

Cation, Anion, Conductivity, and Absorbance Characteristics of Tarawera River Seepage Water Entering the Western Drain, Eastern Bay of Plenty, New Zealand

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Two pulp mills, located downstream of the township of Kawerau, in the Eastern Bay of Plenty region of New Zealand, have for more than 35 years, discharged effluent waters to the Tarawera River. Upstream of the mill discharges river water has a high quality, while downstream water is highly coloured and characterised by diminished dissolved oxygen (BOPCC 1985, McIntosh 1995, Rutherford et al. 1991, Rutherford 1991) and by the presence of significant levels of resin acids (Wilkins et al. 1996a, Judd et al. 1996). During its passage across the Western Rangitaiki Plains the Tarawera River is constrained behind stop banks. At two points the river passes in close proximity to the Western Drain. This drain is one of a series of canals and drains which collect water from surrounding farmland and return it to the Tarawera River shortly before its entry to the sea near the township of Matata.

On some occasions elevated Na levels have been identified in water samples collected from the Western Drain in the vicinity of the Otakiri Road culvert, prompting the suggestion that seepage of Tarawera River water may be responsible (McIntosh, 1995). We have previously reported the levels of resin acids in some water and sediment samples from the Tarawera River, Western Drain, and adjacent bore holes (Wilkins et al. 1996b), however this study did not provide definitive evidence of a river water input to the Western Drain.

In the expectation that cation, anion and colour measurements would prove to be more definitive than resin acid data, we determined the Na, K, Mg, Ca, Fe, Al, Cl, NO₃, SO₄, conductivity and colour levels of two series of Tarawera River, Western Drain, bore hole and some other nearby canal and drain water samples, collected under both summer (low water table) and winter (high water table) conditions.

MATERIALS AND METHODS

Water samples (250 mL), in polyethylene bottles, were collected from the sites listed in Table 1 on 5/2/96 (dry, summer conditions) and 20/7/96 (wet, winter conditions). Shallow bore holes were drilled at the sites shown in Table 1 using a hand auger. Water table depths in the BH/4, BH/6, BH/7, BH/5A, BH/5B, BH/5C and BH/5D bore holes were c -0.20, -0.30, 0.0, 0.10, 0.84, 0.33 and 0.22 m above, or below (-) river water level respectively. Surface levels at these sites were c 1.5, 0.9, 0.5, 0.6, 0.84, 0.51, and 0.45 m respectively above the river water level. Cation, anion and colour levels were determined using filtered (Whatman No 1) solutions. Na, K, Ca, Mg and Fe levels (mean of 3 replicates) were determined at 422.7, 766.5, 589.0, 285.2 and 248.3 nm respectively, using a GBC 909 AA spectrometer and an air-acetylene

Table 1 Sample sites and collection dates (5/2/96 or 20/7/96).

