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Relating terrigenous sediment deposition in Mahurangi Harbour to specific land use in the catchment: a pilot study

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Relating terrigenous sediment deposition in Mahurangi Harbour to specific land use in the catchment: a pilot study

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Contents

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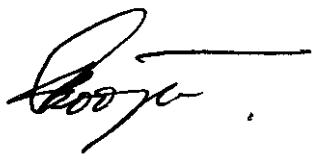

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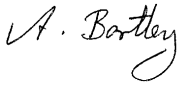


1 Executive Summary

The ecology of Mahurangi harbour is changing, probably as a result of increased sediment loading. Increasing proportions of fine sediment in the upper harbour coincide with decreasing and increasing trends in abundance of species intolerant and tolerant to mud, respectively. The cause has been attributed to catchment disturbance causing erosion and subsequent sediment runoff into the streams draining into the harbour. This pilot study was commissioned by Auckland Regional Council to determine whether it is possible to positively link and apportion observed terrigenous sediment deposition in the upper estuary of Mahurangi Harbour to specific land use practices in the Mahurangi Catchment.

Sediment from three land use types (rural pasture, native forest, and exotic pine forest) were collected as possible sources and sediment from the open mudflats in the upper Mahurangi Harbour was taken as the recipient of the catchment runoff. Sediment from beneath fringing mangroves around the Mahurangi Harbour was also examined to account for possible influences from mangroves. Selected samples representing these 5 sediment types were analysed for a wide range of naturally occurring variables which might reasonably be expected to act as natural tracers for the source sediments into the harbour. The resultant variable matrix was processed through a mixing model which apportioned the % composition of each source in the harbour sediments.

The resin acids, abietic acid and dehydroabietic acid (DHAA), were found in the harbour sediments positively linking these to the exotic pine forest source. The presence of abietic acid, which is normally rapidly degraded to DHAA, indicates that the deposition of exotic pine forest sediment in the harbour was recent. The results were less specific for pasture and native forest sediments.

The mixing model results, using a number of different matrix variables, consistently indicated that 50-54% of the recent sediment in the harbour mud flats was most likely derived from exotic pine forest land use activity. The apportionment of pasture and native forest sediment content was less certain but a realistic estimate was 32-44 % from pasture and 6-14 % from native forest land use.

While this pilot study was successful in positively linking and apportioning the exotic pine forest sediment to the harbour sediments, further work is required to improve the linkages for pasture and native forest sediments.

Additional information: Abietic acid and DHAA are both toxic to aquatic organisms and, while the concentrations measured in the harbour sediments were low, the literature indicates that little is known about the effects of chronic exposure of macrofauna to sublethal levels of these toxins. A potential underlying toxicity effect from resin acids may exist and become important when benthic macrofauna are stressed during high turbidity events.

2 INTRODUCTION

NIWA studies of the biota and ecology in Mahurangi Harbour in recent years (Ellis et al. 2002; Cummings et al. 2003) have demonstrated a persistent gradual change in the distribution of benthic macrofauna which are susceptible to pervasive changes in turbidity. The data (Cummings et al. 2003) show changes in the sediment structure in the mid 1990s with an increase in the proportion of fine sands and mud in the upper Mahurangi Harbour after 1997.

While long-shore transport and strong wave action can bring marine sand into the outer harbour from the sea, increasing pressures on land use for urbanisation, farming, forestry, and roading have the potential to increase the rate of terrigenous sediment input to Mahurangi Harbour due to catchment disturbance and subsequent erosion. To protect the Mahurangi Harbour ecosystem, the Auckland Regional Council want to know where the terrigenous sediment is coming from and the relative importance of each land use type.

This report presents the results of a NIWA pilot study commissioned by Auckland Regional Council to determine whether it is possible to positively link and apportion observed terrigenous sediment deposition in the upper estuary of Mahurangi Harbour to specific land use practices in the Mahurangi Catchment. The pilot study was designed to produce a matrix of naturally occurring variables to determine linkages and provide potentially unique "fingerprint" signatures of each land use type. The interpretation of the data was to use a mixing model to apportion the amount of sediment from each land use type in the sediments of Mahurangi Harbour.

2.1 Rationale

Historically, land clearance for farming and the urban development associated with Warkworth township in the 1800s, altered the natural sediment runoff patterns in the Mahurangi catchment (Swales et al. 1997) resulting in increased turbidity and rates of sedimentation in Mahurangi Harbour. These effects are likely to have had substantial impacts on the biota of the Mahurangi Harbour at the time of initial land clearance and a new ecosystem equilibrium will have established in the intervening years. In the 1970s, large tracts of the south western catchment were planted in exotic pine forest which have now matured and are being harvested and replanted.

Recently, coincidental with the clear-felling of exotic pine forests in the Mahurangi River catchment, there have been gradual declining or increasing trends in intertidal species intolerant (e.g. bivalves *Macomona liliana* and *Austrovenus stutchburyi*) or more tolerant (e.g. *Aricidea sp.*, Cirratulids, and the small bivalve *Theora lubrica*) of finer sediments, respectively (Cummings et al. 2003). There has also been a harbour wide decline in the abundance of the horse mussel, *Atrina zelandica*, and the distribution range has reduced in the upper harbour. As *Atrina* are sensitive to increasing suspended solids (Thrush et al. 1998; Ellis et al. 2002; Hewitt & Pilditch

2004), this distribution change is consistent with increasing sediment loads entering the Harbour (Stroud & Cooper 1997; Stroud 2003). While circumstantial evidence suggests a linkage with forestry activity, it is important to determine the land use contributing the sediment that is causing the present change in ecology, and what measures can be taken to remedy the impact.

The objective of this pilot study was to determine whether it was possible to positively identify sourceof terrigenous sediment entering Mahurangi Harbour using naturally occurring tracers. As there is likely to be more than one land use contributing sediment within the Mahurangi catchment, there is also a need to be able to apportion the amount of sediment from each land use at the impact site. Of key importance is the ability to be able to positively distinguish sediment from three main land uses — rural pasture, exotic pine forest, and native forest / scrub — and determine the relative contribution of each land use type sediment source to the sediments in an estuarine environment where the black mangrove is the dominant vegetation on the intertidal zone. As the sediment history of Mahurangi Harbour is dominated by the original native forest and subsequent land clearance for farming, of specific interest is the ability to positively identify and track sediment from more recent clear-fell exotic pine forestry operations.

3 METHODS

3.1 Study sites

For the pilot study, three main land-use types were used — rural pasture (P), exotic pine (E), and native forest (N) — and the receiving sediments in Mahurangi Harbour were sampled from open intertidal mud flats (H) and from beneath a stand of mangroves (M) on a nearby shore. Urban areas were not included in this study.

