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Accumulation of Resin Acids in Sediments Adjacent to a Log Handling Area, Tauranga Harbour, New Zealand

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Recent analyses of storm runoff from the log handling area at the Port of Tauranga, North Island, New Zealand, have shown that the runoff may contain significant concentrations of resin acids (Tian et al. 1995, 1997). For example, the average total resin acid level of 16 wharf runoff samples collected during 2 storms was 1030 ppb. Since environmentally persistent resin acids such as dehydroabietic acid (DHAA) are known to accumulate in receiving water sediments (Brownlee 1977; Barrick and Hedges 1981; Simoneit 1986; Healy et al. 1997; Wilkins et al. 1996a, 1996b, 1997) we considered it likely that some of the resin acids were being deposited on the sea floor around the stormwater discharge points. In order to define the extent of resin acid deposition we determined the levels of resin acids in a series of the sea bed sediment samples collected from sites adjacent to the log handling area.

MATERIALS AND METHODS

Sea bed sediment samples were collected from ten sites at increasing distances perpendicular to the log handling wharf, adjacent to the southern and northern stormwater outfalls (sites S0-S4 and N0-N4 respectively on Figure 1). Sample collection dates, methods, descriptions, and other parameters are given in Table 1. The area from which samples S0-S4 and N0-N4 were collected was extensively dredged during 1990-1992. Two sediment samples were also collected from the Central Bank (sites LWC and DW, Figure 1), c 2300 m and 2800 m respectively from the log handling area (Figure l), and utilised as control samples to identify background resin acid levels in sediments remote from the log handling area. A blank extraction was performed using an acid washed sand sample (Unilab Auburn, Australia).

The S0 and N0 sea bed sediment samples (typically 0-10 cm) were collected by hand at low tide. Other sediment samples were collected using a grab sampler (S1-S4, N1 and N2 samples) or, where there was too much shell material for the grab sampler to function, by SCUBA divers (N3, N4, LWC and DW samples). Sediment samples were stored at - 18°Cin plastic bags which had been sequentially

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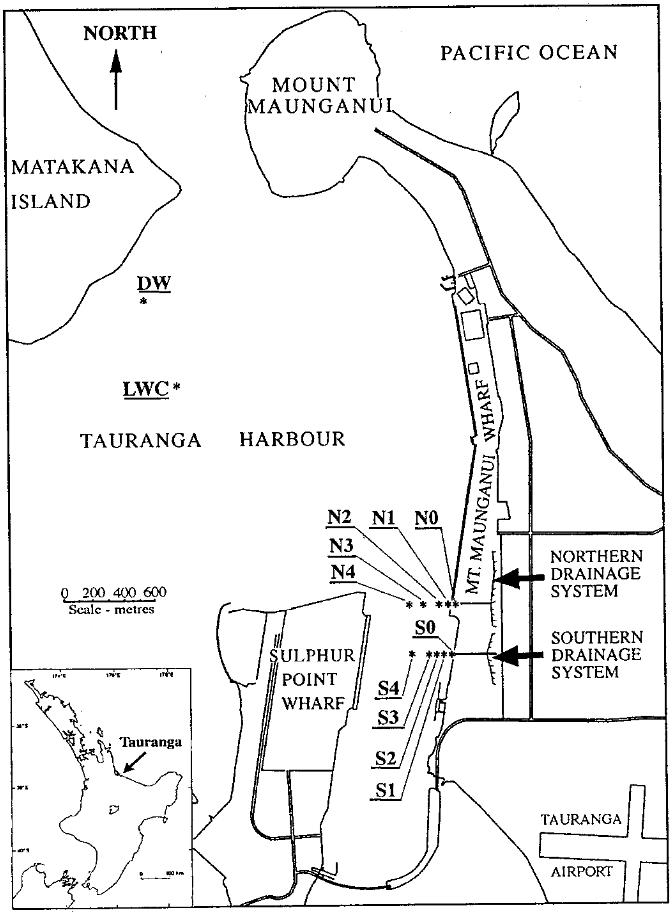


Figure 1. Locations of sediment sampling sites adjacent to the log handling areas and the Central Bank, Tauranga Harbour, North Island, New Zealand. Sites N0-N4 are the locations opposite the northern drainage system; sites S0 - S4 are locations opposite the southern drainage system; sites DW and LWC are the two control sites.

rinsed with 2 M HCl, 2 M NaOH, and distilled water. When required for analyses sediment samples were homogenised, drained and air dried at room temperature (17-23°C). During drying the sediment material was frequently disturbed using a clean class rod, to prevent aggregation. The loss on ignition (loi), representing the total organic content of dried sediment samples, was determined by weight loss after combustion at 550°C for 3 h.