Code	Site	Dist. to sea (km) ^a	date(s)	
			5/2/	20/7
TR/1	Tarawera River, Kawerau Town Bridge	28.5	√	
TR/2	Tarawera River, State Highway 30 Bridge	18.5	√	√
TR/3	Tarawera River, Johnsons Road	15.3	√	√
TR/4	Tarawera River, by wash out	14.0	√	
TR/5	Tarawera River, Otakiri Road	13.0		√
TR/6	Tarawera River, by kiwi fruit orchard	8.3	√	
TR/7	Tarawera River, by tree stump	7.4	√	
TR/8	Tarawera River, Edgecumbe-Matata Road	6.3	√	
TR/9	Tarawera River, State Highway 2	0.7	√	
WD/1	Western Drain, Hallett Road	(16.6)		√
WD/2	Western Drain, Johnsons Road	(16.0)	√	√
WD/3	Western Drain, c 300 m upstream of washout	(14.2)	√	√
WD/4	Western Drain, c 80 m downstream of washout	(13.7)	√	√
Seepage	Seepage water entering Western Drain ^b	(13.3)		√
WD/5	Western Drain, c 200 m upstr. of Otakiri Road	(13.2)		√
WD/6	Western Drain, Otakiri Road culvert	(13.0)	√	√
WD/7	Western Drain, c 700 m downstr. of Otakiri Rd	(12.3)	√	
WD/8	Western Drain, off Soldiers Road	(9.6)	√	
WD/9	Western Drain, by kiwi fruit orchard	(8.3)	√	
WD/10	Western Drain, Edgecumbe-Matata Road	(7.0)	√	
WC/1	Wilsons Creek, Edgecumbe-Matata Road		√	
AKC/1	Awakaponga Canal, Edgecumbe-Matata Road		√	
AKC/1	Awaiti Canal, c 250 m upstream of SH2 bridge		√	
AKC/2	Awaiti Canal, Edgecumbe-Matata Road		√	
OM/1	Omeheu Drain, Edgecumbe-Matata Road		√	
OM/2	Omeheu Canal, Edgecumbe-Matata Road		√	
OM3	Omeheu Adjunct Canal, Edgecumbe-Matata Rd		√	
BH/4	Bore hole, TR/4 site, 1.5 m from river	14.0	√	
BH/6	Bore hole, TR/6 site, 1.7 m from river	8.3	√	
BH/7	Bore hole, TR/7 site, 2.1 m from river	7.4	√	
BH/5A	Bore hole, TR/5 site, 0.6 m from river	13.0		√
BH/5B	Bore hole, TR/5 site, 28 m from river	13.0		√
BH/5C	Bore hole, TR/5 site, 35 m from river	13.0		√
BH/5D	Bore hole, TR/5 site, 63 m from river ^c	13.0		√
FD/1	Field drain, discharging to the Western Drain	(12.7)		√
FD/2	Field drain, discharging to the Western Drain	(12.6)		√
FD/3	Field drain, discharging to the Western Drain	(12.5)		√
FD/4	Field drain, discharging to the Western Drain	(12.3)		√
RD/30	Road side drain, SH30, c 500 m east of TR/2 site	(18.5)		√

^abracketed distances (km) estimated relative to distance of the Tarawera River from the sea; ^bc 300m upstream of the Otakiri Road culvert; ^c 16 m from Western Drain.

flame. AI levels (mean of 3 replicates) were determined at 396.2 nm using a GBC 905 furnace AA spectrometer. Cl, NO₃, and SO₄ level were determined using a Dionex QIC analyser and a Dionex 4x250 mm AS4A-SC column. Absorbances at 270, 340 and 440 nm were determined using 1 cm quartz cells 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. Resin acid levels were determined using previously reported methodology involving liquid-liquid extraction, derivatisation with CH_2N_2 , addition of *O*-methylpodocarpic acid ethyl ester as internal standard, and selected ion mode (SIM) GC/MS detection (Wilkins et al. 1996b).

RESULTS AND DISCUSSION

The pH, conductivity, Na, K, Mg, Ca, Fe and Al levels determined for some Tarawera River, three near-river bank bore holes, Western Drain, and other Western Rangitaiki Plains drain and canal water samples collected on 5/2/96, during an extended period of fine summer weather are presented in Table 2. The increased conductivity, Na, K, Mg, Fe and Al levels identified in the downstream TR/2-9 samples, in comparison to the levels determined for the upstream TR/1 sample, can be predominantly attributed to the influence of the pulp mill discharges (Wilkins et al. 1996a, 1996b), and to a lesser extent, natural geothermal effluents (McIntosh 1995). Elevated Na levels, indicative of a river water contribution, were

Table 2. Cation levels, pH and conductivity of some Tarawera River, Western Drain, and other canal and drain water samples, collected 5/2/96.