Representative sediment samples were collected from a number of sites for each land use type (Figure 1) and chilled on crushed ice for transport to the laboratory for analysis. Samples collected are listed in Table 1. Site photos are presented in Section 11. As the Mahurangi catchment has been developed for many years, there was difficulty in finding "pure" examples of each land use type. Rural pasture is frequently dotted with single and small clumps of pine trees (Photo 9). As these were not being felled, it was assumed that sediment runoff associated with these pines would be minimal and that the pasture samples collected would reflect mainly farming land use activity. Native forest was selected from stands of tall trees which were well established but essentially surrounded by farmland. The sample collected from Duck Road (Photo 1) was from a surface runoff zone from the forest above the normal level of the stream and is assumed to be essentially free from pasture derived sediment. Even the exotic pine forest samples (Photos 4-6), which were associated with recent logging operations, may have an underlying pasture or native forest land use signature, although it is assumed that this will be minimal after 30 years. Typical logging operations are clear fell (Photo 10), exposing large areas of bare earth which is the vulnerable to erosion until plant cover is re-established.

The harbour sediment samples were collected from an upper harbour intertidal mudflat (Photo 7) on a rising tide using a short coring tube and discarding all but the upper 2 cm. Mangrove samples were scraped from the intertidal sediment surface beneath dense mangroves (Photo 8) adjacent to the harbour sediment sites.

All samples were wet sieved through a 1-mm stainless steel mesh prior to analysis to remove woody debris, plant matter, and gravel.

Figure 1 Location map of sampling sites in the Mahurangi catchment and harbour. Circles indicate areas investigated. Codes refer to details in Table 1.

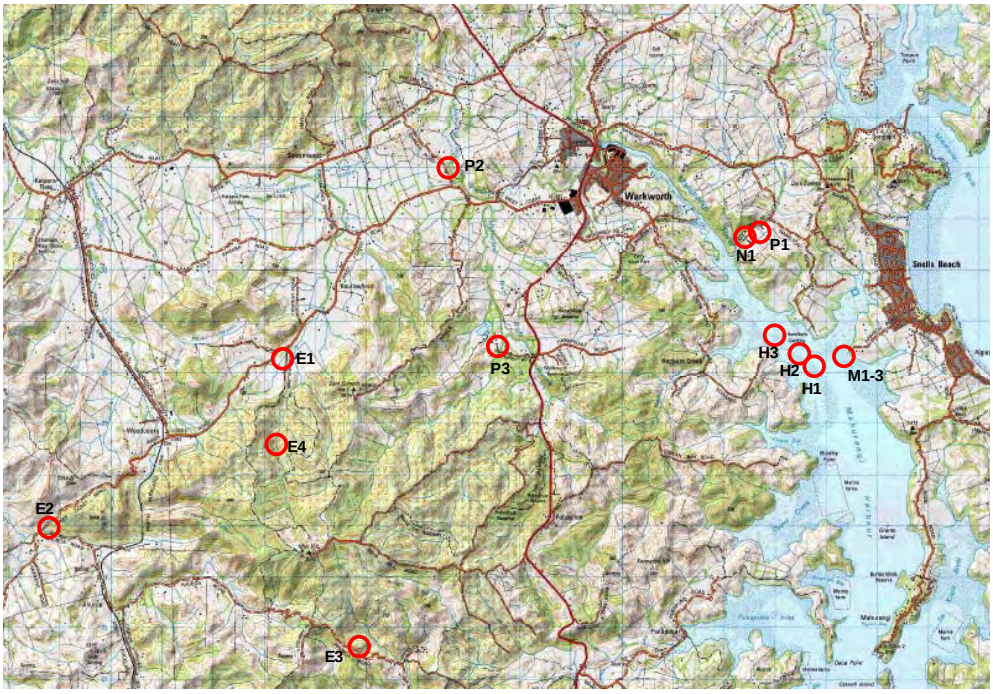


Table 1 Sampling site descriptions from Figure 1. (* site photo in section 10).

Sample		NZ Map grid	
Code	Description	Easting	Northing
P1	Small reed-dominated paddock*	2662847	6531142
P2	Sediment bar on side of Mahurangi River (Carran Rd)*	2656581	6532239
P3	Shallow weedy drain near culvert (Perry Rd)	2657567	6528509
N1	Sediment bar on Duck Creek within native forest*	2662539	6530970
E1	Culvert below recent clear-fell (West Coast Rd)*	2652213	6527371
E2	Skidder pad (West Coast Rd)*	2648736	6525171
E3	Surface sediment from freshly felled pine forest (Ahuroa Rd)*	2654920	6522757
E4	3m from stream, on bank, on edge of clear-felled area	2653283	6526861
H1	Surface sediment (≈2 cm) on bare mudflat in Harbour*	2663260	6528480
H2	Surface sediment (≈2 cm) on bare mudflat in Harbour	2663668	6528443
H3	Surface sediment (≈2 cm) on bare mudflat in Harbour	2663406	6528582
M1	Surface sediment beneath mangroves adjacent to H1*	2664487	6528682
M2	Surface sediment beneath mangroves adjacent to H1	-	-
M3	Surface sediment beneath mangroves adjacent to H1	-	-

3.2 Analyses

Because it was not known which natural tracers, if any, would provide a discrimination between the different land use types, a broad range of analyses were performed, including both standard and stable isotope techniques, to develop a matrix of different analytes which, together, may produce a unique pattern or "fingerprint" for sediment from a specific source. The suite of analyses included grain size, heavy metals, fatty and resin acids, natural abundance stable isotopes, and compound specific stable isotopes. Methods used are those employed by the commercial laboratories R.J. Hill (Hamilton) and Iso-trace New Zealand Ltd (Dunedin), or standard methods used by NIWA for sediment analyses.

4 ANALYTICAL RESULTS

The original proposal was to evaluate the results using a matrix array technique to assess which analytes can best be used to distinguish the 3 land use type sediment sources while eliminating any confounding effects of the mangroves. While simple in principal, it proved difficult for the commercial laboratories to reach the required sensitivities to provide meaningful analytical results. Repeat analyses were required using freeze dried samples rather than wet sediment to achieve suitable detection levels. This raised some problems with contamination from the extraction apparatus for some compounds and repeat extractions were required. Consequently, it was not possible to analyse all the samples collected as originally intended within the time constraints and budget.

