal, Edgecumbe-Matata Road	417	15	3.6	4.2
Awaiti Canal, Edgecumbe-Matata Road	37	24	16	1.5
Omeheu Drain, Edgecumbe-Matata Road	35	25	17	1.5
Omeheu Canal, Edgecumbe-Matata Road	148	23	24	0.95
Omeheu Adjunct Canal, Edgecumbe-Matata Road	2	40	42	0.95

[a] At the junction of Otakiri and Soldiers Road; [b] Source: McIntosh (1995), Environment BOP, Environment Report 95/6, reproduced with permission.

In both the present and previous studies (McIntosh 1995), the Na level determined for Western Drain water at Otakiri Road are appreciably greater than those recorded for water at Johnsons Road. Intriguingly, most of the 1993 calcium levels (and therefore Na/Ca ratios) are 3-4 times greater than those determined in the present study. The diminished sodium level recorded for Western Drain water at the Edgecumbe-Matata Road (6.7 km downstream of Otakiri Road) can be attributed to dilution. At this point, however, the total sodium burden (concentration multiplied by flow) is appreciably greater (see Table 1), indicating sodium inflow continues below Otakiri Road, possibly occurring in the vicinity of site B (Table 1) where the Western Drain is again in close proximity to the Tarawera River.

Appreciable levels of resin acids, including chlorinated dehydroabietic acid isomers were identified (Table 4) in ground water from the site A (Otakiri Road) bore hole adjacent to the Tarawera River (hole 1). Lesser levels were detected in ground water from the second bore hole. Resin acids were also significant components of the sediments recovered from each of these bore holes (Table 5). Only traces of resin acids were detected in ground water and sediments from the third bore hole, adjacent to the Western Drain, indicating negligible river influence at this point. In general the organic results (Tables 4 and 5) exhibit the same trend apparent in the sodium results (Table 3), in that levels decrease with increasing distance from the river.

Table 4. SIM GC-MS determined concentrations (ppb) of resin acids identified in site A (Otakiri Road) water samples, collected 28th September 1995.

	river water	bore hole samples 1	2	3	Western Drain
secodehydroabietic acid-1	4.0	0.6	0.1	-	-
secodehydroabietic acid-2	1.6	0.3	tr	-	-
pimaric acid	3.0	2.9	0.5	tr	-
abietan-18-oic acid	67	19	1.9	0.1	0.2
dehydroabietic acid	32	10	1.8	0.2	0.2
12-chlorodehydroabietic acid	0.3	-	-	-	-
14-chlorodehydroabietic acid	1.2	0.4	0.3	0.1	-
12,14-dichlorodehydroabietic acid	1.7	0.9	0.1	-	-

tr = trace, "-" = not detected

Table 5. SIM GC-MS determined concentrations (ppm) of resin acids identified in sieved (< 250 μm) sediments from bore holes at site A (Otakiri Road), collected 28th September 1995.

	1A[a]	1B	2A	2B	3A	3B
secodehydroabietic acid-1	0.09	0.16	0.60	0.26	-	-
secodehydroabietic acid-2	0.06	0.09	0.32	0.22	-	-
pimaric acid	0.03	0.06	0.16	0.11	0.01	0.01
abietan-18-oic acid	0.87	1.7	4.2	2.0	-	0.03
dehydroabietic acid	1.7	2.4	9.9	4.4	0.26	0.27
12-chlorodehydroabietic acid	-	-	0.03	-	-	-
14-chlorodehydroabietic acid	0.06	0.09	0.47	0.07	-	-
12,14-dichlorodehydroabietic acid	0.01	0.02	0.06	0.02	-	-

[a] 'A' samples taken c 15 cm above ground water level; 'B' samples taken at ground water level.
tr = trace, "-" = not detected

Downstream of Otakiri Road (site A), the distance between the Western Drain and Tarawera River progressively increases to *c* 700 m, then briefly reduces to less than 100 m. Ground water was encountered in a series of five bore holes drilled on 12th October 1995, opposite the Waikamihi Stream (site B), 3.9 km downstream of site A. This site was selected for investigation on the basis of its surface topography, including a boggy field drain linked to the Western Drain, and a 2 m difference between river and drain water levels. At the time of sampling, ground water was present in a coarse white sand lens located 1-1.2 m below the surface. The levels of sodium, calcium and resin acids identified in ground water from the five site B bore holes are given in Tables 6 and 7. Only the first of three bore holes drilled in the vicinity on the river bank exhibited an elevated sodium level. In the absence of

Table 6. Sodium and calcium concentrations (ppm) determined for Western Drain. Tarawera River and ground water samples, collected 30th October 1995.