Site	Na ppm	K ppm	Mg ppm	Ca ppm	Fe ppm	Al ppb	pH	conduct. x 10 ³
<u>Tarawera River</u>								
TR/1 (28.5 km)	40.8	7.6	1.5	3.3	0.2	35	7.7	0.320
TR/2 (18.5 km)	72.1	9.8	2.3	3.3	0.4	99	7.5	0.449
TR/3 (15.3 km)	65.5	9.5	2.3	3.2	0.4	133	7.6	0.440
TR/6 (8.3 km)	63.4	9.3	2.1	3.3	0.4	109	7.5	0.418
TR/7 (7.4 km)	62.0	9.5	2.0	3.1	0.4	197	7.6	0.416
TR/8 (6.3 km)	58.9	8.9	2.0	2.9	0.4	178	7.6	0.402
TR/9 (0.7 km)	59.3	9.1	1.9	3.0	0.4	120	7.6	0.393
<u>Bore holes</u>								
BH/4 (14.0 km)	52.1	13.0	2.7	7.1	4.4	nd	7.1	0.340
BH/6 (8.3 km)	82.7	12.7	3.7	4.3	2.5	98	6.9	0.460
BH/7 (7.4 km)	20.4	25.3	2.6	8.9	4.4	120	7.6	0.406
<u>Western Drain</u>								
WD/2 (16.0 km)	23.6	5.4	1.7	2.0	1.2	11	7.2	0.174
WD/3 (14.2 km)	33.8	5.3	2.1	2.6	2.4	31	7.3	0.225
WD/4 (13.7 km)	40.0	6.7	2.5	2.7	2.5	27	7.4	0.255
WD/6 (13.0 km)	34.3	6.3	2.8	2.7	2.5	32	7.3	0.272
WD/7 (12.3 km)	33.7	7.1	2.6	2.8	2.6	37	7.4	0.278
WD/8 (9.6 km)	33.9	8.2	2.8	3.1	3.2	22	7.6	0.278
WD/9 (8.3 km)	29.6	7.4	3.0	3.4	2.9	19	7.5	0.271
WD/10 (7.0 km) ^a	30.7	6.9	3.5	3.7	2.4	16	7.7	0.273
<u>Other Sites</u>								
Wilsons Creek ^a	20.1	5.0	0.9	1.3	0.6	202	7.3	0.131
Awakaponga Canal ^a	14.5	4.9	0.6	0.8	0.5	70	7.1	0.130
Awaiti Canal (SH2)	44.1	8.2	6.4	5.3	0.7	18	7.8	0.325
Awaiti Canal ^a	33.8	11.7	4.9	4.4	3.7	14	7.4	0.307
Omeheu Drain ^a	30.1	9.6	6.8	4.9	2.9	12	7.5	0.342
Omeheu Canal ^a	21.5	5.5	4.3	3.5	2.5	10	7.5	0.231
Omeheu Adj. Canal ^a	29.4	12.1	8.5	6.1	2.5	14	7.6	0.349

^a Edgumbe-Matata Road

Table 3. Cation and anion levels, pH, conductivity and absorbance at 270, 340 and 440 nm, determined for some Tarawera River, bore hole, Western Drain, field drain and roadside drain water samples collected 20/7/96.