4.1 Particle size analysis

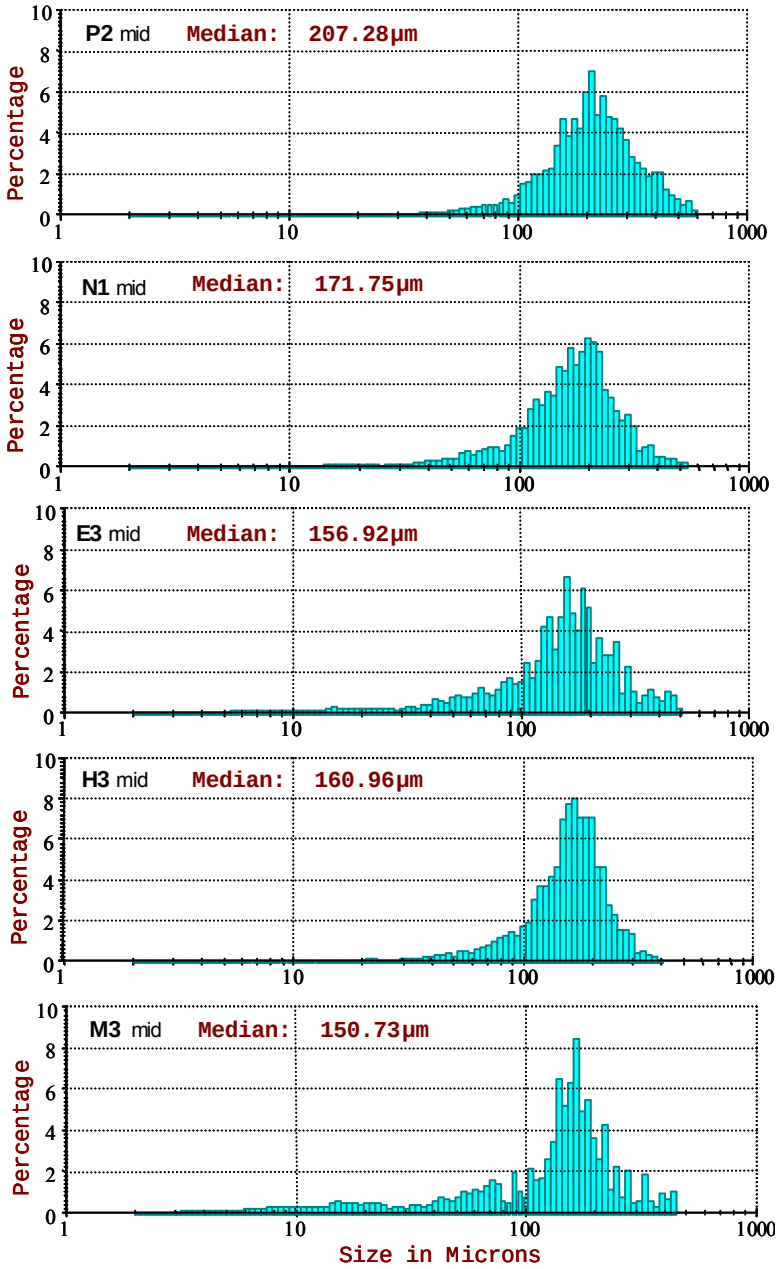
Selected sediment samples from each land use type were analysed at NIWA using a Galai Particle Analyser. Grain size volume density graphs are presented in Figure 2 and the data are summarised in Table 2.

Table 3 Sediment grain size as % volume (Wentworth size class) with mean volume and mean number values as calculated by the particle size analyser.

Sample		Pasture	Native	Exotic	Harbour	Mangrove
Size (µm)	Description	P2	N1	E3	H3	M3
0-6	Clay	0.10	0.23	0.62	0.22	1.23
6-31	Fine silt	0.76	2.11	4.93	1.21	9.29
31-62.5	coarse silt	1.97	4.62	6.83	3.50	8.00
62.5-125	very fine sand	11.05	19.02	20.55	20.10	16.36
125-250	fine sand	53.45	58.66	53.09	67.98	54.72
250-500	medium sand	31.17	15.05	13.97	6.99	10.50
Mean volume density (µm)		223.54	177.82	164.65	161.48	148.35
Mean number density (µm)		6.76	6.14	5.58	5.94	5.21

On a volumetric basis, the sediments from the three source sediments are mainly very fine to medium sands (Wentworth size class) [P2, 95%; N1, 93%; E3, 88%] with the remaining 5-12% in the size range of clay to coarse silts (Table 2). The harbour sample from the exposed mudflats also had a high sand content [H3, 95%] but most of it was in the fine to very fine range. In contrast, the mangrove sediments had a much lower sand content [M3, 81%] and much higher silt and clay content, which is consistent with the expectation of mangroves trapping fine sediments. Numerical modelling of Mahurangi Harbour (Oldman & Black 1997; Oldman et al. 2004) also supports the concept that mangroves are mostly a sediment sink rather than source.

Figure 2 Volume density graphs of particle size for the 5 sediment types analysed.



The volume density graphs show the relative distribution of particles by volume and demonstrate the broader spectrum of small particles in the mangrove sediments. The median values of these curves suggests a closer link between the exotic forest (E3), harbour (H3), and mangrove (M3) sediments than with the pasture (P2) and native forest (N1) sediments.

4.1.1 Data interpretation

These data suggest that the freshly disturbed exotic pine forest sediments have been less leached of fine particles than the native forest or established pasture sediments and thus are likely to produce a higher clay load when disturbed. The higher clay content and lower mean volume density of the mangrove sediments than the open mudflat sediments in Mahurangi Harbour are consistent with the expectation that mangroves trap more fines than would normally settle on the mudflats. It is also consistent with tidal reworking of the surficial sediments to a depth of up to 8 cm on the exposed mudflats as indicated by Swales et al. (2002).

Swales et al. (2002) estimated that sedimentation rates on the intertidal zone could be from 4 – 9 mm yr^{-1} and hence the 20 mm deep harbour sediment cores taken for this pilot study could represent an integration of catchment inputs over the last 3 to 5 years. Consequently, reworking of the sediments could redistribute the catchment sediment load from a runoff event, fractionating the clay and silt into the mangroves around the harbour edge while retaining the heavier sands on the intertidal mudflats.

As natural organic tracers are likely to be associated with the finer particles [higher surface adsorption characteristics], any specific catchment tracers may accumulate in the mangroves at greater rates than in the open sediments of the harbour.

4.2 Heavy metals

The five samples analysed for grain size were also analysed for heavy metal content (table 3). These data show no logical links between the catchment and harbour or mangrove sites for arsenic, copper, nickel, or zinc. These metal concentrations were the same or higher in the harbour and mangrove sediments than in the sediments from potential source catchments and may reflect the presence of the town Warkworth between the land and harbour sites. The concentration of each of these metals was slightly higher in the mangrove sediment than the harbour sediment indicative of redistribution and accumulation in the mangroves.

Cadmium and lead both showed a potential relationship between the native and exotic forest samples and the harbour and mangrove samples. Chromium showed a potential relationship between exotic forest and the harbour and mangroves samples. These data may form part of the data matrix.

None of the metals measured showed any positive relationships for the pasture sample, which is surprising since cadmium is often associated with the application of super phosphate fertiliser to pasture. The low cadmium concentrations may indicate that it is relatively mobile and has been leached from the sample P2.

Table 4 Total recoverable heavy metal (mg/kg dry weight) content of sediments from the 5 sediment types.

