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Pulp Mill-Sourced Substances in Sediments from a Coastal Wetland

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ABSTRACT

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Matata Lagoon, at the mouth of the Tarawera River is an ecologically important coastal wetland, situated some 26 km upstream of two paper mills which discharge their waste waters into the river. A matter of environmental concern is the extent to which pulp mill related organic substances, especially resin and fatty acids, have penetrated the upper and lower reaches of the lagoon. Investigation by GC-FID and GC-MS established that: (1) the lower lagoon sediments possessed resin acid levels similar to that presently within the river bed; (2) upper lagoon sediments were close to natural background levels; and (3) mass spectral ion ratio analyses confirmed that lower lagoon sediments were significantly contaminated by mill-sourced resin acids, whereas upper lagoon sediments were not significantly contaminated.

ADDITIONAL INDEX WORDS: *DHAA, resin acids, fatty acids.*

INTRODUCTION

Matata Lagoon was originally the estuarine mouth of the Tarawera River, but when in 1914 the river was diverted through coastal dunes direct to the sea, the lagoon became established as a flood overspill reservoir (Figures 1 and 2) protected from the open sea by a series of high foredunes (HEALY, 1978; RICHMOND *et al.,* 1984). Subsequently, it has gradually infilled to create a swampy lagoon in the lowland area behind the beach and foredunes (Figure 1). The lagoon comprises upper and lower basins, separated by a causeway and a weir. Highly organic muddy sediments are now accumulating in the basins.

The modern lagoon is freshwater dominated with a high biological primary production, and it contains typical coastal lagoon plant successions. Periodically the lagoon is subject to tidal backflow and episodic storm flooding from the Tarawera River from which it is separated by a semi-permeable peaty deposit. Some 26 km upstream, two paper mills discharge about 200,000 m^3 per day of biologically treated waste waters. Below the mills, the river's appearance changes from clear, fresh, pristine water to a dark brown waterway with a significant odour. Hitherto concentrations of 46 μg/L DHAA and 40 μg/L abietan-18-oic acid have been found (WILKINS and PANADAM, 1987) in water samples taken about 10 km downstream from the two paper mills. Lesser levels were detected in a more recent synoptic survey (SINGH-THANDI, 1993).

A matter of environmental concern is the extent to which mill-sourced organic substances, especially resin acids, have penetrated the upper and lower reaches of the lagoon and become incorporated into the lagoon sediments. This paper investigates the levels of resin acids and fatty acids detected in representative lagoon sediment samples. This information was required by the regional environmental authority as part of the coastal management plan.

PULP MILL ORGANIC CONTAMINANTS

Dehydroabietic acid (DHAA), abietic acid, and pimaric acid (Figure 2) are examples of a group of persistent resin acid diterpene metabolites derived from woody plants (mainly conifers) 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."

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 LC$_{50}$ concentration (lethal dose toxicity test) of DHAA towards rainbow trout is about 1000 μg/L (1 ppm). KINAE *et*

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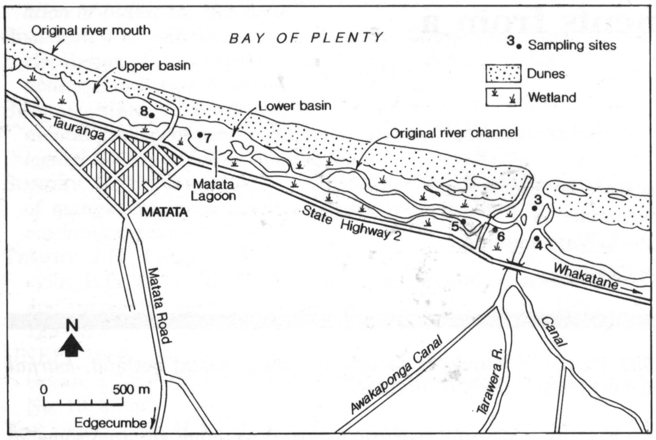

Figure 1. Map of the Matata Lagoon and coastal dunes near the mouth of the Tarawera River. The control sample was collected some 4 km distance along the tributary, parallel to the Whakatane highway.

