Dehydroabietic acid (DHAA) and related organic components in sediments from the Matata Lagoon and Tauranga Harbour, Bay of Plenty, New Zealand

A research report prepared for the
Bay of Plenty Regional Council

A. L. WILKINS[1], T. R. HEALY[2] and T. LEIPE[2]

[1]Department of Chemistry

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Summary

The concentrations and distribution of dehydroabietic acid (DHAA) and related resin acids in sediments at two different sites in the Bay of Plenty were determined to ascertain the extent of sediment contamination by organic compounds derived from wastes arising from wood industry operations (shipping and paper making).

Sediments from the mouth of the Tarawera River, and the Matata Lagoon, are influenced by the effluents discharged from two pulp and paper mills, while waste wood and pine bark from log export operations has been dumped in landfills around the shores of the Tauranga Harbour.

Twenty six sediment samples from 12 locations were collected, freeze dried, and the fraction finer than 0.2 mm was extracted using a Soxhlet apparatus with hexane/isopropanol as solvent. Organic substances were identified and quantified using capillary column gas chromatography with flame ionisation detection (GC-FID) and combined gas chromatography/mass spectrometry (GC/MS).

A variety of resin acids were identified including abietic acid, dehydroabietic acid (DHAA), chlorodehydroabietic acid isomers, abietan-18-oic acid, pimaric acid and sandaracopimaric acid. Additionally fatty acids and hydrocarbons were analysed in selected samples.

Individual resin acid concentrations varied from below the detection limit of 2-3 mg/kg, up to 516 mg/kg, dry weight of sediment sample. The natural (background) level of dehydroabietic acid (DHAA) in control sites was about 20-30 mg/kg. Sediment samples collected from the Tarawera River mouth and the lower (eastern) part of the Matata Lagoon were found to have DHAA and other resin acid concentrations 10-15 times greater than the background level. Some processed modified resin acids, including abietan-18-oic acid and chloro-DHAA isomers, were also detected in these samples.

Sediment samples from the two larger lakes in the upper (western) part of the Matata Lagoon did not appear to be significantly influenced by modern Tarawera River water. DHAA levels were similar to background levels, while modified resin acids (abietan-18-oic acid and chloro-DHAA isomers) were absent.

Multivariate statistical analysis of the data identified correlations between total resin acids and chlorinated DHAA analogues in lower (eastern) Matata Lagoon sediment samples, and between DHAA and fatty acids in upper (western) lagoon sediment samples.

Sediment samples from the vicinity of the bark dumping grounds on the edges of the Tauranga Harbour were found to contain resin acid levels similar to background levels. The range and concentrations of DHAA and other resin acids detected in these samples indicated a lack of substantial diagenetic changes in the deposits. However, the dark brown outflow from the dumping areas after heavy rainfalls indicates lignin mobilisation.

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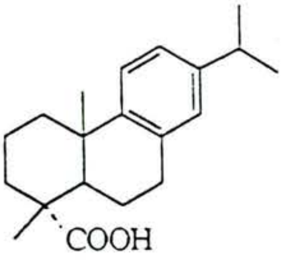
1. Introduction

Dehydroabietic acid (DHAA) is one of a group of persistent resin acid diterpene metabolites which may be encountered in different parts of the environment, especially in sediments (Barrick and Hedges, 1981; Simoneit, 1986; Streibl and Herout, 1969) where they tend to accumulate. Simoneit (1986) has described DHAA as "the major polycyclic diterpenoidal compound present in the geosphere". DHAA, and related compounds, are natural products derived from woody plants (mainly conifers).



Dehydroabietic acid (DHAA)

In New Zealand, the conifer *Pinus radiata* is the basis of commercial exotic forestry and the major source for the paper and timber industry. Substantial quantities of *P. radiata* logs, timber and wood chips are also exported. The content and composition of resin acids and fatty acids in *P. radiata* were investigated by McDonald and Porter (1969), Porter (1969) and Lloyd (1978). However, the distribution and degradation of resin acids in the environment, their diagenetic changes, and their impacts on the biosphere can be variable and complicated to investigate.

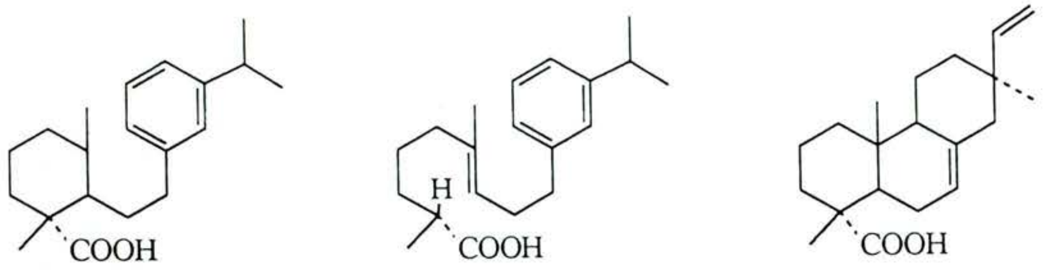
Some of the naturally occurring diterpenoids encountered in woody plants are known to be toxic or mutagenic. Oikari et al. (1980) and Tana (1988) have described the bioaccumulation and the sublethal effects in fish of resin acids from pulp and paper mill effluents. The 96 hour LD_{50} concentration (lethal dose toxicity test) of DHAA towards rainbow trout is about 1000 µg/L (1 ppm). Kinae et al. (1981) have reported mutagenic effects in wild fish and tested this in some experiments with bacteria.

In river water samples, a concentration of about 20-100 µg/L (20-100 ppb) of DHAA can result in a sediment concentration several orders of magnitude greater (e.g. 100 ppm), depending on sediment type, origin and degree of pollution, and distance to the source of pollution. Resin acids are generally of low solubility, but diagenetic processes, or changes in environmental conditions, can results in the release of bound resin acids into the aqueous phase.

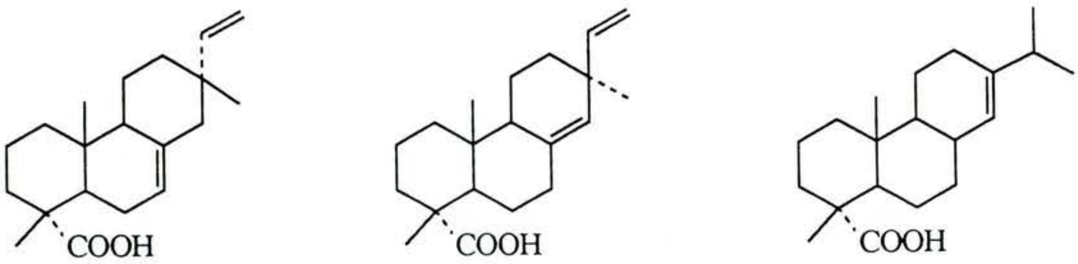
The metabolism and degradation of resin acids can be very different. Some compounds are stable over a long time and also under varying conditions, whilst others are decomposed quickly. Takeda et al. (1968) have discussed the thermal isomerisation of abietic acid while McFarlane and Clark (1988) have investigated the microbiological metabolism of resin acids in anaerobic reactor experiments. Wilkins et al. (1989) have identified a new hydroxylated resin acid (13β-hydroxyabietan-18-oic acid) as an anaerobic degradation product of abietic acid in a treatment system of a New Zealand pulp and paper mill. There are also reports of investigations directed towards the development of biotechnological procedures for the detoxification of pulp and paper mill effluents (Leach et al., 1978), especially for the degradation of DHAA with bacteria (Biellmann et .al., 1973a, 1973b) or fungi (Kutney et al., 1981).

In recent years there has been a marked increase in the emphasis placed on the organic geochemical processes occurring in the environment. However, the necessary analytical techniques are expensive and the evaluation of the results is still very difficult. The variety of organic molecules is huge and there is little knowledge about their specific effects on the environment and biota.

