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Sediment tracking method refinement

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Sediment tracking method refinement

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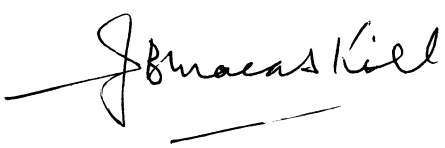

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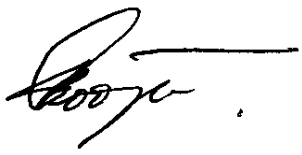

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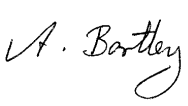


1 Executive Summary

A pilot sediment tracking study using compound specific isotope (CSI) techniques provided "proof-of–concept" that it was possible to apportion the amount of source soils from different land uses in the sediments of the Mahurangi Harbour. The Auckland Regional Council commissioned NIWA to complete the method development required to convert the sediment tracking technique into a robust tool. This report documents the steps taken to refine the methodology and demonstrates the ability of the technique to disciminate between similar land use types from different parts of the Mahurangi River catchment in the estuarine sediments.

Bulk samples of 10 different source soil types from adjacent and distant sites across the whole catchment, and 6 estuarine sites in the upper Manhurangi Harbour including 3 depth-dependent sets of the harbour samples, were processed to a finely ground dry powder. All samples were analysed for a range of resin and fatty acids both as mass concentrations in these potential source soils and their CSI signatures. Analytical methods were refined to produce reliable results at low concentrations. A multiple matrix of selected variables was run through a mixing model (Iso-Source) which was designed to provide a range of feasible solutions for a mixture where there were too many sources to use a linear mixing model.

Method testing included spiking a soil with a known mixture of resin and fatty acids to test the extraction efficiency, and analysing prepared mixtures of source soils to test the mixing model accuracy. With the exception of abietic acid, all resin and fatty acids had a 100% recovery in the spike test. The abietic acid spike recovery, however, was 0% due to assumed decomposition under the aerobic handling procedures. Individual mixing model runs gave good indications of the proportions of source soils in the mixtures but no one result was perfect. However, averaging the upper and lower limits of the feasible ranges of all mixing model runs for each mixture improved the predicted proportions to within 10% for all components in the mixtures and precision was often within 3% of the actual proportion for the major components. At low source soil compositions (i.e., <25%), averaged mixing model results were not as precise.

Testing of the revised method using natural estuarine samples as the mixtures demonstrated that the tracking technique could distinguish between different source soils of the same land use type in different parts of the catchment, and from one side of a valley to the other by the CSI signatures imparted to those soils by the plants growing on those soils. It was also shown to be possible to use a general soil type from an area to give an indication of whether soils from the area were likely to be sources contributing sediment to the estuary.

A detailed description of the method used and the associated protocols is included.

It is concluded that the method can now be used as a robust tool for estimating the source of sediment being deposited in an estuary.

2 Introduction

A pilot sediment tracking study (Gibbs 2004) provided the "proof-of–concept" that it was possible to apportion the amount of sediment from three different land uses in the sediments from the Mahurangi Harbour. That study collated analytical data on naturally occurring chemical compounds (signatures) adhering to the soil particles from the three different land uses, as a means of tracking this as potential source material for sediment deposited in the Mahurangi Harbour. To achieve this, the chemical signatures of the surface sediment from a central mud bank in the upper harbour were compared with those from the potential source materials using a multiple matrix of variables and a mixing model. This technique produced a consistent pattern of source composition in the harbour sediment with some relatively precise %-composition estimates, depending on the matrix of chemical signatures used in the mixing model.

Although it was concluded that the concept had been proved and the technique was promising, there were several concerns identified that needed to be checked before the technique could be used as a robust tool. These concerns included:

- Were the selected chemical signatures of the sediments affected by leaching or biodegradation i.e., is the signature [relatively] stable in the aquatic environment?
- Were the proportions of selected chemical signatures in the sediments uniform with particle size i.e., is the proportion of a chemical signature higher in the fines, which are more easily transported by water into the harbour?
- Does the mixing model accurately apportion the amount of sediment from each source in a mixture of those sediments?