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 result in the release of resin acids into the aqueous phase.

The metabolism and degradation of individual resin acids can be very different. Some compounds are stable over a long time and also under varying conditions, while others are decomposed quickly. TAKEDA *et al.* (1968) and PEREIRA *et al.* (1982) have discussed the thermal isomerisation of abietic acid while LAFLAMME and HITES (1978) have described possible degradation pathways for abietic acid and pimaric acid, leading to metabolites such as dehydroabietin, retene and/or fichtelite. MCFARLANE and CLARK (1988) have investigated the microbiological metabolism of resin acids in anaerobic reactor experiments; WILKINS *et al.* (1989) have identified 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 effluent's (LEACH *et al.,* 1978), especially for the degradation of DHAA with bacteria (BIELLMANN *et al.,* 1973a; 1973b) or fungi (KUTNEY *et al.,* 1981).

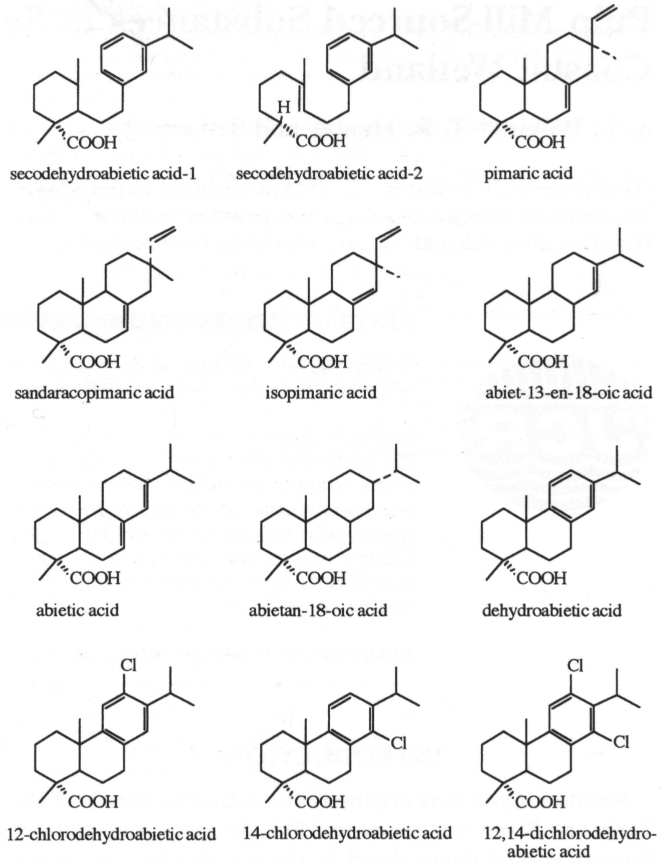

Figure 2. Structural formulae of some resin acids.

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, and lignins and to also occur in deposits derived from volcanic eruptions occurring in the vicinity of coniferous wood (see Table 1). Examples of human-induced concentration and release of resin acids and resin neutrals into the environment include wood, timber, log and

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	Volcanic Ash
Abietic acid	√	√	√	—	√	—	—	—
Pimaric acid	√	√	—	—	—	—	—	—
Dehydroabietic acid	√	√	√	—	√	√	√	√
Abiet-13-en-18-oic acid	—	—	√	—	—	—	—	√
Dehydroabietane	√	√	—	√	√	—	√	√
Dehydroabietin	—	√	—	—	√	√	√	√
Fishtelite	—	—	√	—	√	√	—	—
Retene	—	√	√	√	√	√	√	√

Table 2. *Matata Lagoon samples (for sample sites see Figure 1).*

Sample No.	Sediment Type	Sample Site
1*, 2	black, silty, anoxic mud	control site, SH2 bridge, southern tributary, upstream
3	mainly 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

*Due to transport contamination sample 1 was not suitable for analyses

Table 3. *GC-FID sample sequence and some sample characteristics of the Matata Lagoon and Tarawera River mouth sediment samples.*

No.	Sample Code	Depth (cm)	Loss on Ignition (%)	Weight (g)	Extraction Date[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

[a] Internal standards, 150 μL *n*-nonanoic 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)

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).