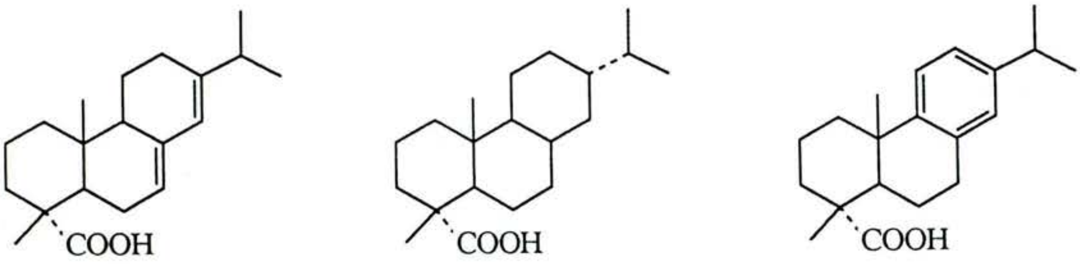
The structural formulae of the resin acids and related degradation products analysed in this study are presented in Figure 1. Possible degradation pathways for abietic acid and pimaric acid, after Osborne (1991) and LaFlamme and Hites (1978) are depicted in Figure 2.



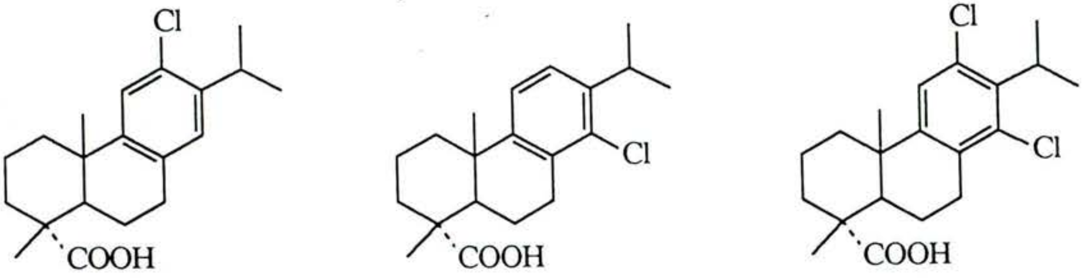
Secodehydroabietic acid-1 Secodehydroabietic acid-2 Pimaric acid



Sandaracopimaric acid Isopimaric acid Abiet-13-en-18-oic acid



Abietic acid Abietan-18-oic acid Dehydroabietic acid



12-chlorodehydroabietic acid 14-chlorodehydroabietic acid 12,14-dichlorodehydroabietic acid

Figure 1. Structural formulae of some resin acids.

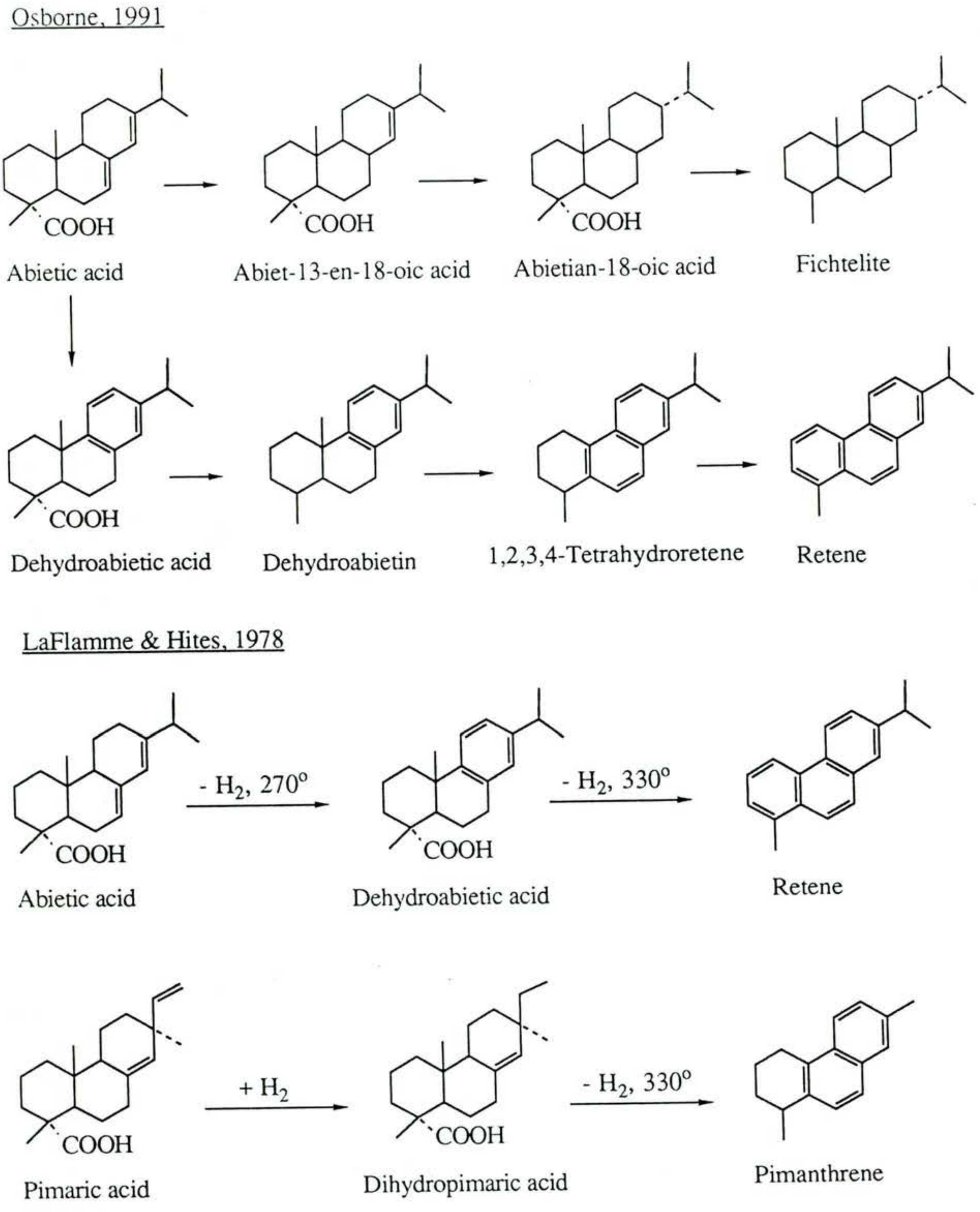


Figure 2. Possible degradation pathways for abietic acid and pimaric acid after Osborne, 1991, and LaFlamme and Hites, 1978.

LaFleur (1983) has discussed biogenic, natural and anthropogenic sources of DHAA and other diagenetic diterpenoids. DHAA has been found to be a constituent of all coniferous plants, wood soils, peat, lignins, and to also occur in deposits derived from volcanic eruptions occurring in the vicinity of coniferous wood (see Table 1 and Figure 2). The heat induced modification of abietic acid has been described by LaFlamme and Hites (1978), and Pereira et al. (1982).

Table 1. Occurrence of diterpenoid organic substances in the environment (after LaFleur, 1983).

Compound	wood extracts	forest soils	peat	coals	freshwater sediments	marine sediments	atmospheric particles	volanic ash
Abietic acid	√	√	√	-	√	-	-	-
Pimaric acid	√	√	-	-	-	-	-	-
Dehydroabietic acid	√	√	√	-	√	√	√	√
Abiet-13-en-18-oic acid	-	-	√	-	-	-	-	√
Dehydroabietane	√	√	-	√	√	-	√	√
Dehydroabietin	-	√	-	-	√	√	√	√
Fichtelite	-	-	√	-	√	√	-	-
Retene	-	√	√	√	√	√	√	√

Examples of human induced concentration and release of resin acids, and resin neutrals, into the environment include wood, timber, log and paper production processes, tar production, the dye industry and the use of conifer wood for heating purposes. These, and other activities, release DHAA and other diterpenoids into the geosphere where they finally accumulate in organisms and sediments, possibly far away from the original sources (Simoneit, 1977; Yamaoka, 1979).

From the point of view of geochemistry, organic molecules such as resin acids and resin neutrals are excellent chemical fossils and biological markers. These compounds can be used to reconstruct the geological development of organic deposits and sediments (Venkatesan et al., 1980; Johns, 1986; Yen and Moldowan, 1988), the distribution of modern and fossil resins (Thomas, 1969) or the history of human impacts in the sedimentary records (LaFlamme and Hites, 1978; Wakeham et al., 1980a, 1980b; Tan and Heit, 1981).

The aim of the present study was to determine the levels of DHAA and related resin acids in sediments collected from two different sites in the Bay of Plenty, both of which were believed to have been exposed to wood product effluents.

The first site, the Matata Lagoon (Figures 3,4), is adjacent to the mouth of the Tarawera River. This river is the receiving water for the effluents from two pulp and papers mills, located about 16 km upstream.

The second site, in the reclaimed land fill site in Tauranga Harbour (Figures 5, 6), was believed to have been ultilised (more than a decade previously) as pine-bark dump, for the bark residues accumulated during the trans-shipment of export logs.