It was also recognised that the sampling technique used to obtain the sediment samples in the harbour needed to be standardised for the specific application of the technique in the environment:

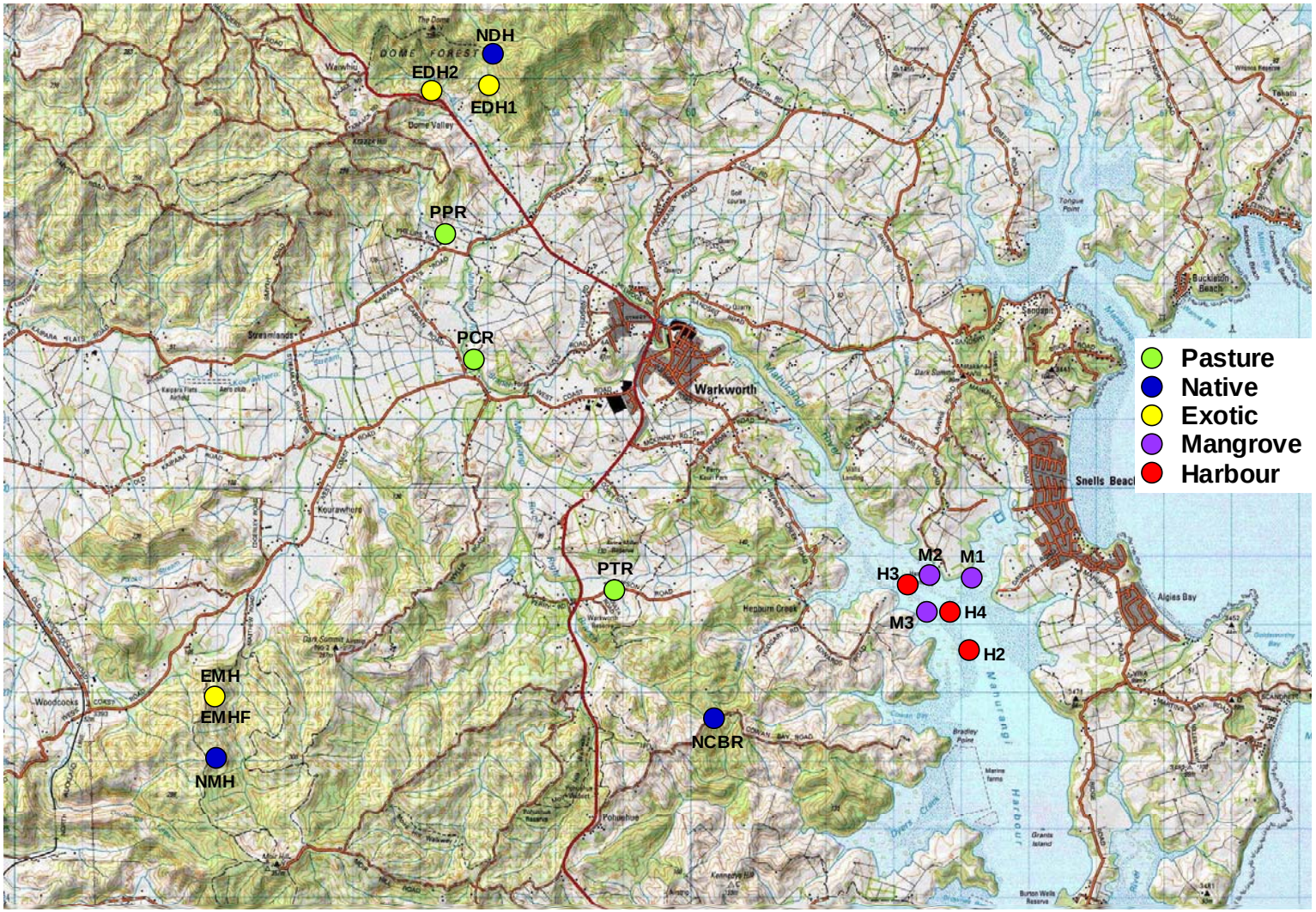
- How deep does the harbour sediment core need to be to apportion the source of terrestrial material deposited over the last 5 years versus material deposited during a recent event?

This study addresses the above concerns by obtaining robust source sample reference signatures and systematically confirming the mixing model predictions to validate the technique. It also included a preliminary evaluation of the depth of sediment required to assess long-term deposition versus recent deposition events.