site	Na ppm	K ppm	Mg ppm	Ca ppm	Fe ppm	Al ppb	Cl ppm	NO ₃ ppm	SO ₄ ppm	pH	conduct. x 10 ³	absorbance		
												270 nm	340 nm	440 nm
<u>Tarawera River</u>														
TR/2 (28.5 km) ^a	48.7	6.0	7.0	3.4	0.14	174	46.8	1.3	22.1	7.4	0.378	0.149	0.051	0.012
TR/3 (15.3 km)	48.9	6.0	6.8	3.4	0.14	168	47.7	1.1	22.3	7.4	0.378	0.157	0.054	0.014
TR/5 (13.0 km)	45.3	5.7	6.2	3.2	0.21	176	48.0	1.5	20.8	7.4	0.340	0.144	0.050	0.013
<u>Bore holes</u>														
BH/5A (13.0 km)	7.6	2.6	9.9	2.5	0.19	495	5.7	0.5	31.4	6.6	0.147	0.161	0.089	0.036
BH/5B (13.0 km)	5.2	5.4	2.5	2.4	0.33	469	8.3	5.2	3.8	6.5	0.085	0.418	0.179	0.039
BH/5C (13.0 km)	6.6	2.8	5.7	2.5	0.58	394	6.5	0.5	7.5	6.6	0.100	0.377	0.152	0.034
BH/5D (13.0 km)	4.0	4.1	3.5	3.9	0.12	520	6.1	7.9	27.5	6.0	0.100	0.280	0.154	0.083
<u>Western Drain</u>														
WD/1 (16.6 km)	10.8	4.3	16.5	6.0	0.46	36	11.2	3.4	55.5	7.3	0.232	0.131	0.045	0.009
WD/2 (16.0 km)	12.1	4.3	13.0	5.4	0.65	29	10.9	3.7	46.2	7.1	0.224	0.138	0.050	0.010
WD/3 (14.2 km)	16.7	4.1	6.7	4.1	0.88	54	15.3	3.8	25.7	7.1	0.185	0.162	0.064	0.012
WD/4 (13.7 km)	15.7	4.5	6.7	4.0	0.84	39	17.2	3.8	23.7	7.1	0.185	0.165	0.068	0.014
Seepage ^b (13.0 km)	41.5	6.1	7.7	3.5	0.08	60	47.2	3.0	31.6	7.0	0.340	0.092	0.039	0.007
WD/5 (13.2 km)	16.1	4.6	6.3	4.3	0.99	85	18.4	3.9	22.8	7.1	0.185	0.172	0.070	0.015
WD/6 (13.0 km)	16.3	4.4	6.4	4.2	0.69	125	18.9	4.2	24.8	6.9	0.201	0.177	0.072	0.016
<u>Field drains</u>														
FD/1 (12.7 km)	28.8	5.8	10.1	5.8	0.97	234	29.9	0.4	54.7	7.1	0.278	0.378	0.161	0.034
FD/2 (12.6 km)	34.5	6.5	9.8	4.8	1.2	134	37.5	2.9	24.1	7.1	0.309	0.299	0.142	0.042
FD/3 (12.5 km)	36.6	9.3	7.8	5.3	1.0	118	42.9	1.5	38.0	7.3	0.332	0.255	0.117	0.032
FD/4 (12.3 km)	15.2	4.5	10.2	8.9	0.56	169	15.7	5.6	81.4	6.6	0.270	0.217	0.090	0.017
<u>Roadside drain</u>														
RD/30 ^c	8.0	3.8	4.6	5.1	0.74	22	12.7	5.5	20.9	6.8	0.147	0.135	0.050	0.010

^a distance to sea (km); ^b seepage water, left hand bank, c 0.5 m above drain water level; ^c State Highway 30 (SH30), c 500 m east of Tarawera River bridge.

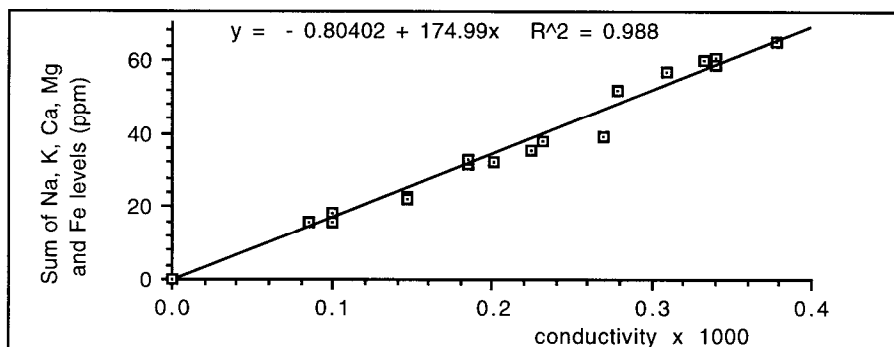


Figure 1. Plot of the sum of Na, K, Mg, Ca and Fe (ppm) levels versus conductivity x 1000 determined for some Tarawera River, bore hole, Western Drain and field drain water samples, collected 20/7/96.

identified in the near-bank BW4 and BH/6 bore hole water samples. The upward trend in Na and conductivity levels exhibited by the WD/2 and WD/3 samples, while suggestive of a moderate river input via ground water seepage between these sites, must be interpreted with caution since some of the other near-by drain and canal water samples, collected from sites along the Edgumbe-Matata Road, also exhibited similar Na and conductivity levels (Table 2).