The natural (background) level of resin acids in some the uncontaminated (control site) sediments were also determined, and it was anticipated that in the case of the Matata lagoon sediments, a pulp and paper mill contribution to the resin acid levels would result in the accumulation of the chlorinated analogues of DHAA (12-chloro-, 14-chloro- and 12,14-dichloro-DHAA) known to be formed from DHAA during pulp bleaching (Wilkins and Panadam, 1987).

2. Geographical setting

2.1. Matata Lagoon (Figure 3)

The lagoon is located at 37°54‘ S and 176°47‘ E in the Bay of Plenty near the village of Matata on state highway 2 between Tauranga and Whakatane. The lagoon formed after the original mouth of the Tarawera River was diverted to the sea in 1914. It has gradually infilled, to create a swampy lagoon in the lowland area behind the beach and foredunes. The lagoon was influenced by brackish water of the tidal backflow as well as storm water in the river mouth area.

Today the western part of the lagoon, with the two larger lakes is cut off from the river water inflow by weirs and dams. Thus the modern lagoon is freshwater dominated with a high biological primary production, and typical coastal lagoon plant successions in the shore area. Highly organic muddy sediment is accumulating in the basins.

The Tarawera River is about 60 km long and is sourced from Lake Tarawera near Rotorua, 290 metres above mean sea level. Its mean annual flow rate, a few kilometres upstream from the mouth, is about 30 m^3/s. The river catchment consists mainly of Quaternary acidic volcanic rocks of the Taupo Volcanic Zone (Rhyolites, Ignimbrites) and the river bed is predominantly composed of gravel, sand and pumice detritus derived from those rocks. Only on the lee side of the meanders in the current shadow, and between water plants along the river bank are found some finer (silty) deposits, enriched with organic material.

At the town of Kawerau, 30 km from the river mouth, two pulp and paper mills discharge about 200 000 m^3 per day (around 10% of the river flow rate) of waste water into the river. Below Kawerau, the river's appearance changes from that of a clear, fresh, pristine river, to a dark brown waterway, with a significant odour.

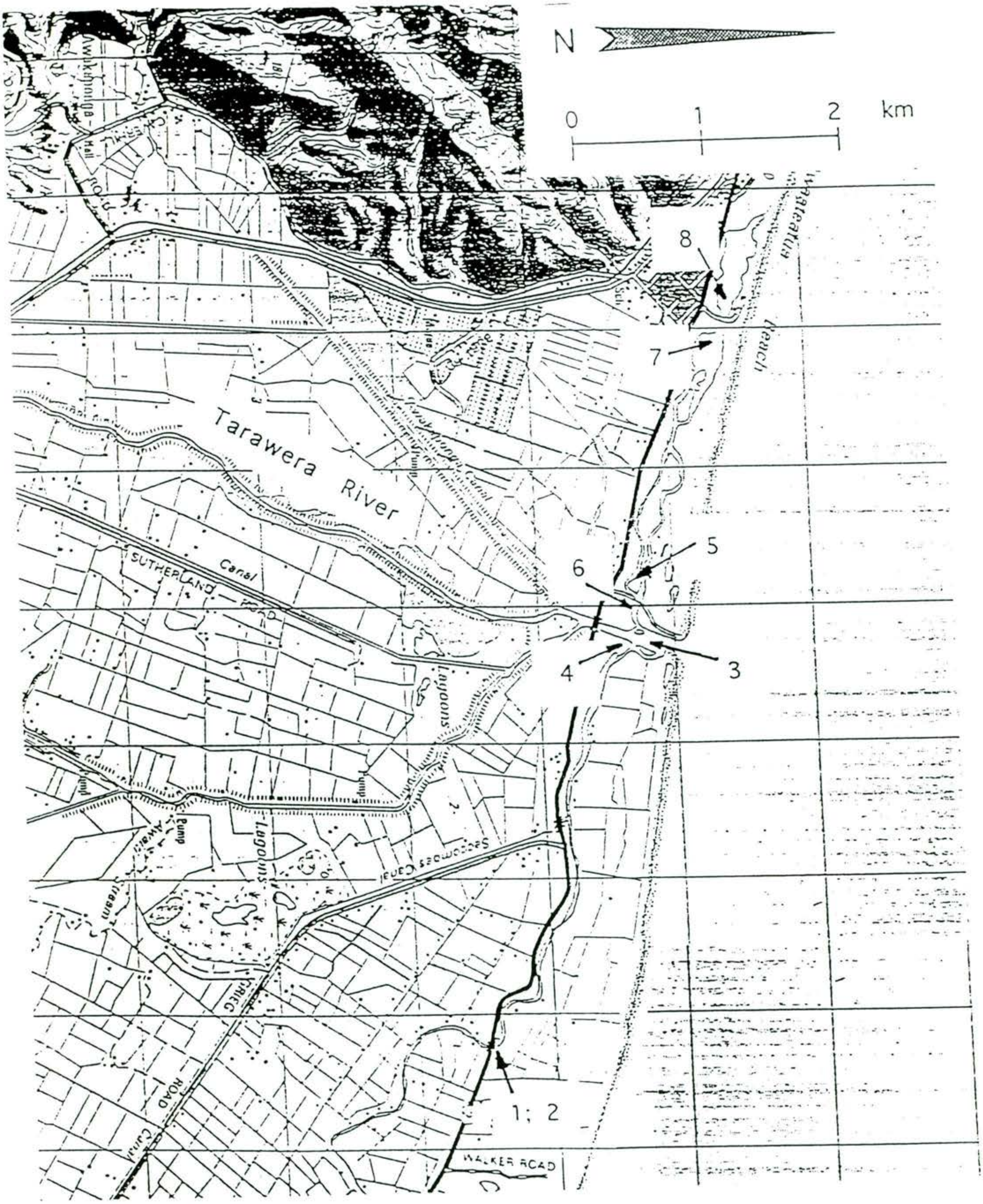


Figure 3. Map of the Matata Lagoon and Tarawera River Mouth, showing sample sites (site codes ML1-ML8).

Figure 4. Aerial view of the Matata Lagoon.

In 1989, effluent water samples from Tasman's biological treatment system were found to contain more than 2600 μg/L resin acids (Wilkins et al., 1989), including 800 μg/L DHAA and 1200 μg/L abietic acid. Concentrations of 46 μg/L DHAA and 40 μg/L abietan-18-oic acid are still found (Wilkins and Panadam, 1987) in water samples taken about 10 km downstream from the mill outfall.

In 1991 Osborne investigated the resin acid and fatty constituents of some Tarawera River water and sediment samples. Palmitic acid, and oleic acid group isomers (mainly 18:1 and 18:2 isomers) were identified as the dominant fatty acids, while dehydroabietic acid (DHAA) and abietan-18-oic acid were identified as the dominant resin acids. Lesser levels of a variety of other resin acids including abietic acid, abiet-13-en-18-oic acid, pimaric acid, secodehydroabietic acid-1, secodehydroabietic acid-2, 12-chloro-DHAA, 14-chloro-DHAA and 12,14-dichloro-DHAA were also detected.

2.2. Tauranga Harbour (Figure 4)

The investigation area in the Tauranga Harbour is situated 37°41' S; 176°12' E near the city of Tauranga in the Bay of Plenty. The Port of Tauranga is a major bulk timber and log exporting port. Many trees are stripped of bark in the port area and the bark may escape into the harbour where it becomes incorporated in the sediment.

During the 1960's tonnes of bark were dumped along parts of the shoreline in the harbour area. Close to the south of the Tauranga Airport, a large rubbish dump area covers the former swampy lowland of Te Ngaiopapa Point. This dumping ground is believed to contain the majority of the wood waste and bark from the port (N. Sinclair, Port of Tauranga Ltd., pers. comm.).