Sample	Pasture	Native	Exotic	Harbour	Mangrove
Metal	P2	N1	E3	H3	M3
Cadmium	0.03	0.13	0.19	0.06	0.05
Lead	3.67	9.98	7.13	8.03	8.98
Chromium	16.8	15.0	31.2	27.3	28.9
Arsenic	1.5	2.6	1.9	9.1	6.4
Copper	4.3	10.4	13.5	13.5	14.6
Nickel	6.9	6.9	6.9	9.0	9.5
Zinc	32.2	42.0	32.5	51.8	57.1

4.3 Resin and fatty acids

Resin acids are tricyclic diterpenoids which occur naturally in conifers such as *Pinus radiata*. The major acid is often dehydroabietic acid (DHAA) which has an aromatic C-ring and is the most stable resin acid. DHAA is a breakdown product of abietic acid (Osborne 1991) which has two conjugated double bonds and hence it is one of the least stable resin acids.

Initial wet sample analyses for resin and fatty acids by normal commercial methods had high detection limits and thus low sensitivity to the compounds of interest. Repeating the analyses using freeze-dried samples enhanced the sensitivity, although there were major changes in the concentrations of some fatty acids that could not be explained. The repeat analyses of the key resin acids, abietic acid and DHAA, showed good agreement with original analyses. The concentrations of the more common resin acids are listed in Table 4 along with several fatty acids found in the sediment samples.

The presence of abietic acid in the harbour sediments is indicative of recent arrival as this resin acid is reported to breakdown rapidly (McMartin 2003). How recently is unknown as data on degradation rates is not presently available (Section 6).

Because DHAA is highly resistant to chemical degradation, it offers a potential tracer for apportioning exotic forest sediment proportions in the harbour sediments. It has previously been used in New Zealand as a tracer for organic matter from bark dumps and pulp mills (Wilcock et al. 1991; Judd et al. 1995; Healy et al. 1997). However, while the relatively low concentration found in the harbour sediment compared with the concentrations in the potential source sediment may truly reflect the proportion of sediment from exotic forest land use in the harbour at that point, it may also indicate that the coring technique used to collect the harbour sediments was too coarse (i.e., integrating 3-5 years rather than, say, months), and that finer sectioning of sediment cores is needed for quantification, depending on the application (Section 6.1).

Table 5 Resin and fatty acid concentrations (mg/kg dry weight) in selected sediment samples including the original 5 samples analysed in table 3.

Compound	P2	P3	N1	E3	E4	H3	M3
RESIN ACIDS							
Abietic acid	<0.01	0.19	0.27	4.30	1.09	0.76	0.02
Dehydroabietic acid	<0.13	0.04	0.13	5.94	3.68	0.13	0.12
Neoabietic acid	<0.01	<0.03	<0.04	0.41	<0.03	<0.03	<0.03
Pimaric acid	<0.01	<0.03	0.08	2.14	0.40	0.05	<0.03
Sandaracopimaric acid	<0.01	0.09	0.15	0.20	0.05	0.14	0.12
Isopimaric acid	<0.01	0.18	0.09	0.75	0.25	0.05	0.09
Palustric acid	<0.01	<0.03	<0.04	0.30	<0.03	<0.03	<0.03
FATTY ACIDS							
Myristic (C14:0)	<0.08	0.06	0.04	<0.03	<0.03	0.05	<0.06
Palmitic (C16:0)	<0.36	1.60	1.30	1.73	0.70	0.80	2.4
Stearic (C18:0)	<0.53	1.50	1.10	1.72	0.80	0.08	1.70
Oleic (C18:1)	<0.01	0.70	0.12	0.70	0.80	0.80	1.20
Linoleic (C18:2)	<0.01	<0.02	0.20	<0.20	0.20	0.20	0.40
Arachidic (C20:0)	0.03	0.92	1.09	2.85	0.28	0.48	1.90
Behenic (C22:0)	0.10	7.10	7.68	17.4	1.81	4.48	7.30
Lignoceric (C24:0)	0.20	18.9	20.5	34.9	7.37	17.0	28.0

Cautionary note: The analyst from RJ Hill Laboratory notes "that Sandaracopimaric acid was higher than Pimaric acid in some samples. Generally it is expected to be at 10% of the Pimaric acid." He also noted "that high levels of fatty acids were detected in all samples. These levels were not seen in the job previously submitted by the client (344656), and may be artefacts of the sample preparation process."

The initial sample submission was of wet sediment. The second sample submission was of material freeze dried at NIWA. Neither of these processes should affect the fatty acid content of the sediments samples submitted.

4.4 Stable isotopes

Differences in natural abundance of the heavy isotopes of carbon (^{13}C) and nitrogen (^{15}N) may provide some discrimination between land use types based on the difference in plant derived C and N in the catchment soils. There was no measurable difference between the pasture and native forest $\delta^{13}C$ isotopic signatures. However, while these are different from the exotic pine, harbour ,and mangrove samples, the level of difference is < 5 ‰ (Table 5) which may reduce the precision of the mixing model results. The $\delta^{15}N$ isotopic signature differences are less than one trophic step[1] and thus may not be usable as these are often biologically modified in wet sediments.

[1] A tropic step is the level of isotopic fractionation that occurs when stable isotopes pass through one biological process: ^{13}C = 1‰; ^{15}N = 3.5-4‰.

The total C and N results show that the pasture sample P2 was highly leached in comparison with the other samples.

In contrast with natural abundance isotopic signatures of bulk sediments, the compound specific stable isotopic analyses show several possible compounds that might be used as tracers to discriminate between catchment land use types (Table 6).

These compound specific isotopic differences are due to isotopic fractionation of $^{13}C/^{12}C$ during plant growth, which results in different isotopic signatures being imparted to the same natural chemicals derived from the different land use types. Consequently, these natural markers may be used to characterise those sediment sources.

Of particular interest are the fatty acids, 11-dodecenoic acid and myristoleic acid, which may characterise pasture. Palmitic and palmitoleic acids appear to characterise exotic pine forest. Palmitoleic acid also appears to be produced by mangroves but, as these are most likely a sediment sink rather than source (section 4.1.1), it can be assumed that the mangroves are likely to have little effect on sediment chemistry in the open mudflats. The more enriched isotopic signature of palmitoleic acid in the mangrove samples suggests that, were mangroves having a major effect on the open mudflats, the isotopic signature of the palmitoleic acid from the open mudflats would be much closer to the mangrove signature than to those of the terrigenous sediments. However, a small influence cannot be discounted.

For reasons as yet unknown, the published method for methylating resin acids in the sediment extracts for compound specific stable isotopic analysis gave very low conversions and hence none of the resin acid compounds identified in Table 4 were detected above the confidence level above background noise. Further work is needed on these methods.

Table 6 Stable isotopic composition of bulk sediment samples from the 5 original land use types. Results for isotopic ratios of ▫C:▫C and ▫N:▫N are expressed in standard delta (δ) notation with units of per mil (‰). C and N are expressed as % of total sediment.

Compound	P2	N1	E3	H3	M3
$\delta^{13}C$ ‰	-26.88	-26.88	-23.04	-24.87	-24.70
$\delta^{15}N$ ‰	5.44	3.35	4.74	4.40	5.64
C %	0.33	2.51	3.81	2.01	3.66
N %	0.03	0.18	0.26	0.15	0.28

Table 7 Compound specific isotopic analysis of methylated fatty acid extracts from the 5 original land use types. Results for isotopic ratios of ¹³C:¹²C are expressed in standard delta (δ) notation with units of per mil (‰). Carbon = number of carbon atoms in molecule. Relative concentration is expressed as peak height in mV. Blank cells indicate the peak was not resolved from the background by more than 200 mV. i.e., confidence limit.