Results for a second set of Tarawera River and Western Drain samples, collected on 20/7/97 during an extended period of wet, rainy weather, are presented in Table 3. On this occasion the river level at the Awakaponga gauging station was 2.04 m above sea level (c 0.24 m higher than normal) (Pang, 1993). The flow in the Western Drain on 20/7/97 was appreciably greater (c 2-3 fold greater by visual inspection) than was the case under summer conditions. Bore holes drilled on farm land between the Tarawera River and the Western Drain adjacent to the Otakiri Road culvert revealed that in vicinity of the stop bank (the base of which is c 1-2 m above the river level) the ground water table was within 5-10 cm of the surface level. It appears that under winter conditions there is a ground water outflow from the stop bank to the river. Water samples were also collected from four field farm drains discharging to the Western Drain c 300-700 m downstream of the Otakiri Road culvert, and from a road side drain 500 m east of the SH30 Tarawera River bridge (near the TR/2 site). Close inspection of the left-hand bank of the Western Drain identified a zone, c 300 m upstream of the WD/6 site and 0.3-0.5 m above the drain's water-line, at which a seepage water outflow was visible.

The Na and conductivity levels determined for the winter (20/7/96) Tarawera River and the Western Drain water samples (Table 3) were lower than those determined for the summer (5/2/96) samples (Table 2). Of particular note is the moderate downward trend in conductivity observed for the winter WD/1-WD/5 samples (Table 3), compared to an upward trend observed for the corresponding summer samples (Table 2). We interpret the trends in Na and conductivity levels as indicative of an appreciable rain water contribution (dilution) to the winter samples. The conductivity of the 20/7/96 samples correlated strongly with the sum of the Na, K, Mg, Ca and Fe levels (Figure 1). A similar correlation between conductivity and cation levels was also observed for the 5/2/96 samples. The increased Na level, decreased Fe level, and increased conductivity of the seepage water sample, relative to Western Drain water samples, are consistent with the view that the seepage water is comprised principally of Tarawera River water.