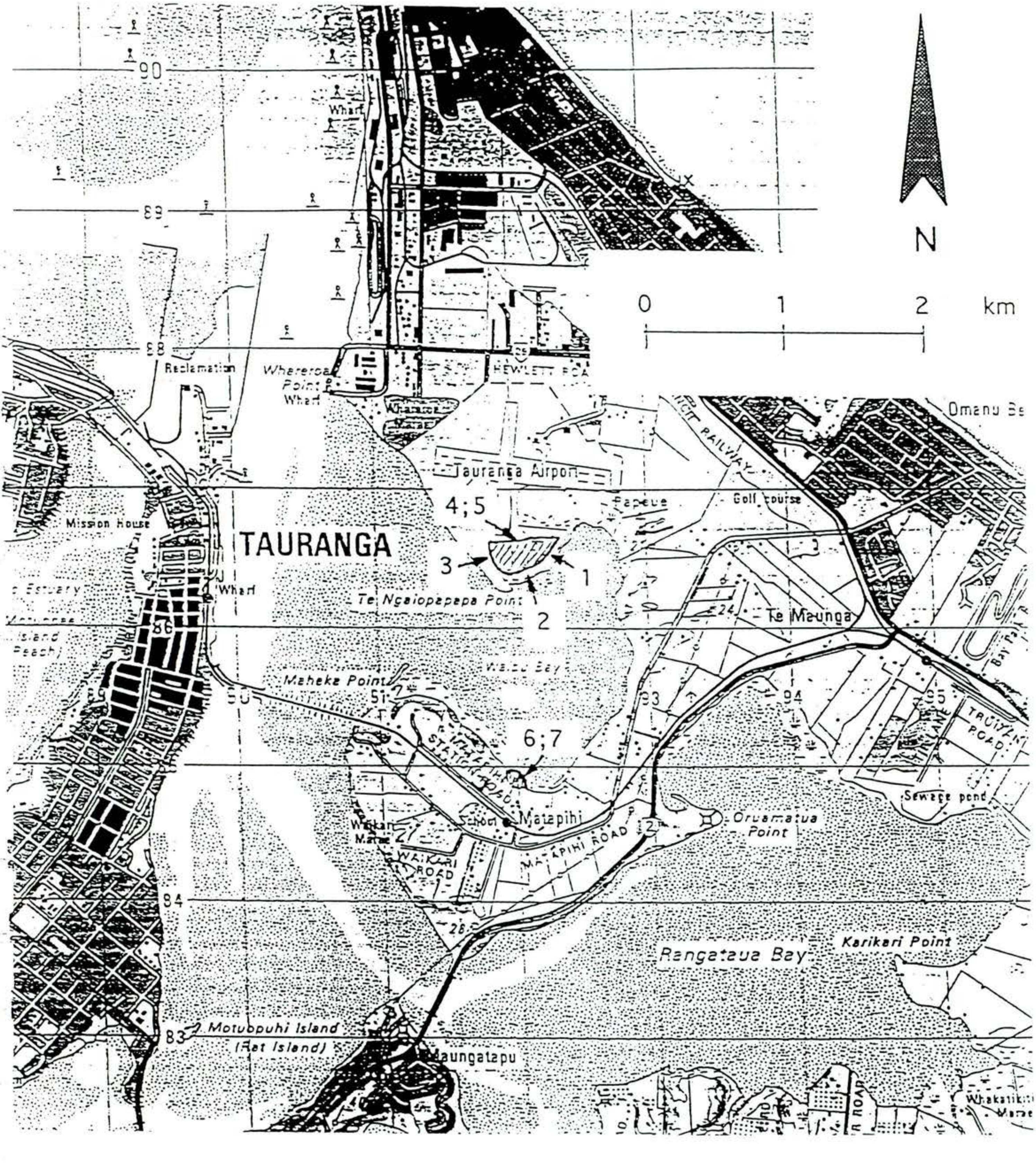


Figure 5. Map of the Tauranga Harbour, showing sample sites (site codes TH1-TH5).

Figure 6. View of one of the bark dumps on the South side of Waipu Bay, Tauranga Harbour.

Today the area is overgrown with grass, but some ditches drain the area into the harbour. Other bark and wood dumping grounds are found on the southern shore of Waipu Bay near Matapihi; one of these dumps is still operating. Leachate from these dumps also drain into the harbour. After heavy rainfalls and at low tide a dark brown outflow can be observed.

The typical sediment of the intertidal flats of the investigation area can be described as fine and medium sand with a relatively low proportion of fine sized particles, and organic material. Descriptions of Tauranga Harbour sediments and their dynamics are in Davies-Colley (1976) and from Dahm (1983), although there have been no previous studies of the harbour sediments specifically at this site.

3. Sediment sampling and description

Samples were taken either as sediment surface samples using a box-dredge, or in short plastic core tubes. Samples were collected by hand and with the help of scuba diving equipment. Normally, the depth interval of sampling was about 0 to 10 cm. Where possible, short cores were collected and divided into 10 cm depth interval segments. Subsamples of the cores were designated (after the slash mark) by the number of the sampling station and by the average depth of the core segment.

Before sampling, equipment was sequentially rinsed with 2 M acid (HCl) and base (NaOH) solutions and hot water. Sampling stations are shown in Figure 3 (Matata Lagoon), and Figure 5 (Tauranga Harbour). Sample descriptions are given in Table 2.

Table 2. Sample descriptions.

Matata Lagoon samples (for sample sites see Figure 3)

sample no.	sediment type	sample site
1, 2	black, silty, anoxic mud	control site, SH2 bridge, southern tributary, upstream
3	sand and gravel	Tarawera River bed, between SH2 bridge and coastline
4	peaty sand	Tarawera River bank, periodically flooded swamp, overgrown
5, 6	black-grey, silty anoxic mud	old lagoon arms and pond close to the Tarawera River
7, 8	dark grey, sandy, muddy silt	western lagoon lakes near Matata village

Tauranga Harbour samples (for sample sites see Figure 5)

sample no.	sediment type	sample site
1, 2, 3	brown-grey, sandy, artificial soil, rubble	southern border of the airport dumping ground, drain-ditch
4, 5	black, sandy mud	drain/ditch along the northern border of the dumping ground
6, 7	black-grey, muddy sand	Waipu Bay, Matapihi, at the foot of the active wood dump

4. Sample extraction and analysis

Samples were homogenized and suspended in distilled water and wet-sieved through a 200 µm mesh sieve. The sieved sediment was then centrifuged and the recovered solid fraction was freeze dried to afford a salt free, dry, homogeneous fraction, finer than 0.2 mm. Sediment samples were extracted for 24 h using a Soxhlet extractor with hexane/isopropanol as solvent. n-Nonanoic acid was introduced onto the sediment samples in the Soxhlet extractor immediately before extraction, while n-octadecane (C_{18} hydrocarbon) was added to the extractive solutions after the extraction period. Response factors for resin acid and fatty acids were determined using a standard solution of abietic acid, palmitic acid and n-octadecane in hexane/isopropanol (1:1).

Extractive solutions were concentrated to ca 2 mL using a rotary evaporator. After the addition of diazomethane (to convert the acids to methyl esters), the extractive solutions were analysed by gas chromatography using a HP-1 (methyl silicone) capillary column installed in a Hewlett Packard 5890 Series II GC instrument fitted with a flame ionisation detector (FID) The GC-FID sample sequence and other sample parameters are given in Table 3.

The following compounds were quantified: palmitic acid (16:0), oleic acid group isomers (cis/trans 18:1; 18:2, isomers etc), stearic acid (18:0), other fatty acids (22:0, 24:0, 26:0, 28:0: and 30:0), pimaric acid, isopimaric acid group (up to four contributing resin acids), abietan-18-oic acid, dehydroabietic acid (DHAA), abietic acid and C_{22} to C_{32} hydrocarbons.

Peak identifications were verified using a Hewlett Packard 5890 GC system interfaced to a Hewlett Packard 5970 Mass Selective Detector (MSD). Selected ion GC/MSD analysis was also used to determine the levels of DHAA, 12-chloro-DHAA, and 14-chloro-DHAA, 12,14-dichloro-DHAA.