An accurately weighed portion of the < 0.2 mm fraction, obtaining by sieving of air-dried sediment material, was extracted in a Soxhlet apparatus for 16 h with hexane-isopropanol (1:1). *O*-Methylpodocarpic acid (PDA), prepared as a 0.103 mg/mL solution in chloroform, was added to the sediment samples as surrogate (recovery) standard immediately before extraction commenced. After extraction, *O*-methylpodocarpic acid ethyl ester (PDA-Et), prepared as a 0.100 mg/mL solution in chloroform, was added to the hexane-isopropanol extract as internal (quantification) standard. The sample weight and addition rates of PDA and PDA-Et were derived from the estimated resin acid levels in different sediment samples from trial extractions, performed in advance. The extracts were concentrated to c 1-2 mL under reduced pressure using a rotary evaporator and derivatised using an ethereal solution of diazomethane (CH_2N_2). Reaction mixtures were allowed to stand at room temperature for 30 min and then placed in a refrigerator (1-3°C) for 24 h. Excess diazomethane was blown off under a stream of oxygen free nitrogen.

Table 1. Sample collection details [site, date, collection method, fraction size for analysis and % loss on ignition (loi) determined for sediment samples].

Code	Site, distance from wharf	Date	Method	Fraction	loi (%)
S0	southern outfall, 1 m	10/3/95	hand	< 0.2 mm	1.6
S1	southern outfall, 15 m	10/3/95	grab	< 0.2 mm	1.8
S2	southern outfall, 50 m	10/3/95	grab	< 0.2 mm	7.2
S3	southern outfall, 120 m	10/3/95	grab	< 0.2 mm	6.7
S4	southern outfall, 250 m	10/3/95	grab	< 0.2 mm	5.5
N0	northern outfall, 1 m	10/3/95	hand	< 0.2 mm	34.7
N1	northern outfall, 40 m	10/3/95	grab	< 0.2 mm	4.8
N2	northern outfall, 80 m	10/3/95	grab	< 0.2 mm	5.3
N3	northern outfall, 160 m	2/11/95	diver	< 0.2 mm	3.8
N4	northern outfall, 290 m	2/11/95	diver	< 0.2 mm	3.8
LWC	Central Bank, 2300 m	2/11/95	diver	< 0.5 mm[a]	0.7
DW	Central Bank, 2800 m	2/11/95	diver	< 0.5 mm[a]	0.7

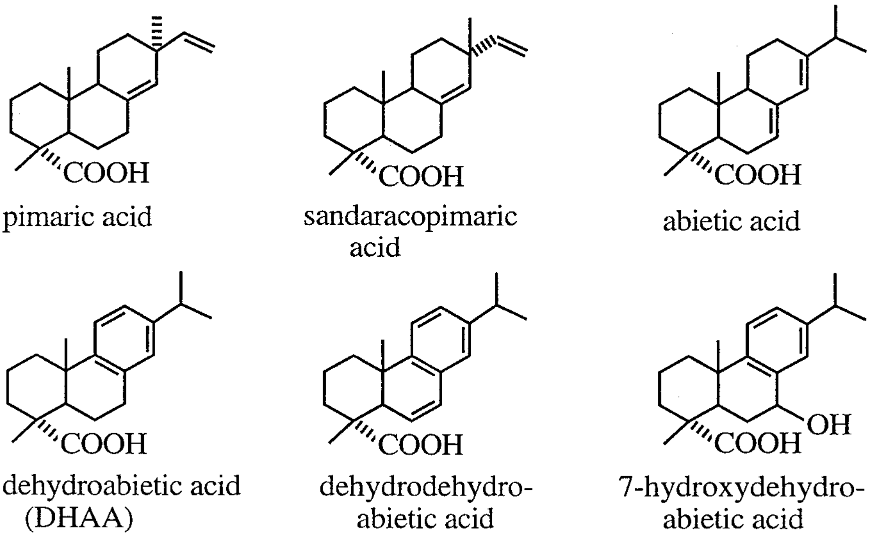
[a] combined with < 0.2 mm fraction to afford sufficient material for Soxhlet extraction.

Resin acids were quantified using a previously reported selected ion mode (SIM) GC-MS detection protocol (Wilkins et al. 1996a, 1996b). The ions used in the SIM GC-MS analyses are listed in Table 2. SIM GC-MS response factors were determined using either a reference solution containing known amounts of

Table 2. Ions used for SIM GC-MS analyses.