Compound	Carbon	P2	N1	E3	H3	M3
$\delta^{13}C$ ‰						
methyl caprate	C10:0		-39.41	-39.04		-39.47
methyl 11-dodecenate	C12:0	-39.66	-41.62	-43.28	-40.10	-43.23
methyl myristoleate	C14:0	-39.00	-45.72	-45.02	-38.71	-44.73
methyl palmitate	C16:0		-47.65	-32.67	-35.73	-38.32
methyl palmitoleate	C16:1	-41.22	-44.34	-36.87	-39.23	-30.01
methyl oleate	C18:1		-38.65	-37.15		
methyl vaccenate	C18:1	-41.45	-40.29	-35.56	-42.94	
methyl linoleate	C18:2	-44.96	-42.03	-43.69	-42.76	-45.43
methyl linolenate	C18:3	-42.12	-41.33	-41.31	-41.48	-42.05
methyl eicosapentaenoate	C20:5			-38.65		
methyl docosatetraenenoate	C22:4					-43.09
methyl docosahexaenoate	C22:6			-41.17		
methyl nervonate	C24:1				-41.96	
cholesterol				-40.44	-37.68	-39.56
CONCENTRATION (peak height)						
methyl caprate	C10:0		325	322		422
methyl 11-dodecenate	C12:0	204	506	694	230	342
methyl myristoleate	C14:0	228	733	616	445	1663
methyl palmitate	C16:0		417	288	258	1035
methyl palmitoleate	C16:1	1294	2581	2655	1954	4199
methyl oleate	C18:1		628	649		
methyl vaccenate	C18:1	475	1263	1732	261	
methyl linoleate	C18:2	200	366	358	211	319
methyl linolenate	C18:3	1162	1503	1394	1242	1324
methyl eicosapentaenoate	C20:5			1206		
methyl docosatetraenenoate	C22:4					418
methyl docosahexaenoate	C22:6			1465		
methyl nervonate	C24:1				270	
cholesterol				375	256	569

5 MIXING MODEL

The original intention of the pilot study was to determine whether it was possible to positively link and apportion observed terrigenous sediment deposition in the upper estuary of Mahurangi Harbour to specific land use practices in the Mahurangi Catchment. This pilot study has identified a number of naturally occurring variables that provide positive linkages between sediment in Mahurangi Harbour and terrigenous sediment from exotic forest land use in the Mahurangi River catchment. The linkages between rural pasture and native forest land use types are not as clear but must be occurring. To determine the proportional contribution of source sediment from each land use type in the harbour sediment, it was proposed to use a mixing model. To achieve this, a matrix of variables is needed for the apportioning.

5.1 Selection of matrix variables

If it is assumed that the marginal mangroves are a sediment sink rather than source, then these variables (Table 7) could be used in a mixing model with three sources (the land use types) and the harbour and mangrove sediments as sinks. The second assumption made is that sediment derived from open coastal waters does not reach the upper harbour i.e., the sediment in the upper estuary is a composite of sediment erosion from the three sources (pasture, native forest, and exotic pine forest).

If these assumptions are true then the value for each variable selected in the harbour and mangrove sediments must be intermediate to the values of that variable in the three land use type sources. Values higher or lower than all of the sources indicate accumulation or local production, and cannot be used. Other specific requirements for using mixing models are that the variables selected are stable (i.e., are not biologically degraded) and are present in all the sources and sinks at more than trace levels. A special requirement for stable isotopes is that the difference between the isotopic signatures of the sources and sink be significant. This means a difference of more than one trophic step which, for carbon means $\delta^{13}C$ value differences of >1 ‰ and for nitrogen, $\delta^{15}N$ value differences of >3.5-4 ‰.

Applying these criteria to the matrix of variables (Table 7) we see that several possible variables can be eliminated. The metals lead and cadmium appear to be leached from the sample P2. Cadmium, lead, and chromium potentially may also come from industry in Warkworth. The resin acids, although positive markers for exotic pine forest sediment, may be biologically degraded between source and sink. The $\delta^{15}N$ values are all much less than one trophic step. The $\delta^{13}C$ value of myristoleic acid is more enriched in the harbour sediments than in the sources and thus myristoleic acid cannot be used. Myristic, dodecanoic, and linoleic acids are present only at trace levels which means they cannot be used either.

From the potential matrix of variables listed in Table 7, a revised matrix of variables was produced that meet the mixing model criteria (Tables 8). Some variables marked

with a single asterisk (*) are of questionable reliability as acknowledged by the analyst (section 4.3). The values used are from the final analytical result sheet so that all samples experienced the same extraction procedure. The mangrove data marked with a double asterisk (**) may indicate that mangroves produce or accumulate that compound and hence there is need for caution in the use of those values, and the final interpretation of the data. For the purpose of this pilot study, the mixing model was not applied to the mangrove data as a sink.

Table 8 Selected potential matrix variables for testing in mixing models for apportioning terrigenous sediment from three land use type sources in Mahurangi Harbour sediments from open mud flats and marginal mangroves. (* = caution [see text]; ** = may be produced by mangroves; † value used is half detection limit).

Variable	Source concentrations			Sink concentrations	
	Pasture	Native	Exotic	Harbour	Mangrove
HEAVY METALS					
Cadmium	0.03	0.13	0.19	0.06	0.05
Lead	3.67	9.98	7.13	8.03	8.98
Chromium	16.8	15.0	31.2	27.3	28.9
RESIN ACIDS					
DHAA	0.04	0.13	3.68	0.13	0.12
Sandaracopimaric acid*	0.09	0.15	0.05	0.14	0.12
Fatty acids					
Myristic acid	0.06	0.04	0.015†	0.05	-
Arachidic acid*	0.92	1.09	0.28	0.48	1.90**
Behenic acid*	7.1	7.68	1.81	4.48	7.30**
Lignoceric acid*	18.9	20.5	7.37	17.0	28.0**
Stable isotopes (‰)					
Whole sediment ($\delta^{13}C$)	-26.88	-26.88	-23.04	-24.87	-24.70
Whole sediment ($\delta^{15}N$)	5.44	3.35	4.74	4.40	5.64
COMPOUND SPECIFIC STABLE ISOTOPES ($\delta^{13}C$)					
methyl 11-dodecenate (‰)	-39.66	-41.62	-43.28	-40.10	-43.23**
methyl 11-dodecenate (mV)	204	506	694	230	342**
methyl myristoleate (‰)	-39.00	-45.72	-45.02	-38.71	-44.73
methyl myristoleate (mV)	228	733	616	445	1663**
methyl palmitoleate (‰)	-41.22	-44.34	-36.87	-39.23	-30.01**
methyl palmitoleate (mV)	1294	2581	2655	1954	4199**
methyl linoleate (‰)	-44.96	-42.03	-43.69	-42.76	-45.43**
methyl linoleate (mV)	200	366	358	211	319**
methyl linolenate (‰)	-42.12	-41.33	-41.31	-41.48	-42.05**
methyl linolenate (mV)	1162	1503	1394	1242	1324**

Table 9 Potential matrix of variables that meet the mixing model criteria.