Table 3. GC-FID sample sequence and some sample characteristics.

no.	sample code	depth (cm)	loss on ignition (%)	weight (g)	extraction date
Matata Lagoon samples[a]					
1	ML2/1[b]	5	21.6	3.135	28-5-92
2	ML2/1[b]	5	21.6	3.135	28-5-92
3	ML2/2	15	19.5	3.092	28-5-92
4	ML3[b]	5	15.0	0.592	28-5-92
5	ML3[b]	5	15.0	0.592	28-5-92
6	ML4/1	5	16.8	3.188	28-5-92
7	ML4/2	15	14.9	3.600	9-6-92
8	ML5/1[b]	5	20.9	3.494	9-6-92
9	ML5/1[b]	5	20.9	3.494	9-6-92
10	RF standard	-	-	-	-
11	ML5/2	15	24.2	3.296	9-6-92
12	ML5/3	25	10.0	3.723	9-6-92
13	ML6/1	5	14.1	3.415	31-5-92
14	ML6/2	15	15.6	3.179	31-5-92
15	ML7/1	5	10.9	3.167	31-5-92
16	ML7/2	15	7.6	3.261	31-5-92
17	ML7/3	25	9.3	3.183	31-5-92
18	ML8/1	5	13.0	3.319	31-5-92
19	ML8/2	15	11.6	3.156	3-6-92
20	RF standard	-	-	-	-
21	ML8/3	25	9.4	3.274	3-6-92
Tauranga Harbour samples[a]					
22	TH1	5	29.2	3.187	3-6-92
23	TH2	5	16.7	3.114	3-6-92
24	TH3	5	29.9	3.107	4-6-92
25	TH4	5	13.9	3.278	4-6-92
26	TH5	5	10.7	3.120	4-6-92
27	TH6/1	5	6.7	3.480	4-6-92
28	TH6/2	15	5.9	3.741	5-6-92
29	TH6/3	25	6.7	3.421	5-6-92
30	TH6/3 (clay)	25	20.8	3.904	5-6-92
31	TH7	5	3.6	5.057	5-6-92
32	RF standard	-	-	-	-

[a] internal standards, 150 μL n-nonanoic acid acid (0.570 mg/mL) added before extraction and 150 μL n-octadecane (0.569 mg/mL) added after extraction, except for sample ML3 (30 μL of each standard added).

[b] split sample (for duplicate analysis).

The experimental procedures were generally similar to those describe by Wilkins and Panadam (1987). Other similar investigations have been described by Morales et al. (1992) and Remberger et al. (1990). For general information concerning the analysis and identification of organic pollutants see Eglinton and Murphy (1969), Keith (1976) and Holmbom (1980).

The loss on ignition (l.o.i.), was determined by weight loss of the dry samples after combustion at 550ºC for 3 h.

5. Calculation of Concentrations

Representative GC-FID and GC-MSD profiles, obtained using the FID and MSD systems respectively, are given in Figures 7 and 8. Compound concentrations were computed using a purpose written EXCEL spreadsheet.

Concentrations were calculated using the following protocols:

<u>Response Factor (RF) Calculation</u>

A_{Sub} = Area of selected substance peak

V_{Sub} = Volume of selected substance solution (mL)

$[conc]_{Sub}$= concentration of selected substance solution

M_{Sub} = mass (weight) of selected substance in RF solution

$= V_{Sub} * [conc]_{Sub}$

A_{IntS} = Area of internal standard peak

V_{IntS} = Volume of internal standard solution (mL)

$[conc]_{IntS}$ = concentration of internal standard solution (µg/mL)

M_{IntS} = mass (weight) of internal standard in RF solution

$= V_{IntS} * [conc]_{IntS}$

$RF = (A_{Sub} / M_{Sub}) / (A_{IntS} / M_{IntS})$

<u>GC-FID and GC/MS Analyses</u>

A_{TS} = Area of target substance peak

M_{Sed} = mass (g) of sediment used in the extraction

RF = response factor of target substance

A_{IntS} = Area of internal standard peak

V_{IntS} = Volume of internal standard solution (mL)

$[\text{conc}]_{IntS}$ = concentration of internal standard solution (µg/mL)

M_{IntS} = mass of internal standard added to extractive solution (µg)

$$= V_{IntS} * [\text{conc}]_{IntS}$$

M_{TS} = Mass of target compound in extractive solution (µg)

$$= \frac{(A_{TS} / RF) * M_{IntS}}{(A_{IntS})}$$

$[\text{conc}]_{TS}$ = concentration of target compound in sediment sample (µg/g = mg/Kg = ppm)

$$= M_{TS} / M_{Sed}$$

$$= \frac{(A_{TS} / RF) * M_{IntS}}{(A_{IntS} * M_{Sed})} \quad (\mu g/g = mg/Kg = ppm)$$

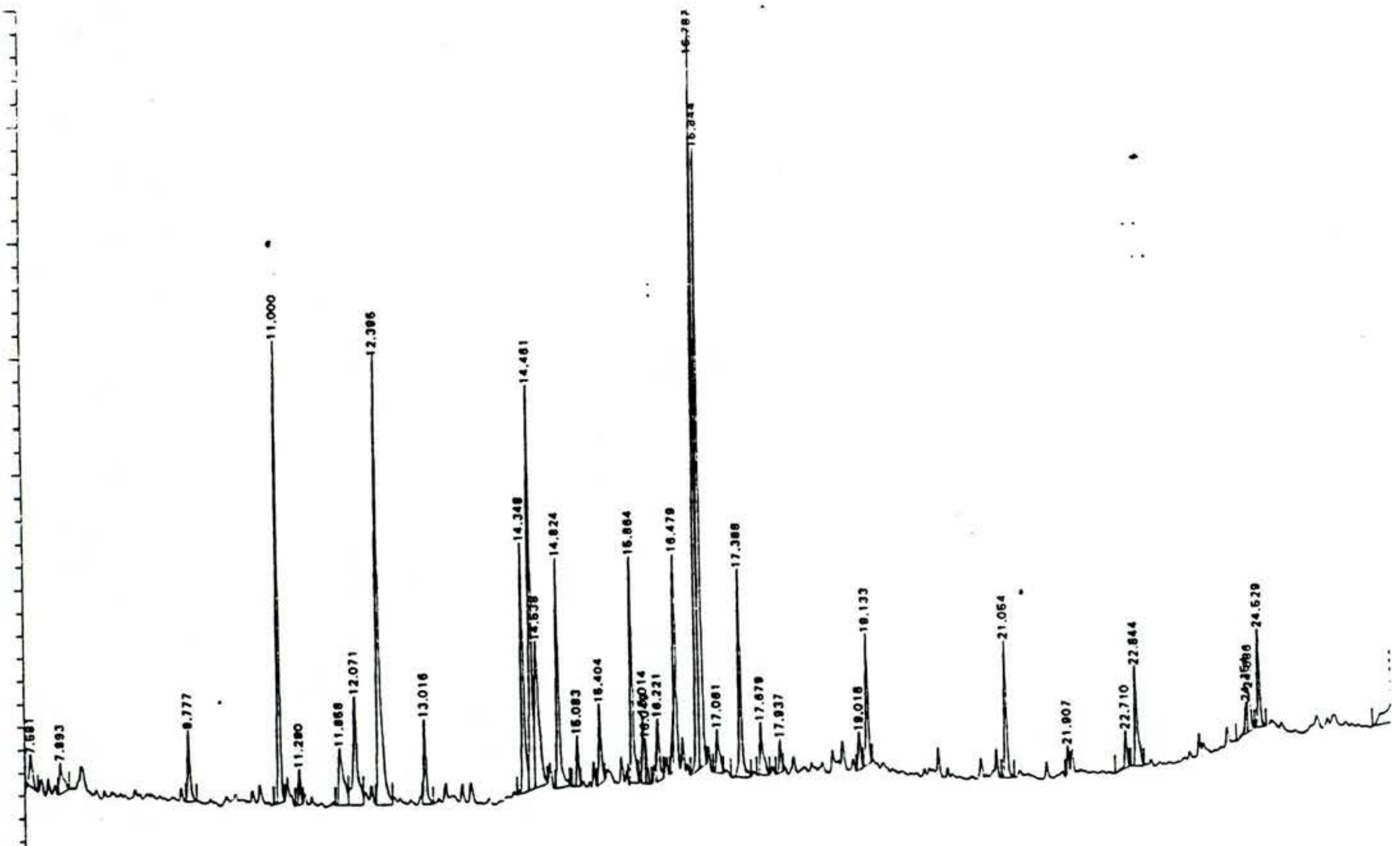


Figure 7. GC-FID profile of the Matata Lagoon sample ML5 (see Table 2 for site description).