Organic molecules such as resin acids (eg DHAA) and resin neutrals (fichtelite) are excellent chemical and biological marker species. 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). We therefore anticipated that a pulp and paper mill contribution to the Matata Lagoon sediments would result in the accumulation of 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).

METHODS

Sample Collection

Samples were collected 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. Where possible, short cores were collected and divided into 10 cm depth interval subsamples, 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 1 and sample descriptions are given in Table 2.

Sample Extraction and Analysis

Samples were homogenised 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 (1:1) 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. Extractive solutions were concentrated to about 2 mL using a rotary evaporator. After the addition of an ethereal diazomethane (to convert the acids to methyl esters), the extractive solutions were analysed by gas chromatography using a 20 m × 0.22 mm HP-1 (methyl silicone) capillary column installed in a Hewlett Packard 5890 Series II GC instrument fitted with a flame ionisation detector (FID). GC-FID analyses were temperature programmed from 125°C to 285°C at 6°C/min. The GC-FID sample sequence and other sample parameters are given in Table 3. Peak identifications were verified by combined gas chromatography/mass spectrometry (GC-MS) using a 20 m × 0.25 mm HP-1 (methylsilicone) capillary column installed in a Hewlett Packard 5890 GC instrument interfaced to a Hewlett Packard 5970B Mass Selective Detector.

Experimental procedures were generally similar to those described 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 GC-FID response factors applied to resin acids and fatty acids (as classes) were determined using authentic specimens of abietic acid, palmitic acid and *n*-octadecane. The following compounds were quantified by GC-FID: palmitic acid

(16:0), oleic acid group isomers (*cis/trans* 18:1; 18:2, isomers etc) and stearic acid (18:0), pimaric acid, isopimaric acid and abiet-13-en-18-oic (a co-eluting pair), abietan-18-oic acid, dehydroabietic acid (DHAA) and abietic acid. Selected ion mode (SIM) response factors were determined using authentic specimens of DHAA, 12-Cl and 14-Cl DHAA and 12,14-Cl DHAA. The levels of secodehydroabietic acids-1 and 2 were also calculated (Table 4) using the GC-FID determined level of these compounds in sample ML3 (Table 3) to derive the corresponding SIM GC-MS response factor.

The loss on ignition (l.o.i.), representing the total organic content of the samples, was determined by weight loss of the dry samples after combustion at 550°C for 3 h.

Calculation of Concentrations

Responses factors (RF) and compound concentrations [conc] were computed using a purpose written EXCEL spreadsheet using the following protocols:

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

where:

A_{Sub} = area of selected substance peak
M_{Sub} = mass (weight) of selected substance in RF solution
A_{IntS} = area of internal standard peak
M_{IntS} = mass (weight) of internal standard in RF solution
$[\mathrm{conc}]_{\mathrm{TS}}$ = concentration of target substance in sediment sample (µg/g = mg/Kg = ppm)

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

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

where:

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

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

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

RESULTS

Table 4 gives the GC-FID determined concentrations of resin acids and fatty acids detected in sieved sediments recovered from the control site, Tarawera River bed and Matata Lagoon sediment samples. Since the levels of some of the resin acids (e.g., chlorodehydroabietic acid isomers) were close to or below the nominal GC-FID detection limit, the sediment extracts were also analysed using SIM GC-MS detection. Table 5 gives the SIM GC-MS determined concentrations of secodehydroabietic acids-1 and 2, DHAA, 12-chloro-DHAA, 14-chloro-DHAA and 12,14-dichloro-DHAA. Caution must be exercised in comparing the higher levels reported here for sieved samples with the generally lower levels determined for whole samples, since sieving affords a fraction with an elevated fine clay-like material content with a high affinity for organic substances.