Variable	Source concentrations			Sink concentrations	
	Pasture	Native	Exotic	Harbour	Mangrove
FATTY ACIDS					
Arachidic acid*	0.92	1.09	0.28	0.48	1.90**
Behenic acid*	7.1	7.68	1.81	4.48	7.30**
Lignoceric acid*	18.9	20.5	7.37	17.0	28.0**
STABLE ISOTOPES (‰)					
Whole sediment ($\delta^{13}C$)	-26.88	-26.88	-23.04	-24.87	-24.70
COMPOUND SPECIFIC STABLE ISOTOPES ($\delta^{13}C$)					
methyl palmitoleate (‰)	-41.22	-44.34	-36.87	-39.23	-30.01**
methyl palmitoleate (mV)	1294	2581	2655	1954	4199**
methyl linolenate (‰)	-42.12	-41.33	-41.31	-41.48	-42.05**
methyl linolenate (mV)	1162	1503	1394	1242	1324**

5.2 Mixing Model: IsoSource

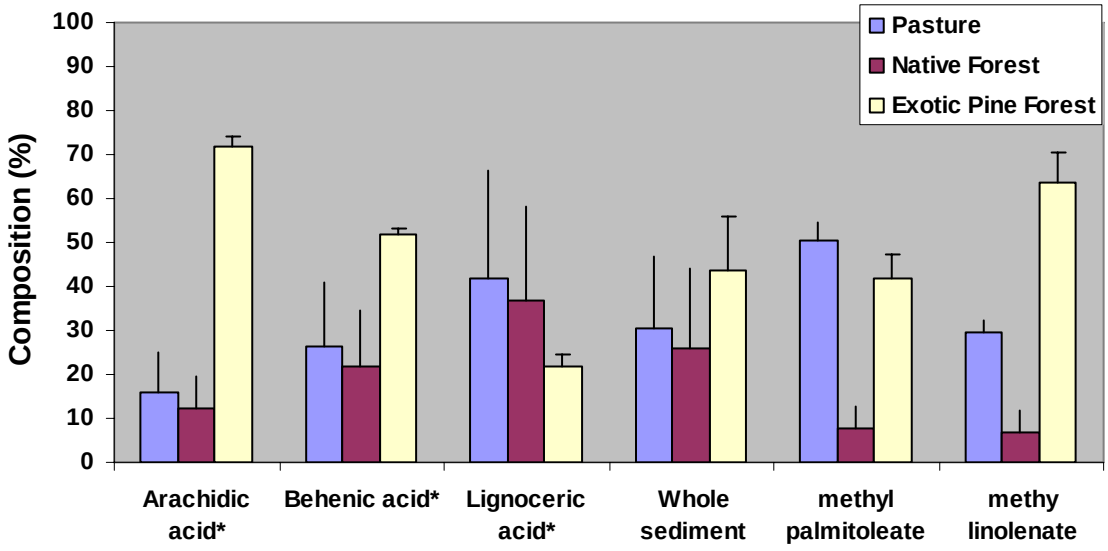
Mixing models are used to estimate the % contribution of a specific source in a mixture from two or more sources (endmembers). A simple two-endmember mixing model which might be used for estimating the % contribution of terrestrial material in samples taken along the gradient to pure marine sediments is:

$$\% \text{ terrestrial} = (d^{13}C_{sample} - d^{13}C_{marine})/(d^{13}C_{terrestrial} - d^{13}C_{marine}) \times 100$$

This type of model produces a result which is unique for each sample along the gradient. Many mixing models have been developed for research into food web structures using stable isotopes. In general, the proportional contributions of n+1 different sources can be uniquely determined by the use of n different isotope system tracers with linear mixing models based on mass balance equations. When there are more than n+1 potential sources, there can be no unique solution of source proportions. Don Phillips, USEPA, has produced a mixing model, "IsoSource" (Phillips & Gregg 2003), which is designed to evaluate samples where there are too many sources and produce a range of feasible solutions from which the frequency and range of potential source contributions can be determined. Phillips & Gregg (2003) caution that "*To avoid misrepresenting the results, users of this product should report the distribution of feasible solutions rather than focusing on a single value such as the mean.*"

While IsoSource was primarily designed for use with stable isotope data, it works equally well for non-isotopic variables in the mixture which are linearly related to the same variables in the source and have distinctly different concentrations or characteristics. This model has been used to evaluate the results obtained in this pilot study.

Figure 3 Mean results from IsoSource for each potential matrix variable identified in Table 8 as a first approximation for apportioning % contribution of each catchment land use type sediment in the harbour sediments. These data are not unique solutions but mean values of a range of feasible solutions. (Error bar = 1 SD).



Notwithstanding the cautionary note above regarding the use of mean values, the mean values give a quick method of checking whether the range of possible mixture proportions are realistic. They can also highlight potential problems in sampling, analysis, or the sample selection process. Graphical presentation of the individual matrix element mean proportions show that some proportions have large SD values but, although there is a range of proportional compositions for the three sources, most individual results indicate a high proportion of exotic pine forest sediment in the harbour sediments (Figure 3).

The mixing model was then used with several multiple matrix element combinations of these variables (Table 9).

Considering the feasible solutions graphs (Figure 4), the results show a consistent pattern that suggests about 50 – 54 % of the sediment in the upper 2 cm of harbour sediment at the location given for sample H3 (Table 1) was derived from exotic forest land use type activity. These results, sequentially from A) to E), demonstrate an improving estimate of the proportion of the source sediment in the harbour sediment.