Compound	Quantification ion (*m/z*)	Confirmation ion(s) (*m/z*)
O-Methylpodocarpic acid[a]	227	
O-Methylpodocarpic acid ethyl ester	227	
Pimaric acid[a]	121	316
Sandaracopimaric acid[a]	121	316
Abietic acid[a]	256	241, 316
Dehydrodehydroabietic acid[a]	237	
7-hydroxydehydroabietic acid[a]	237	
Dehydroabietic acid[a]	239	299, 314
Isopimaric acid[a]	241	256

[a] acids were detected and quantified as the corresponding methyl esters.


pimaric acid

sandaracopimaric acid

abietic acid

dehydroabietic acid (DHAA)

dehydrodehydroabietic acid

7-hydroxydehydroabietic acid

Figure 2. Chemical structures of the dominant resin acids identified in sediment samples.

commercially available standards (DHAA, pimaric acid, sandaracopimaric acid) purchased from Helix Biotech, Richmond BC, Canada, or reference solutions containing GC-FID determined levels of target compounds, quantified on the basis of unit response factors relative to DHAA. The SIM GC-MS detection limit applied in this study was 10 ppb.

RESULTS AND DISCUSSION

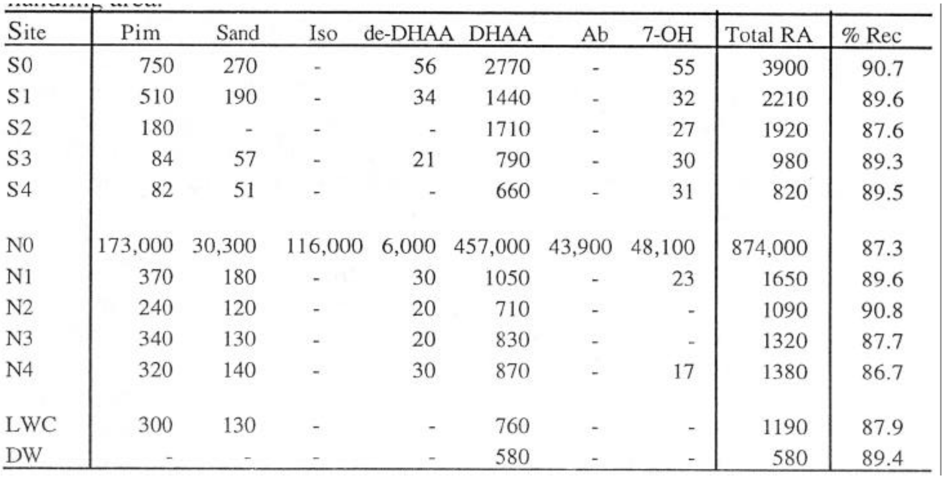
The levels of resin acids identified in the sediment samples using selected ion mode (SIM) GC-MS detection are presented in Table 3. The chemical structures of the dominant resin acids identified in the sediment samples are shown in Figure 2. An elevated level of resin acids (total of 874,000 ppb) was identified in the N0 sample, collected from the bottom of a small perched pool beside the northern stormwater outfall. Close examination of the NO sediment material revealed the presence of a significant amount of bark residue. The very high loss on ignition (34.7%, see Table 1) determined for this sample is consistent with an appreciable bark contribution, which would be expected to have a very high resin acid concentration.

The total resin acid levels identified in each of the other sediment samples (excluding the NO sample) were in the range of 820-3900 ppb. These levels are substantially lower than those identified in sediments collected adjacent to a bark dumping ground in the Tauranga Harbour (31-84 ppm) (Healy at al. 1997) and in sediments from a coastal wetland at the mouth of the Tarawera River, Western Bay of Plenty, New Zealand (65-1231 ppm) (Wilkins et al. 1997).

Extensive dredging and widening of Tauranga Harbour's shipping channels, including the area adjacent to the log handling wharf in the vicinity of Sulphur Point (Figure 1), occurred during 1990-1992 when about 5,000,000 m^3 of sediments were dredged (Healy et al. 1991). Thus, it follows that when the samples were collected in March, or November, 1995, the sea bed sediments had been exposed to the wharf stormwater discharge impacts for a maximum period of 36, or 44 months, respectively.

The resin acid levels of the N3 and N4 sites sediments were similar (1320 and 1380 ppb), and slightly higher than the level determined for N2 site sediment sample (1090 ppb). This difference can be attributable to the collection of the N3 and N4 samples (by SCUBA divers) 8 months after the N2 sample. During the extra 8 month period it is likely that additional resin acids will have accumulated at the N3 and N4 sites. Based on the mean total resin acid levels determined for the S3 and S4 samples (900 ppb; 36 months accumulation) and N3 and N4 samples (1350 ppb, 44 months accumulation), the net accumulation rate of resin acids in sediment in the shipping channel between the Mount Maunganui and Sulphur Point wharves, at distances of c 100-300 m from the Sulphur Point wharf, can be estimated to be currently of the order 300 ppb/year (southern outfall) and 370 ppb/year (northern outfall) respectively, assuming a linear accumulation rate to date. Further study is required to accurately quantify the long term balance of resin acid deposition (accumulation) and degradation (removal) in harbour sediments.