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 the upper lagoon sediment samples (sites ML7 and ML8) and control site (uncontaminated) sediment samples taken from an site (ML2) remote from the Tarawera River mouth. On the other hand, elevated levels of resin acids (150-1235 ppm) were detected in the river bed sample (ML3) and the abandoned river channel samples (ML5 and ML6 sites). The river bed sample was found to be comprised of mainly pumice and gravel material, however sieving realised a modest quantity of fine, silt-clay material. OSBORNE (1991) has noted that compared to samples with a high clay-like material content, samples comprised mainly of river bed pumice and fine gravel/sand have little affinity for resin acids. In our analyses, it is apparent that the level of resin acids associated with the sieved river bed silt-clay material is similar to that determined for equivalently sieved and extracted river bank and abandoned river channel sediment samples.

A notable aspect of the investigation was the detection in some of the samples of biological or chemically modified resin acids. For example, abietan-18-oic acid has hitherto been identified by WILKINS *et al.* (1987) as the major resin acid constituent of the biologically treated pulp mill effluents discharged into the Tarawera River. This resin acid which was not detected in control site samples is believed to be derived from abietic acid by biologically moderated hydrogenation of abietic acid. Chloro-DHAA isomers, formed from DHAA during pulp bleaching operations, were also detected in the river bed and the abandoned channel 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 (Table 5).

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

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 in respect to the characterisation of a possible pulp and paper mill contribution can be attached to the fatty acid levels.

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

	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
Abandoned channel 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

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 1

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. From the correlation matrix (Table 6) in which r = 0.48 is significant at the 95% level, a number of trends are evident. Firstly, a high positive correlation occurs 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. Secondly, a negative correlation occurs 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 abandoned river channel sites exhibited high levels of resin acids, whereas the upper lagoon sites display resin acid levels less than those of the fatty acids.

A principal components analysis (PCA) (Table 7) identified three factors which accounted for 91.6% of the data variance. The first PCA factor accounting for 58.9% of the variance shows a strong association of the concentrations of DHAA, chlorinated DHAA's, and total resin acids. This factor is negatively related to sample depth and fatty acid levels and reflects a relatively uniform level of fatty acids compared to the influence of mill source resin acids, particularly the abandoned river channel sites (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 PCA factor (9.5%) is associated with random variations in total fatty acid concentration.

SIM GC-MS 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 both compounds exhibit a strong mass spectral ion of m/z 121, the relative levels can be conveniently assessed by integrating the respective m/z 121 SIM GC-MS responses. The native (natural) ratio of these ions is around 0.40-0.43 (*e.g.,* ML2 samples, see Table 8), while biological treatment results in a ratio of around 0.19-0.24 (ML4, ML5 and ML6 samples). 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. The m/z 146 ion responses of secodehydroabietic acids-1 and 2 (0.67-0.76 in native sediments; 0.49-0.60 in sediments exposed to a water column carrying biologically treated pulp mill effluent's) (see Table 4) also serves to define the extent

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

	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
Abandoned channel 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

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 shown in Figure 1

to which pulp mill effluents have contributed to the deposition of these substances in the Matata Lagoon.

DISCUSSION

The sediments of the upper (western) parts of Matata Lagoon including the lakes near Matata village do not appear to be influenced by modern Tarawera River water. In accord with this observation biologically or chemically modified resin acids, such as abietan-18-oic acid (believed to be derived from abietic acid by hydrogen addition) and chloro-DHAA isomers (bleaching by-products), were not detected in the ML7 and ML8 samples; 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.