	Na (ppm)	Ca (ppm)	Na/Ca ratio
Western Drain, Johnsons Road	14	1.8	7.8
Western Drain, Otakiri Road	39	2.5	16
Tarawera River, opp. Waikamihi Stream	69	2.1	33
bore hole 1	53	4.6	12
bore hole 2	20	1.9	11
bore hole 3	20	2.1	9.5
bore hole 4	16	1.4	11
bore hole 5	17	3.1	5.5
Western Drain, opp. Waikamihi Stream	31	3.3	9.5
Western Drain, Edgecumbe-Matata Road	36	3.8	9.5

Table 7. SIM GC-MS determined concentrations (ppb) of resin acids identified in Tarawera River and ground water samples at site B (opposite the Waikamihi Stream), collected 30th October 1995.

	river water	bore hole sites				
		1	2	3	4	5
secodehydroabietic acid-1	1.6	tr	0.1	-	0.3	-
secodehydroabietic acid-2	0.8	tr	tr	-	0.2	-
pimaric acid	3.0	0.2	0.6	0.1	1.2	tr
abietan-18-oic acid	19	0.5	1.0	0.2	3.5	0.1
dehydroabietic acid	10	0.5	0.9	1.1	2.7	0.2
12-chlorodehydroabietic acid	0.2	-	-	-	-	-
14-chlorodehydroabietic acid	0.8	tr	0.3	-	0.1	-
12,14-dichlorodehydroabietic acid	2.6	-	0.1	-	-	-

tr = trace, "-" = not detected,

Table 8. SIM GC-MS determined concentrations (ppm) of resin acids identified in seived (< 250 µm) sediments from the Tarawera River and bore holes at site B (opposite the Waikamihi Stream), collected 30th October 1995.

	river	1A [a]	2A	2B	3A	4A	4B	5A
secodehydroabietic acid-1	50	0.11	-	-	-	-	-	-
secodehydroabietic acid-2	25	0.06	-	-	0.03	-	-	-
pimaric acid	61	0.03	0.01	tr	0.01	tr	tr	tr
abietan-18-oic acid	1184	3.30	0.22	0.28	0.75	0.13	0.08	tr
dehydroabietic acid	212	0.77	0.12	0.12	0.25	0.16	0.12	0.35
12-chlorodehydroabietic acid	2.7	0.01	-	-	-	-	-	-
14-chlorodehydroabietic acid	12	0.03	-	-	-	-	-	-
12,14-dichlorodehydroabietic acid	11	0.01	-	-	-	-	-	-

[a] 'A' samples taken c 15 cm above ground water level; 'B' samples (were available) taken at ground water level. tr = trace, "-" = not detected,

hydrological data, little significance can be attached to the variable levels of resin acids identified in ground water from the five bore holes.

Low levels of resin acids were detected in sediments from the five bore holes (Table 8). It is clear that on 30th October 1995 site B ground water was not significantly influenced by river water. None the less, the detection of resin acids in sediments from the five bore holes indicates there may be circumstances (for example during periods of high river flow) when significant outflow of river water occurs at this site.

It is likely that river water primarily reaches the site A and B near bank bore holes by a lateral permeation process (attenuated with increasing distance from the river bank), whereas more distance bore holes will only be influenced by river water if there is a significant aquifer flow through (for example) a coarse sand lens, as appears to be the case for bore hole 2 at site A on the 28th September 1995, but not 12th October 1995.

The levels of resin acids identified in the site A and site B water and sediment samples can be compared with those found in water and sediment 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), and a coastal lagoon adjacent to the Tarawera River (Wilkins, Healy and Leipe 1996).

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