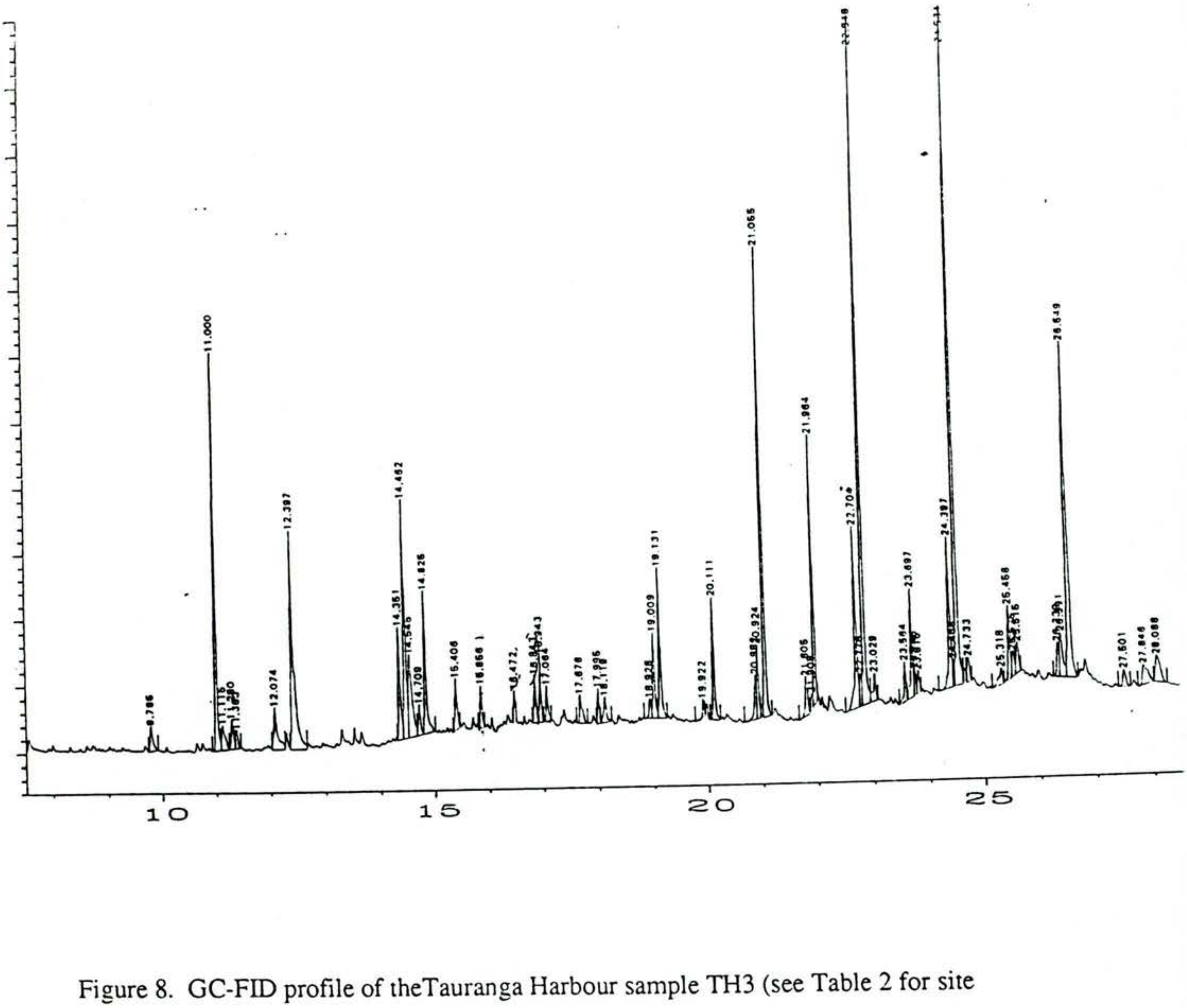


Figure 8. GC-FID profile of theTauranga Harbour sample TH3 (see Table 2 for site description).

6. Results and Discussion

6.1. Matata Lagoon

Table 4 gives the concentrations of resin acids and fatty acids detected in the control site, Tarawera River bed and Matata Lagoon sediment samples using the GC-FID protocol. Since the levels of some of the resin acids (eg chlorodehydroabietic acid isomers) were close to, or below the nominal GC-FID detection limit the sediment extracts were also analysed using selected ion GC-MSD detection. Table 5 gives the concentrations of DHAA, 12-chloro-DHAA, 14-chloro-DHAA and 12,14-dichloro-DHAA determined using selected ion acquisition with response factors determined for these compounds using authentic specimens of the foregoing compounds. The levels of secodehydroabietic acids 1 and 2 (given in brackets in Table 5) was also indirectly calculated using the GC-FID determined level of these compounds in the sample ML3 to derive the corresponding SIM GC/MSD response factor.

The results given in Tables 4 and 5 can also be compared with those determined by Singh-Thandi (pers. comm.) in a parallel study of other Tarawera River sediment samples (Table 6). These samples were dried, sieved, extracted and analysed in an manner identical to that applied in this study.

6.1.1. Resin acids

Comparatively low levels of resin acids (50-70 ppm) (mainly dehydroabietic acid, pimaric acid, isopimaric acid and/or abiet-13-en-18-oic acid) were detected in control site sediment samples, taken from an uncontaminated site (ML2) remote from the Tarawera River Mouth sediment (ML3) and in the upper lagoon sediment samples (ML7 and ML8 sites). On the other hand elevated levels of resin acids (150-1235 ppm) were detected in the river bed sample (ML3) and the lower lagoon sample samples (ML5 and ML6). Generally similar levels of resin acids were also detected in a parallel investigation other Tarawera River bank sediment samples (see Table 6).

Table 4. GC-FID determined concentration of resin acids and fatty acids detected in some Matata Lagoon and Tarawera River sediment samples (ppm).

Abbreviations: Pim = pimaric acid; Iso/13 = isopimaric and/or abiet-13-en-18-oic acids; Ab-18 = abietan-18-oic acid; DHAA = dehydroabietic acid; Abiet = abietic acid; 16:0 = palmitic acid; 18:1 gp = oleic (18:1) and linolenic (18:2) acid isomers; 18:0 stearic acid.
Sample sites are as shown in Figure 3.

	resin acids					fatty acids		
	Pim	Iso/13	Ab-18	DHAA	Abiet	16:0	18:1 gp	18:0
Control site								
ML2/1 (5 cm)	14	15	-	21	#	68	149	31
ML2/2 (15 cm)	16	14	-	21	6	47	119	20
River bed site								
ML3 (5 cm)	112	203	471	319	100	#	#	#
Site near river bank								
ML4/1 (5 cm)	124	142	516	330	119	65	149	36
ML4/2 (15 cm)	83	72	193	227	101	25	75	16
Lower lagoon sites								
ML5/1 (5 cm)	45	49	134	115	44	46	85	22
ML5/2 (15 cm)	61	61	182	164	68	59	83	13
ML5/3 (25 cm)	32	23	41	75	29	16	50	10
ML6/1 (5 cm)	102	96	337	278	114	36	75	27
ML6/2 (15 cm)	74	63	92	205	89	54	121	26
Upper lagoon sites								
ML7/1 (5 cm)	19	18	-	23	5	99	142	27
ML7/2 (15 cm)	21	17	-	27	5	52	120	20
ML7/3 (25 cm)	23	21	-	38	21	41	122	25
ML8/1 (5 cm)	20	17	-	28	13	63	120	23
ML8/2 (15 cm)	21	23	-	31	18	35	114	10
ML8/3 (25 cm)	18	18	-	32	16	33	100	9

- not detected; # not quantified.

Table 5. Selected ion GC/MS determined concentrations of dehydroabietic acid and related resin acids in Matata Lagoon and Tarawera River sediment samples (ppm).

Abbreviations: Seco-1 = secodehydroabietic acid-1; Seco-2 = secodehydroabietic acid-2; DHAA = dehydroabietic acid; 12-Cl = 12-chlorodehydroabietic acid; 14-Cl = 14-chlorodehydroabietic acid; 12,14-Cl_2 = 12,14-dichlorodehydroabietic acid.
Sample sites are as shown in Figure 3.

	Seco-1	Seco-2	DHAA	12-Cl	14-Cl	12,14-Cl_2
Control site						
ML2/1 (5 cm)	#	#	39	-	-	-
ML2/2 (15 cm)	#	#	24	-	-	-
River bed site						
ML3 (5 cm)	(32)[a]	(16)[a]	333	7	41	57
Site near river bank						
ML4/1 (5 cm)	(25)	(12)	297	5	17	12
ML4/2 (15 cm)	(16)	(9)	211	3	9	4
Lower lagoon sites						
ML5/1 (5 cm)	(8)	(4)	125	2	12	10
ML5/2 (15 cm)	(10)	(6)	179	4	20	8
ML5/3 (25 cm)	(4)	(2)	74	1	6	1
ML6/1 (5 cm)	(17)	(10)	252	8	26	9
ML6/2 (15 cm)	(11)	(7)	196	6	24	6
Upper lagoon sites						
ML7/1 (5 cm)	(2)	(2)	31	-	-	-
ML7/2 (15 cm)	(3)	(2)	32	-	-	-
ML7/3 (25 cm)	(3)	(2)	46	-	-	-
ML8/1 (5 cm)	(3)	(2)	32	-	-	-
ML8/2 (15 cm)	(3)	(2)	34	-	-	-
ML8/3 (25 cm)	(3)	(2)	34	-	-	-

- not detected; # not quantified; [a] see text.