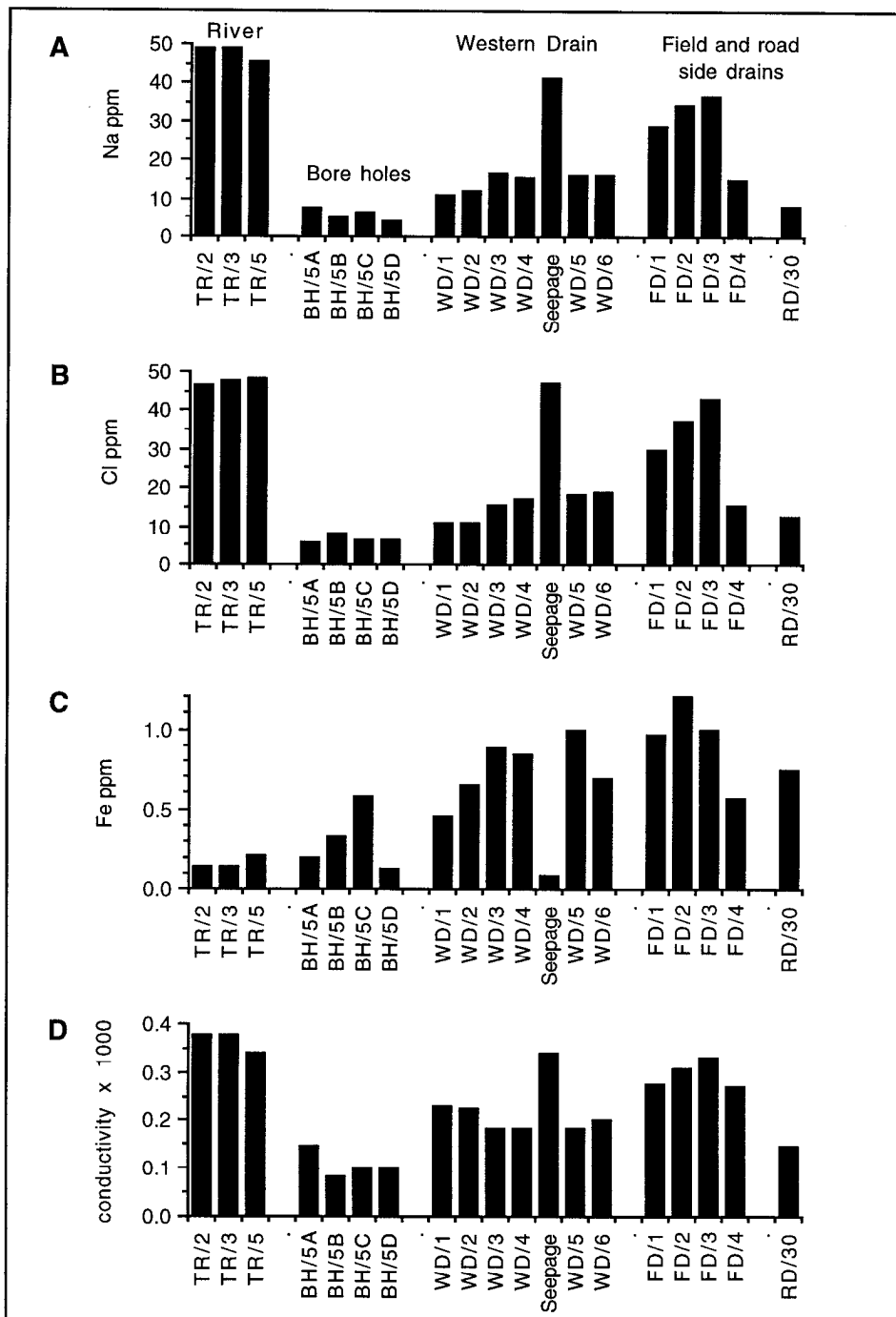


Figure 2. A: Na levels, **B:** Cl levels, **C:** Fe levels, and **D:** conductivity of some Tarawera River, bore hole, Western Drain, field drain and road side drain water samples, collected 20/7/96.

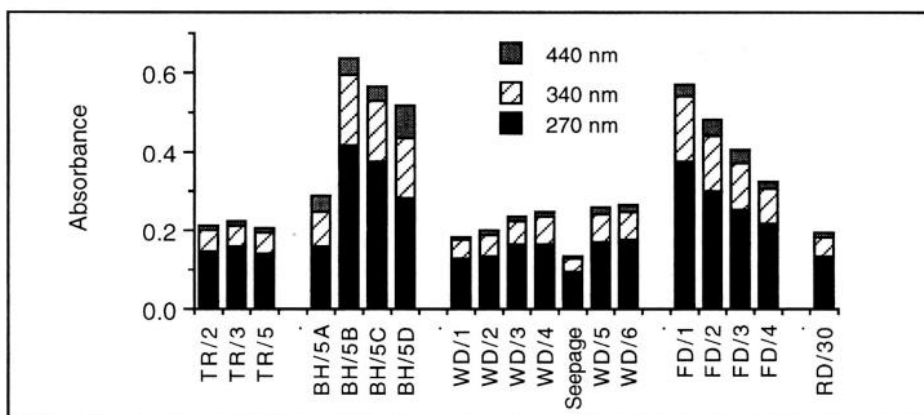


Figure 3. Absorbance of some Tarawera River, bore hole, Western Drain, field drain and road side drain water samples, collected 20/7/96.