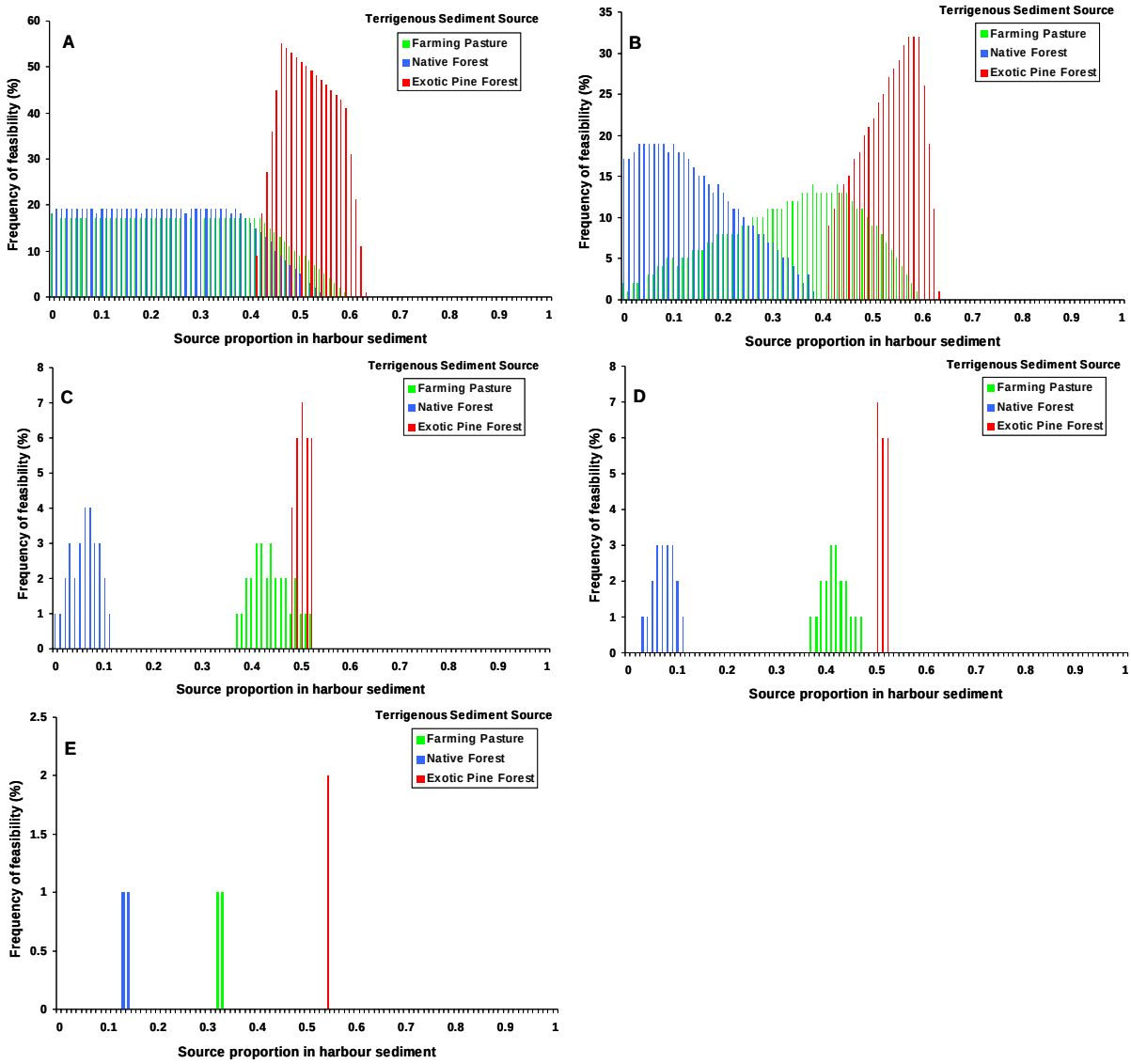
Using purely mass data (Figure 4A) produced a very coarse estimate of the proportions. The mass results rely on the accuracy of quantitation and thus are affected by sampling technique, sample handling, and the amount of dilution due to moisture content of the sample. Sequentially replacing the mass data with stable isotope parameters improves the apparent reliability of the model output (Figure 4B to E). The stable isotope signature is not affected by dilution or sample handling.

Table 10 Mean (± 1SD) % composition results from IsoSource for a range of endmembers in matrix combination for harbour sediment (H3). Graphs of the distribution of feasible solutions for each combination of endmembers are presented in Figure 4. (* = whole sediment).

Matrix combination	Graph (Figure 4)	Pasture	Native	Exotic
Archidic acid, Behenic acid, Lignoceric acid	A	25.5 (15.4)	23.0 (13.9)	51.5 (5.4)
Archidic acid, Behenic acid, methyl palmitoleate	B	33.2 (13.6)	13.9 (9.5)	52.9 (5.6)
Behenic acid, methyl palmitoleate	C	44.0 (4.0)	5.9 (2.9)	50.1 (1.4)
$\delta^{13}C$*, Behenic acid, methyl palmitoleate	D	41.8 (2.7)	7.3 (2.2)	50.9 (0.8)
$\delta^{13}C$*, methyl palmitoleate, methyl linolenate	E	32.5 (0.7)	13.5 (0.7)	54.0 (0.0)

These results indicate that the harbour site had a sediment composition of about 50-54 % exotic pine forest, 32-44 % farmland pasture, and 6-14 % native forest sediment.

Figure 4 Graphs of the distribution of feasible solutions for each combination of endmembers modelled in . This selection of results sequentially for A) to E) demonstrate increasing confidence in the estimated proportion of the three catchment sources in the harbour sediments. (X-axis scale is 0 to 1 representing 0 to 100% of the three catchment type sediments in the harbour sample).



6 DISCUSSION

This pilot study has demonstrated that it is possible to positively link and apportion terrigenous sediment deposition in the upper estuary of Mahurangi Harbour to specific land use practices in the Mahurangi Catchment. The data positively identify sediment from exotic pine forests in the upper 2 cm of the upper estuary and the mixing model indicates that the exotic pine forest sediment component is in the order of 50–54 % for the variable matrices used in Figure 4C-E.

Apportioning of the sediment from native forest and pasture was less certain and the mixing model variously gave % proportions of 32-44 % and 6–14 %, respectively, for these two sources in the harbour sediment mixture, depending on the variables selected. The variability in relative proportions of these two sources may reflect the difficulty in obtaining "pure" reference sediments from native forest and pasture catchments or the problems encountered by the commercial laboratories during analyses, or the lack of a complete set of variables for matrix selection. However, as four different sets of variables produced comparable results for exotic pine forest % contribution, there is reasonable confidence in those results. It should also be possible to provide results of similar confidence for the pasture and native forest % contributions once the appropriate variables have been identified and analytical methods have been perfected.

To produce the results obtained from the mixing model, sets of three independent variables were required that were not subjected to biological degradation or did not accumulate in the sediments of the harbour. The latter condition was not met for the mangrove sediments and, consequently, the mixing model was not tested using the mangrove sediments. While it is possible that the mangroves could be influencing the chemical composition of the open mudflat sediments, this is unlikely on the broad expanses sampled. Grain size analyses from this study and modelling results from Mahurangi Harbour (Oldman et al. 2004) suggest that fine sediment accumulates in the natural sediment trap of the fringing mangroves, which is consistent with the observed progradation of the mangroves. The compound specific $\delta^{13}C$ isotopic signature of -30 ‰ for the methyl palmitoleate is 6 – 14 ‰ more enriched in the mangrove sediments than in the other three sources (Table 6) and would have had a substantial effect on the harbour sediment isotopic signature if mangroves were a source rather than a sink.

Leaching was identified in the pasture sample and this raises the question as to whether this would affect the model output. Leaching is a process which selectively removes a compound from the soil substrate e.g., nitrate is highly soluble in water and thus easily leached. Although we can measure the nitrate concentration in whole pasture soil, leaching means that we are not able to relate sediment from pasture to sediment in the harbour using the nitrate concentration in the harbour sediment. However, as the δ13C signature of the carbonate that makes up the soil substrate is not changed by leaching, it can be used. Similarly, any compound that strongly binds to the soil and is effectively uniformly bound to all soil particles can also be used, even though part of the soil is washed away, as occurred with the pasture sediment [P2].