Table 3. SIM GC-MS determined resin acid concentrations (ppb) identified in some Tauranga Harbour sediment samples collected from sites adjacent to the log handling area.



Site	Pim	Sand	Iso	de-DHAA	DHAA	Ab	7-OH	Total RA	% Rec
S0	750	270	-	56	2770	-	55	3900	90.7
S1	510	190	-	34	1440	-	32	2210	89.6
S2	180	-	-	-	1710	-	27	1920	87.6
S3	84	57	-	21	790	-	30	980	89.3
S4	82	51	-	-	660	-	31	820	89.5
N0	173,000	30,300	116,000	6,000	457,000	43,900	48,100	874,000	87.3
N1	370	180	-	30	1050	-	23	1650	89.6
N2	240	120	-	20	710	-	-	1090	90.8
N3	340	130	-	20	830	-	-	1320	87.7
N4	320	140	-	30	870	-	17	1380	86.7
LWC	300	130	-	-	760	-	-	1190	87.9
DW	-	-	-	-	580	-	-	580	89.4

Abbreviations: Pim: pimaric acid; Sand: sandaracopimaric acid; Iso: isopimaric acid; de-DHAA: dehydrodehydroabietic acid; DHAA: dehydroabietic acid; Ab: abietic acid; 7-OH: 7-hydroxy-dehydroabietic acid; Total RA: total resin acids; % Rec: % recovery of *O*-methylpodocarpic acid.

Care must be exercised in comparing the levels of total resin acids identified in the S3, S4, N3 and N4 samples (820-1380 ppb) and the control site LWC and DW

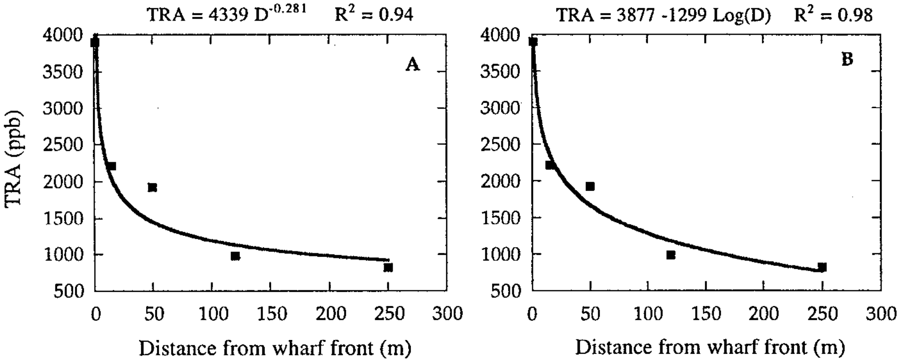


Figure 3. Curve fitting results using (A) a power equation and (B) a logarithmic equation, where TRA = total resin acids in ppb, D = distance in m from wharf front.

samples (580 and 1190 ppb respectively) since the former sediments have only been exposed to resin acid influenced storm runoff for c 3-4 years, while the levels identified in the control site samples can be attributed to the long term (> 30 years) accumulation of low levels of resin acids. Our results are consistent with view that the 1990-1992 dredging program reduced the background resin acid to negligible levels in 0-10 cm surface sediments in the immediate vicinity of the log handling wharf.

Curve fitting using either a power equation, or a logarithmic equation (KaleidaGraph software), was applied to model the total resin acid levels in sediment samples collected up to 250 m from the southern stormwater outfall (Figure 3). Storm runoff input from the Sulphur Point wharf, which also contains significant levels of resin acids (Tian et al. 1995), may limit the use of the first predictive equation, $TRA = 4339D^{-0.281}$ ($R^2 = 0.94$), to the region 250 m away from the Mount Maunganui wharf. The second equation, TRA = 3877 - 1299*logD ($R^2 = 0.98$), does however appear to have some validity beyond 250 m, in so much as it tends towards zero (the likely level immediately after dredging) at increasing distance from the Mount Maunganui wharf front.

In summary, it is apparent from both the results presented in Table 3, and the modelling equations, that total resin acid levels are attenuated with increasing distance from the northern and southern stormwater outfalls. Further monitoring is however required to establish the general validity of either (or both) of equations A and B, as predictive models for the deposition of resin acids in Tauranga Harbour sediments, and to define the long-term accumulation, redistribution and degradation characteristics of resin acid laden sediments in the tidal shipping channel adjacent to the log handling area.

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