Anion and colour data support this conclusion. For example, the Cl level of the 20/7/96 seepage water sample was similar to those of the Tarawera River water samples, and markedly different from Western Drain water samples (Table 3). The colour levels exhibited by the 20/7/96 bore hole and drain water samples (Table 3) can be attributed to the presence of humic material in leachate from the organic (peaty) soils of the lower Rangitaiki Plains (McIntosh, 1995). The Na, Cl, Fe, conductivity and colour levels of these samples are compared in Figures 2 and 3. The downward trend in colour levels and the upward trend in Na and Cl levels exhibited by the FD/1, FD/2 and FD/3 field drain water samples is suggestive of a moderate river water contribution to these samples. Our results indicate that river water colour (Table 3) and resin acid levels (Table 4) are appreciably attenuated

Table 4. SIM GC/MS detected levels (ppb) of resin acids identified in some 5/2/96 and 20/7/96 Tarawera River, Western Drain and bore hole water samples.

Site	date	Seco-1	Seco-2	Pim	18-Ab	DHAA	Cl-DHAA	Cl ₂ -DHAA
TR/2	5/2/96	2.2	1.0	5.7	55.9	16.9	1.8	2.4
TR/6	5/2/96	1.8	1.0	5.0	49.5	14.4	1.9	2.3
TR/9	5/2/96	1.4	0.7	4.3	45.1	12.4	1.4	1.9
BH/4	5/2/96	-	-	1.7	11.9	7.7	1.6	0.5
BH/6	5/2/96	1.0	0.4	4.6	25.2	14.6	3.3	0.7
BH/7	5/2/96	-	-	2.0	-	2.0	-	-
TR/2	20/7/96	4.4	2.3	4.8	40.5	8.1	1.1	1.2
TR/3	20/7/96	4.0	2.0	4.8	38.3	8.0	1.0	1.0
TR/5	20/7/96	3.6	1.8	4.4	37.4	7.2	0.9	1.0
BH/5A	20/7/96	tr	tr	tr	0.1	0.4	-	-
BH/5B	20/7/96	-	-	tr	tr	0.1	-	-
BH/5C	20/7/96	-	-	-	-	0.1	-	-
BH/5D	20/7/96	-	-	-	-	0.1	-	-
WD/6	20/7/96	0.1	tr	tr	0.1	0.4	-	-
Seepage	20/7/96	tr	tr	0.1	0.3	0.5	tr	tr

"tr" indicates < 0.05 ppb. Abbreviations: Seco-1 = secodehydroabietic acid-1, Seco-2 = secodehydroabietic acid-1, Pim = pimelic acid, 18-Ab = abietan-18-oic acid, DHAA = dehydroabietic acid, Cl-DHAA = 14-chlorodehydroabietic acid, Cl₂-DHAA = 12,14-dichlorodehydroabietic acid.

during passage of river water to the Western Drain, presumably via one of the many shallow, pumice and sand aquifers of the Western Rangitaiki Plains (McIntosh, 1995).

The attenuation of resin acid and colour levels observed in this investigation is consistent with the results of an earlier laboratory investigation using soil columns and effluent from another New Zealand pulp mill (Williams 1986). The resin acid data presented in Table 4 shows that the 20/7/97 (winter) near-river bank BH/5A bore hole water sample is not significantly influenced by river water, whereas the 5/2/97 (summer) near-river bank BH/4 and BH/6 bore hole water samples are significantly influenced by river water. This data is consistent with the proposal that an inflow of ground water from the stop bank to the river may occur under winter conditions, whereas an outflow of river water to ground water may occur under summer conditions.

In summary, our investigations have identified a point flow (seepage) from the Tarawera River into the Western Drain c 300 m upstream of the Otakiri Road culvert and provided evidence for a possible river water input to three field drains discharging to the Western Drain c 300-700 m downstream of the Otakiri Road culvert.

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