Table 6. GC-FID determined concentration of resin acids and fatty acids detected in Tarawera River sediment samples (ppm).

Abbreviations: Pim = pimaric acid; Iso/13 = isopimaric and/or abiet-13-en-18-oic acids; Ab-18 = abietan-18-oic acid; DHAA = dehydroabietic acid; Abiet = abietic acid; Other = other resin acids; 16:0 = palmitic acid; 18:1 gp = oleic (18:1) and linolenic (18:2) acid isomers; 18:0 stearic acid; Other = other fatty acids..

	resin acids						fatty acids			
	Pim	Iso/13	Ab-18	DHAA	Abiet	Other	16:0	18:1 gp	18:0	Other
Kawerau Bridge	13	-	-	28	13	traces	48	108	15	38
below Caxton	9	15	-	13	10	traces	32	25	18	33
below Tasman	40	88	213	144	42	106	47	36	16	32
SH30 Bridge	98	187	470	270	107	206	42	82	18	48

- not detected; # not quantified.

The river bed sample was found to be comprised of mainly pumice and gravel material. However sample seiving realised a modest quantity of fine, silt-clay material. Hitherto Osborne has noted that river bed pumice and gravel has little affinity for resin acids. It is apparent that the level of resin acids associated with the seived river bed silt-clay material is similar to that determined by Singh-Thandi (pers. comm.) for equivalently seived and extracted river bank and lower lagoon sediment samples.

A notable feature of the results was the detection in the ML3, ML4, ML5 and ML6 samples of process modified resin acids. Abietan-18-oic acid has hitherto been identified by Wilkins et al. (1987) as the major resin acid constituent of the biologically treated effluents discharged into the Tarawera River by the Tasman Pulp and Paper Company. Abietan-18-oic acid, which is not a constituent of Pinus radiata extracts (or the tall oil fraction recovered during the recycling of cooking liquors), is believed to be derived from abietic acid by successive hydrogenation of the two double bonds (see also Figure 2). Similarly chloro-DHAA isomers, formed from DHAA during pulp bleaching operations, were detected in the river bed and lower lagoon samples, but not the upper lagoon samples. The level of the chloro-DHAA isomers was such that while they could not be adequately quantified by GC-FID, they were readily quantified using SIM GC/MS data (see Table 5).

The results presented in Tables 4 and 5 demonstrate that sediments from the lower lagoon sites possess resin acid levels similar to those encountered in river bed and river bank samples. It is clear that river water is continuing to penetrate the lower lagoon (adjacent to the river (sites ML4 and ML5 respectively). This penetration may take the the form of either or both of ground water seepage and periodic flooding of the low lying ground in the vicinity of the river mouth.

6.1.2. Fatty acids

Fatty acids [mainly palmitic acid, oleic acid group isomers (18:1, 18:2, etc) and stearic acid] were detected in all of the sediment samples. Since the levels detected in the river bed and lagoon sediments were not significantly different from those determined for the control site sediment, little significance (at least in respect of the characterisation of a possible a pulp and paper mill contribution) can be attached to the fatty acid levels.

6.1.3. GC/MS selected ion ratio data

In the course of the investigation it was noted that a relationship appeared to exist between the levels of pimaric acid and sandaracopimaric acid. Since each of these compounds exhibited a strong mass spectral ion of m/z 121, the relative levels of these these compounds can be conveniently assessed by integrating the m/z 121 SIM GC/MS responses of these compounds. The native ratio of the these ions is around 0.40-0.43 (eg ML2 samples, see Table 7), while biological treatment results in a ratio around 0.19-0.24 (ML4, ML5 and ML6 samples).

Table 7. SIM-GC/MS determined dehydroabietic acid concentrations (ppm) and resin acid ion ratios in Tarawera River Mouth and Matata Lagoon sediment samples.

Abbreviations: l.o.i. = loss on ignition; DHAA = dehydroabietic acid; Seco-1 = secodehydroabietic acid-1; Seco-2 = secodehydroabietic acid-2; Sand = sandaracopimaric acid; Pim = pimaric acid. Sample sites are as shown in Figure 3.

	depth (cm)	l.o.i (%)	DHAA (ppm)	Seco-2/Seco-1	Sand/Pim
ML2/1	5	21.6	39	0.76	0.43
ML2/2	15	19.5	24	0.74	0.40
ML3	5	15.0	333	0.49	0.31
ML4/1	5	16.8	297	0.49	0.19
ML4/2	15	14.9	211	0.52	0.20
ML5/1	5	20.9	125	0.49	0.21
ML5/2	15	24.2	179	0.58	0.20
ML5/3	25	10.0	74	0.51	0.24
ML6/1	5	14.1	252	0.57	0.23
ML6/2	15	15.6	196	0.60	0.24
ML7/1	5	10.9	31	0.73	0.39
ML7/2	15	7.6	32	0.69	0.38
ML7/3	25	9.3	46	0.69	0.33
ML8/1	5	13	32	0.73	0.37
ML8/2	15	11.6	34	0.71	0.35
ML8/3	25	9.4	34	0.67	0.44

The sandaracopimaric acid/pimaric acid ratios exhibited by the ML7 and ML8 samples (0.33-0.44) are consistent with the view that these samples have not in recent times been exposed to a water column carrying biologically treated pulp mill effluents. To a lesser extent the ratio of the m/z 146 ion responses of the pair of secodehydroabietic acids (0.67-0.76 in native sediments; 0.49-0.60 in sediments exposed to a water column carrying biologically treated pulp mill effluents) (see Table 7) also serves to define the the extent to which pulp mill effluents have entered the Matata Lagoon.

6.1.4 Matata Lagoon Data Multivariate Statistical Analysis

A multivariate analysis involving bivariate correlations and principal components analysis was undertaken for the data set of 17 cases, comprising the variables of sample depth, loss on ignition, concentrations of DHAA's, chlorinated DHAA's, total resin acids, and total fatty acids.

Table 8. Pearson moment correlation matrix for Matata Lagoon data.

	Depth (cm)	Loss on ignition	DHAA	chlorinated DHAA's	total resin acids	total fatty acids
depth (cm)	1.000					
loss on ignition	-0.496	1.000				
DHAA	-0.363	0.191	1.000			
chlorinated DHAA's	-0.379	0.146	0.897	1.000		
total resin acids	-0.384	0.152	0.990	0.877	1.000	
total fatty acids	0.112	-0.028	0.563	-0.696	-0.539	1.000

Table 9. Principle component analysis of Matata Lagoon data. Only loadings exceeding 0.5 are listed.

parameter	factor 1	factor 2	factor 3
depth (cm)	0.509	0.694	
Loss on ignition		-0.824	
DHAA	-0.954		
chlorinated DHAA's	-0.949		
total resin acids	-0.944		
total fatty acids	0.699		-0.557
% total variance	58.9	22.3	9.5

From the correlation matrix (Table 8) in which r = 0.48 is significant at the 95% level, the following trends are evident:

- there is a high positive correlation between the concentrations of DHAA and chlorinated DHAA's and total resin acids, and between the chlorinated DHAA's and total resin acids. This is consistent with the predominant origin of the three classes of resin acids from a common source, i.e. the Tasman mill which is known to discharge resin acids, including chlorinated DHAA's which are produced as a by-product of bleaching operations.

- There is a negative correlation between the concentrations of fatty acids and DHAA, and between chlorinated DHAA's and total resin acids. This can be ascribed to a relatively uniform level of fatty acids throughout the lagoon sediments. In contrast the lower lagoon sites exhibits high levels of resin acids, whereas the upper lagoon sites display resin acid levels less than those of the fatty acids.

The principal components analysis (Table 9) identified three factors which accounted for 91.6% of the data variance. The first factor accounting for 58.9% of the variance shows a strong association of the concentrations of DHAA, chlorinated DHAA's, and total resin acids, being negatively related to sample depth and fatty acid levels, reflecting a relatively uniform level of fatty acids compared to the influence of mill source resin acids, particularly the lower lagoon sites (see Table 4).