Table 7. *Principal component analysis of Matata Lagoon sediment sample 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

Differences between the mean concentrations of the resin acids (calculated as the sum of the resin acid levels given in Table 4) and those at the four other sites were examined using *t*-tests. At a 95% confidence level, each of the other sites were found to contain significantly higher levels of resin acids than was the case for the control site. Based on mean levels, the average enrichment factors for resin acids relative to the control site were 1.4 (upper lagoon sites), 6.6 (abandoned channel sites), 12.5 (site near river bank), and 16.4 (river bed site). These enrichment factors are in keeping with the view that the upper parts of the Matata lagoon have not been significantly influenced by the pulp mill effluents discharged into the Tarawera River. The sediment 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 are usually only observed in sediments exposed to paper mill effluent discharges. For example in Lake Superior, Canada, FOX (1976) has reported DHAA concentrations of the order 100 mg/kg dry weight of sediment for sediment material collected from the mouth of a contributing (polluted) river; REMBERGER *et al.* (1990) have reported the concentrations of chloro-DHAA isomers in some Scandinavian sediments to be of order 130-450 mg/kg organic carbon content. If it is assumed that in the present study approximately ⅓ of the loss on ignition arises from organic carbon, it follows that the level of chloro-DHAA isomers in the sieved Tarawera River sediments is of the order 600 mg/kg organic carbon.

CONCLUSIONS

The main findings of the present investigation are: (1) abietan-18-oic acid and chloro-DHAA isomers are absent in the

Table 6. *Pearson moment correlation matrix for Matata Lagoon sediment sample 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 8. *SIM-GC/MS determined resin acid ion ratios in Tarawera River mouth and Matata Lagoon sediment samples.*

	Depth (cm)	Seco-2/Seco-1	Sand/Pim
ML2/1	5	0.76	0.43
ML2/2	15	0.74	0.40
ML3	5	0.49	0.31
ML4/1	5	0.49	0.19
ML4/2	15	0.52	0.20
ML5/1	5	0.49	0.21
ML5/2	15	0.58	0.20
ML5/3	25	0.51	0.24
ML6/1	5	0.57	0.23
ML6/2	15	0.60	0.24
ML7/1	5	0.73	0.39
ML7/2	15	0.69	0.38
ML7/3	25	0.69	0.33
ML8/1	5	0.73	0.37
ML8/2	15	0.71	0.35
ML8/3	25	0.67	0.44

Abbreviations: Seco-1 = secodehydroabietic acid-1; Seco-2 = secodehydroabietic acid-2; Sand = sandaracopimaric acid; Pim = pimaric acid Sample sites are as shown in Figure 1.

control site samples and are thus good indicators of pulp and paper mill originated contribution(s) to sediments; (2) sediment samples from the abandoned river channels draining the Matata Lagoon, but not the upper lagoon basins, are influenced by pulp mill sourced organic contaminants from the modern Tarawera river water, as evidenced by the present of abietan-18-oic acid and chloro-DHAA isomers; and (3) DHAA concentrations in sediments from the polluted area(s) are typically 10 times higher than samples from the control sites.

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LITERATURE CITED

Barrick, R. C. and Hedges, J. I., 1981. Hydrocarbon geochemistry of the Puget Sound region. II. Sedimentary diterpenoid, steroid and triterpenoid hydrocarbons. *Geochimica et Cosmochimica Acta,* 45, 381–392.

Biellmann, J. F.; Branlant, G.; Gero-Robert, M., and Poiret, M., 1973a. Degradation bacterienne de l'acide dehydroabietique par Flavobacterium resinovorum. *Tetrahedron,* 29, 1227–1236.

Biellmann, J. F.; Branlant, G.; Gero-Robert, M., and Poiret, M., 1973b. Degradation bacterienne de l'acide dehydroabietique par un Pseudomonas et une Alcaligenes. *Tetrahedron,* 29, 1237–1241.