The consistency of the mixing model results suggests that the variables selected meet this criterion.

Notwithstanding this, it is surprising that the multiple matrix mixing model consistently indicated that around 50 % of the surficial sediment in the harbour was derived from exotic pine forest when exotic pine forest comprises <10 % of the catchment land use. The expectation would be for a much higher proportion of pasture and native forest sediment if sediment runoff occurred at a uniform rate across all catchments. Possible explanations for this include:

- A higher proportion of exposed bare sediment in the exotic pine forest catchments available for erosion than in the other catchments;
- The harbour sampling caught an 'event' following recent rainfall;
- The mechanism of sediment deposition differs along the estuary. In the upper estuary, newly eroded 'clay'-based sediment will float in the freshwater layer on top of seawater and deposit as a surface scum on the sediments on the ebb tide (Photo 11). Further down the harbour, turbulent mixing and flocculation will cause particle aggregation and sedimentation out of the water column.
- The flocculation and sedimentation pattern across the upper harbour intertidal mudflats is not uniform i.e., sediment can only deposit on the intertidal mudflat when it is immersed. At other times the terrigenous sediment will be carried down the channel and potentially mix with resuspended sediments further down the harbour.
- Sediment reworking through bioturbation and channel migration will redistribute and mix the new terrigenous sediment with older sediments.
- The presence of abietic acid in the harbour sediment at the concentration measured would tend to support the 'event' concept, without excluding the other possibilities.

Laboratory studies have found that abietic acid is degraded about 5 times faster than DHAA under strong artificial sunlight (UV254-radiation source), with DHAA having a half life of about 190 hours independent of starting concentration (McMartin 2003). Another group of researchers measured apparent DHAA half-life values of up to a month in natural water and up to 21 years in sediment (Volkman et al. 1993). The lower concentrations of DHAA than abietic acid in the harbour sediment in this study suggests that the DHAA from earlier deposition events has been worked into the sediments through bioturbation or redistributed by wave action and tidal erosion of the intertidal zones. It could also mean that the DHAA measured is the beginning of the breakdown of the abietic acid from the recent event.

From the above, it is apparent that the results from this pilot study have several limitations. The intention of this study was to identify "fingerprint" compounds in the first of each sample set and then analyse the remaining samples for these "fingerprint" compounds as confirmation. Due to analytical problems and thus timing as well as financial constraints, the confirmation work was not completed.

As discussed above, there are a number of questions about the quality of samples taken for the sources and for the sinks. Consequently, while this pilot study shows that it is feasible to identify and apportion the catchment sediment sources in the harbour sediments, it does not yet provide a robust analytical result. Further work is required to complete the method development and it's application.

6.1 Application

How the technique is used depends on the questions being asked.

If it were important to know the dispersal pattern of sediment from a single rainfall event, the harbour samples would need to include only the upper few mm of surficial sediment to exclude older sediments and thus older event signals. While thinner layers may increase the possible effects of bioturbation by feeding animals, sampling shortly after a sediment producing storm event could overcome that problem. A fine spatial grid of harbour sediment samples would need to be processed to draw a contour map of the source sediment content.

If the objective were to determine the mean influence of a particular catchment source, deeper cores of up to 10 cm length to integrate over a 5 year period [based on 210Pb profiles (Swales et al.2002)] would need to be taken from a coarser spatial grid and processed to produce a contour map of the source sediment content. The coarser grid pattern recognises the likely effect of sediment reworking and thus blending of the terrigenous sediment sources over time. If the distribution pattern required covered the whole of the Mahurangi Harbour, additional sediment sources would need to be considered e.g., transport of coastal sediments into the harbour, effects of aquaculture, etc.

7 CONCLUSIONS

While the use of multiple variable matrices and mixing models has the potential to be a powerful tool in determining the % contribution of sediment from a range of catchment sources to the harbour sediment at a specific location, the tool is not ready to use just yet. The pilot study has shown the potential but the methodology needs to be refined to make a rigorous tool and improve quantification. Specifically:

- The reference source samples need to be improved i.e. the soil from which the sediment is derived should be used as the starting point rather than partially leached material from the sediment bars in the stream channels.
- The sampling technique used in the harbour should be appropriate to the application and the question being asked.
- Analytical methods need to be sorted out to ensure reliable and consistent extraction efficiencies for resin and fatty acids, and compound specific isotopic analyses. These methods may need to be developed in-house within NIWA as the commercial laboratories are not geared up for research-type studies along with their routine analyses.
- The final methods and matrices modelled need to be confirmed using sediments spiked with the variables selected or known weight-percent mixtures of the three reference source sediments, or both.

8 TOXICITY

While the objective of this pilot study was to identify the source of terrigenous sediment impacting on the biodiversity of Mahurangi Harbour through increasing suspended solids and thus turbidity of the harbour waters, it should be noted that some of the chemical compounds measured during this study are known to be toxic to aquatic organisms.

Of particular interest are the resin acids from exotic pine forest. Both abietic acid and DHAA, which were found in the harbour sediments, have LC_{50}[2] values for fish in the range of 0.4-1.7 mg l^{-1} (Wilcock et al. 1991; Volkman et al. 1993), but enzyme activity changes were observed when rainbow trout were exposed to DHAA concentrations as low as 0.005 mg l^{-1} (Volkman et al. 1993).

While the levels found in the sediments were below the LC_{50} values for fish and were much less than those found downstream of pulp mill effluent discharges (Wilcock et al. 1991; Volkman et al. 1993; Judd et al. 1995), they were comparable with levels found in the sediments near a coniferous bark dump beside Tauranga Harbour (Healy et al. 1997) and the log handling operations at the port of Tauranga (Tian et al. 1997). The literature acknowledges that little is known about the effects of chronic exposure to sublethal levels of these compounds either in the water column or in the sediments.

While the levels of resin acids in the Mahurangi harbour are likely to be low, their presence during periods of high turbidity may be an exacerbating factor on organisms which are under stress due to increased turbidity.

Further investigation of the extent of resin acid contamination of the sediments, their transport mechanisms in the water column, and the effects on marine organisms of chronic exposure to sublethal levels of these compounds is required to understand the full ecological effects of exotic pine forestry operations in the catchment on the estuary.

[2] LC_{50} value is the concentration that is lethal to 50% of the test organism that has been exposed to that toxicant for 96 hours.

9 ACKNOWLEDGEMENTS

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11 SITE PHOTOS

Photo 1 Native forest site N1 adjacent to Duck Creek. Sediment taken from true right bank at runoff area above normal stream flow level.

Photo 2 Pasture site P1. Sediment taken from shallow drain from reedy area.

Photo 3 Pasture site P2. Sediment taken from the silt accumulations along the side of the Mahurangi River.