A second independent pattern in the data accounting for 22.3% of the variance, links sample depth negatively with loss on ignition, indicating a reduction in organic matter with depth. A third factor (9.5%) is associated with random variations in total fatty acid concentration.

6.1.5. Discussion

The sediments of the western parts of Matata Lagoon including the lakes near Matata village do not appear to be influenced by modern Tarawera River water. Process modified resin acids, such as abietan-18-oic acid and chloro-DHAA isomers, were not detected in the ML7 and ML8 samples while DHAA concentrations were only marginally higher than those determined for the control sites. Nevertheless, there is the suspicion of a higher input in the past since the DHAA concentrations in the ML7 and ML8 cores show a weakly increasing trend with sediment depth.

The resin acid concentrations determined in this study are typically 10^3 and 10^4 times higher than those found in the overlying water column. DHAA concentrations of more than 100 mg/kg sediment are extraordinary and usually only obtained in paper mill effluent discharge areas. Sediment samples in Lake Superior, Canada, had maximum concentrations of 100 mg DHAA per kg dry weight at the mouth of a polluted river (Fox, 1976).

Remberger et al. (1990) has reported the concentrations of chloro-DHAA's in some Scandinavian sediments to be of order 130 and 450 mg/kg organic carbon content. If it is assumed that in the present study approximately 1/3 of the loss on ignition arises from organic carbon, it follows that the level of chloro-DHAA isomers in the Tarawera is of the order 600 mg/kg organic carbon.

6.2. Tauranga Harbour Bark Dump Samples

6.2.1 Resin acid and fatty acids

Table 10 presents the concentrations of some resin acids, fatty acids and hydrocarbons in the Tauranga Harbour sediment samples. While significant levels of resin acids such as pimaric acid, dehydroabietic acid and abietic acid were detected, none of the process modified resin acids (abietan-18-oic acid and chlorinated DHAA isomers) were detected in the Tauranga Harbour samples.

Table 10. GC-FID determined concentration of resin acids, fatty acids and hydrocarbons detected in some Tauranga Harbour sediment samples (ppm).

Abbreviations: Pim = pimaric acid; Iso/13 = isopimaric and/or abiet-13-en-18-oic acids; Ab-18 = abietan-18-oic acid; DHAA = dehydroabietic acid; Abiet = abietic acid; 16:0 = palmitic acid; 18:1 gp = oleic (18:1) and linolenic (18:2) acid isomers; 18:0 stearic acid; Other FAs = Sum of 20:0, 22:0, 24:0, 26:0, 28:0 and 30:0 fatty acids; C_{22}-C_{32} = sum of C_{22}-C_{32} hydrocarbons.
Sample sites are as shown in Figure 5.

	resin acids				fatty acids				hydrocarbons
	Pim	Iso/13	DHAA	Abiet	16:0	18:1 gp	18:0	Other FAs	C_{22}-C_{32}
TH1 (5cm)	20	12	28 (40)[a]	12	40	115	13	98	34
TH2 (5 cm)	14	9	18 (27)	11	48	94	12	65	23
TH3 (5 cm)	10	7	11 (14)	#	37	60	18	269	132
TH4 (5 cm)	14	8	17 (22)	6	21	81	10	109	29
TH5 (5 cm)	17	11	22 (28)	11	35	112	9	83	14
TH6/1 (5 cm)	15	9	20 (24)	9	28	103	15	52	9
TH6/2 (15 cm)	6	1	6 (8)	#	16	25	9	36	10
TH6/3 (25 cm)	8	2	8 (11)	#	21	35	9	57	15
ML6/3 clay (25 cm)	11	4	10 (13)	#	47	55	19	246	65
TH7 (5 cm)	6	2	6 (8)	#	16	28	7	20	3

Not determined, [a] SIM GC/MS determined concentration.

Generally, the levels of resin acids detected in the Tauranga Harbour samples were low. The observed DHAA levels (Table 10) are comparable to those found in the Matata Lagoon investigation control site sample (ML2), or a Kawerau Town Bridge sample (see Table 6). A series of long chain fatty acids, ranging primarily from palmitic acid to tricontanoic acid (16:0 to 30:0) were also detected in all of the samples. Samples TH3 and TH6/3 clay (the clay fraction of sample TH6/3) exhibited the highest concentrations of long chain fatty acids.

6.2.2 Tauranga Harbour Data Multivariate Statistical Analysis

A multivariate analysis involving bivariate correlations and principal components analysis was undertaken for the data set of 10 cases, comprising the variables of sample depth, loss on ignition, concentrations of DHAA, total resin acids, 16:0/18:1/18:0 fatty acids, other fatty acids and C_{22}-C_{32} hydrocarbons (see Table 11).

Table 11. Pearson moment correlation matrix for Tauranga Harbour samples.

	depth (cm)	Loss on ignition	DHAA	total resin acids	16:0/18:1/18:0 fatty acids	other fatty acids	hydro-carbons
depth (cm)	1.000						
loss on ignition	-0.152	1.000					
DHAA	-0.540	0.413	1.000				
total resin acids	-0.566	0.394	0.995	1.000			
16:0/18:0/18:1 fatty acids	-0.432	0.561	0.905	0.923	1.000		
other fatty acids	0.190	0.759	-0.046	-0.050	0.253	1.000	
hydrocarbons	0.010	0.788	-0.087	-0.092	0.171	0.928	1.000

Table 12. Principle component analysis of Tauranga Harbour data. Only loadings exceeding 0.5 are listed.

parameter	factor 1	factor 2	factor 3
depth (cm)	0.556		0.728
loss on ignition	-0.730	0.610	
DHAA	-0.891		
total resin acids	-0.895		
16:0/18:1/18:0 fatty acids	-0.943		
other fatty acids		0.906	
C_{22}-C_{32} hydrocarbons		0.902	
% total variance	51.1	36.1	9.5

From the correlation matrix (Table 11) in which $r = 0.63$ is significant at the 95% level, the following trends are evident:

- Very high correlations are evident between DHAA and total resin acids and between DHAA and 16:0/18:1/18:0 fatty acids, suggesting that the resin acids and fatty acids have a common source.

- A very high correlation is evident between hydrocarbons and other fatty acids, suggesting a common source.

- Significant correlations occur between loss on ignition and hydrocarbons and other fatty acids. This is not unexpected given the combustible nature of these compounds.

The principal components analysis identified 3 factors (Table 12) accounting for 96.7% of the data variance. The first factor accounting for 51.1% of the variance shows strong association of concentrations of fatty acids with total resin acids, DHAA, and loss on ignition, all of which are negatively associated with sample depth. i.e. concentrations of those materials occur predominantly within the surface sediments.

A second independent pattern in the data accounting for 36.1% of the variance, links high values of loss on ignition with other fatty acids and hydrocarbon concentrations, as noted in the table of correlations. A third factor (9.5%) is associated with random variations in sample depth.

6.2.3 Discussion

The chemical results indicate that the wood and bark material from the modern dump grounds around Tauranga Harbour are in a relatively undecomposed condition and have not yet changed significantly due to diagenetic processes.

The depositional environment of Tauranga Harbour site is oxic and well drained. Moreover, the permeability of the harbour sands, and the regular washing by the tidal water movements probably contributes to the dispersal of organic contaminates originating from the dump grounds. Clearly the situation in Tauranga Harbour is very different to that encountered in the vicinity of the Tarawera River and Matata Lagoon.

Future environmental investigations of the dumping grounds should include some other parameters: eg nutrient mobilisation and heavy metal analyses (if rubbish was dumped together with the bark waste). Sediment and water samples should be secured from the bottom of the dump depositions. The bioaccumulation of resin acids, and other substances, in benthic animals from the vicinity of the dumping area should also be examined.

7. Summary of results

The main findings of the present investigation are:

Matata Lagoon Investigation

(i) Abietan-18-oic acid and chloro-DHAA isomers are absent in the control site samples and are thus good indicators of pulp and paper mill originated contribution(s) to sediments.

(ii) Sediment samples from the lower regions of the Matata Lagoon, but not the upper regions, are influenced by modern Tarawera river water, as evidenced by the present of abietan-18-oic acid and chloro-DHAA isomers.

(iii) DHAA concentrations in sediments from the polluted area(s) are typically 10 times higher than samples from the control sites.

Tauranga Harbour Investigation

(i) Resin acid levels in the bark dump zone sediments were similar to those determined for reference (uncontaminated) sites.

(ii) Modified resin acids, such as abietan-18-oic acid, were not detected in the sediment samples.

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