Eglinton, G. and Murphy, M. T. J. (eds.), 1969. *Organic Geochemistry—methods and Results.* Berlin: Springer Verlag, 828 p.

Fox, M. E., 1976. Fate of selected organic compounds in the discharge of kraft paper mills into Lake Superior. *In:* Keith, L. H. (ed.), *Identification and Analysis of Organic Pollutants in Water.* Ann Arbor, Michigan: Ann Arbor Science Publishers, 718 p.

Healy, T. R., 1978. Some Textural and Mineralogical Investigations of the Rangitaiki Plains Foreshore and River Sands. *Bay of Plenty Coastal Survey Report 78/4,* Bay of Plenty Catchment Commission, 44 p.

Holmbom, B., 1980. A procedure for analysis of toxic compounds in pulp and paper mill waste waters. *Paperi ja Puu,* 9, 523–531.

Johns, R. B. (ed.), 1986. Biological markers in the sedimentary record. *Methods in Geochemistry and Geophysics, No. 24,* Amsterdam: Elsevier, 364 p.

Keith, L. H., (ed.), 1976. *Identification and Analysis of Organic Pollutants in Water.* Ann Arbor Michigan: Ann Arbor Science Publishers Inc., 718 p.

Kinae, N.; Hashizume, T.; Makita, T.; Tomita, I.; Kimura, I., and Kanamori, H., 1981. Studies on the toxicity of pulp and paper mill effluent's. 1. Mutagenicity of the sediment samples derived from kraft paper mills. *Water Research,* 15, 17–24.

Kutney, J. P.; Singh, M.; Hewitt, G.; Salisbury, P. J.; Worth, B. R.; Servizi, J. A.; Martens, D. W., and Gordon, R. W., 1981. Studies related to biological detoxification of kraft pulp mill effluent. I. The biodegradation of dehydroabietic acid with Mortierella isabellina. *Canadian Journal of Chemistry,* 59, 2334–2341.

LaFlamme, R. E. and Hites, R. A., 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochimica et Cosmochimica Acta,* 42, 289–303.

LaFleur, L. E., 1983. Chemical fossils of diterpenes. *Report of the National Council of the Paper Industry for Air and Stream Improvement, Inc.,* New York, 25p.

Leach, J. M.; Mueller, J. C., and Walden, C. C., 1978. Biological detoxification of pulp mill effluents. *Process Biochemistry,* 13, 18–21.

Lloyd, J. A., 1978. Distribution of extractives in Pinus radiata earlywood and latewood. *New Zealand Journal of Forestry Science,* 2, 288–294.

McDonald, I. R. C. and Porter, L. J., 1969. The resin and fatty acid composition of Pinus radiata D. Don whole wood, and its relation to the yield and composition of New Zealand tall oil. *New Zealand Journal of Science,* 12, 352–362.

McFarlane, P. N. and Clark, T. A., 1988. Metabolism of resin acids in anaerobic systems. *Water Science and Technology,* 20, 273–276.

Morales, A.; Birkholz, D. A., and Hrudey, S. E., 1992. Analysis of pulp mill effluent contaminants in water, sediment, and fish bile—fatty and resin acids. *Water Environment Research,* 64, 660–668.

Oikari, A.; Holmbom, B.; Anas, E., and Bister, H., 1980. Distribution in a recipient lake and bioaccumulation in fish of resin acids from kraft pulp mill waste waters. *Paperi ja Puu,* Special number 4a, 193–200.

Osborne, P. J., 1991. Some Chemical Studies of Water and Sediment from the Tarawera River. M.Sc. thesis, University of Waikato, Hamilton, 134p.

Pereira, W. E.; Rostad, C. E.; Taylor, H. E., and Klein, J. M., 1982. Characterization of organic contaminants in environmental samples associated with Mount St. Helens 1980 volcanic eruption. *Environmental Science and Technology,* 16, 387–396.

Porter, L. J., 1969. The resin and fatty acid content of living Pinus radiata wood. *New Zealand Journal of Science,* 12, 687–693.

Remberger, M.; Hynning, P. A., and Neilson, A. H., 1990. Gas chromatographic analysis and gas chromatographic-mass spectrometric identification of components in the cyclohexane-extractable fraction from contaminated sediment samples. *Journal of Chromatography,* 508, 159–178.

Richmond, B.; Nelson, C. S., and Healy, T. R., 1984. Sedimentology and evolution of Ohiwa Harbour, a tidally-dominated estuary in the Bay of Plenty. *N.Z. Journal of Marine and Freshwater Research,* 18, 461–478.

Singh-Thandi, M., 1993. Some aspects of the organic chemistry of the Tarawera River. M.Sc. thesis, University of Waikato, Hamilton, 154p.

Simoneit, B. R. T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochimica et Cosmochimica Acta,* 41, 463–476.

Simoneit, B. R. T., 1986. Cyclic terpenoids of the geosphere. *In:* Johns, R. B. (ed.), 1986: Biological markers in the sedimentary record. *Methods in Geochemistry and Geophysics, No. 24,* Amsterdam: Elsevier, 364p.

STREIBL, M. and HEROUT, V., 1969. Terpenoids—especially oxygenated mono-, sesqui-, di-, and triterpenes. *In:* EGLINTON, G. and MURPHY, M. T. J., (eds.), *Organic Geochemistry—methods and Results.* Berlin: Springer Verlag, 828p.

TAKEDA, H.; SCHULLER, W. H., and LAWRENCE, R. V., 1968. The thermal isomerization of abietic acid. *Journal of Organic Chemistry,* 33, 1683–1684.

TAN, Y. L. and HEIT, M., 1981. Biogenic and abiogenic polynuclear aromatic hydrocarbons in sediments from two remote Adirondack lakes. *Geochimica et Cosmochimica Acta,* 45, 2267–2279.

TANA, J. J., 1988. Sublethal effects of chlorinated phenols and resin acids on rainbow trout (Salmo gairdneri). *Water Science and Technology,* 20, 77–85.

THOMAS, B. R., 1969. Kauri resins—modern and fossil. *In:* EGLINTON, G. and MURPHY, M. T. J. (eds.), *Organic Geochemistry—methods and Results.* Berlin: Springer Verlag, 828p.

VENKATESAN, M. I.; BRENNER, S.; RUTH, E.; BONILLA, J., and KAPLAN, I. R., 1980. Hydrocarbons in age-dated sediment cores from two basins in the Southern California Bight. *Geochimica et Cosmochimica Acta,* 44, 89–802.

WAKEHAM, S. G.; SCHAFFNER, C., and GIGER, W., 1980a. Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta,* 44, 403–413.

WAKEHAM, S. G.; SCHAFFNER, C., and GIGER, W., 1980b. Polycyclic aromatic hydrocarbons in recent lake sediments—II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta,* 44, 415–429.

WILKINS, A. L. and PANADAM, S., 1987. Extractable organic substances from the discharges of a New Zealand pulp and paper mill. *Appita,* 40, 208–212.

WILKINS, A. L.; LANGDON, A. G.; MILLS, G. N.; PANADAM, S. S., and STUTHRIDGE, T. R., 1989. Kinleithic acid: a new hydroxylated resin acid from the biological treatment system of a New Zealand kraft pulp and paper mill. *Australian Journal of Chemistry,* 42, 983–986.

YAMAOKA, Y., 1979. Identification of terpenoid compounds in the sediment in Hiro Bay by gas chromatography-mass spectrometry. *Agricultural Biology and Chemistry,* 43, 1143–1144.

YEN, T. F. and MOLDOWAN, J. M. (eds), 1988. *Geochemical biomarkers.* London: Harwood Academic Publishers, 438p.