This report includes all analytical results and the output from the mixing model runs. Recommendations and a protocol for the use of the method as a general tool are presented.

Figure No.1

Location map of sampling sites used in this report. Colour coding indicates the soil type. Refer to Table 1 for details of site labels. (Site H1 not shown).



3 Methods

3.1 Sampling

Bulk natural soil samples (Table 1) were collected on 28 February and 1 March 2005 from each of 3 terrestrial land use types, pasture, native forest, and exotic forest, and placed in 5-litre plastic buckets with sealable lids and stored at 4 °C pending processesing and analysis. Samples from mangrove and harbour sites were collected on 10 March 2005. (Site map: Fig.1; Site photos are presented in Section 8).

Table No. 1

Soil and sediment land-use types and sampling site locations. (H1 not used –see text).

Soil	Site	description	Easting	Northing
Pasture				
PTR	Thompson Rd	Rolling hill-side pasture	2658490	6528350
PCR	Carran Rd	Flat flood-plain near stream	2656710	6531670
PPR	Phillips Rd	Flat flood-plain near stream	2656250	6533580
Native forest				
NDH	Dome Hill	Nikau, Rimu, Titoke plus small native understorey (above cutover pine)	2656410	6536390
NMH	Moir's Hill	Nikau, Rimu, Titoke, Taraire plus small native understorey (Block in pine forest)	2652870	6526740
NCBR	Cowan Bay Rd	Kauri, Rimu, Tanekaha, Titoke with Kanuka edge (Block by pastured land)	2660310	6526590
Exotic forest				
EDH1	Dome Hill (far)	Tall pines with native understorey, on ridge (above cutover pine and ginger)	2656640	6536280
EDH2	Dome Hill (near)	Eroded soil/subsoil in recent cutover pine with pine debris lying on dry ground (ginger present)	2656200	6535750
EMH	Moir's Hill	Tall pines about to be cut, native understorey (surface soil only)	2652970	6527110
EMHF	Moir's Hill frit	Subsoil exposed by log-hauler	2652970	6527090
Mangrove forest (upper harbour)				
M1	Mahurangi Harb.	Edge of large expanse (left bank)	2664030	6528391
M2	Mahurangi Harb.	Under large trees (left bank)	2663720	6528393
M3	Mahurangi Harb.	Under large trees (Right bank)	2663648	6528182
Harbour sediment (upper harbour, right bank)				
H1*	Mahurangi Harb	Middle of mud bank near island	2663578	6528235
H2	Mahurangi Harb	Upstream of island on mud bank	2663402	6528352
H3	Mahurangi Harb	Downstream of island on mud bank	2663909	6528092
H4	Mahurangi Harb	Outside edge of mud bank near island	2663754	6528189

The pasture sites were animal-cropped, grassy swaths on flat or gently sloping land adjacent to streams. Samples were taken from upstream of the road-crossing of stream channels. Soil from each pasture sample was shaken from the roots of a grass sod cut to a depth of about 10 cm. Large root material, worms, insect larvae, and stones were removed by hand while crumbling the sample through a 10-mm mesh plastic sieve before the sample was put in a 5-litre sample bucket and sealed.

The native forest sites were taken from natural ephemeral drainage channels beneath a forest canopy with a variety of tall species (Table 1). The forest floor was relatively open with a sparce understorey of small native plants and a thick layer of leaves. The exotic forest sites were beneath mature (30 yr old?) *Pinus radiata* on sloping ground above natural streams. There was a relatively dense understorey of native plants and a thick layer of pine needles on the ground. There was an extensive infestation of wild ginger in the cutover pine forest near the Dome Hill sites, but no ginger in the immediate vicinity of where the soil samples were taken. Before collecting the soil from the forest sites, leaf litter and large woody debris was raked back to expose the soil surface. Soil was then dug to a depth of about 5 cm and crumbled through the 10-mm plastic sieve as for the pasture soil. The exotic forest frit from Moir's Hill was the result of the rubbing of the log-hauler hauser on the steep clay bank. Samples of this subsoil were shaken through a 1-mm mesh stainless steel sieve directly into a 5-litre sample bucket and sealed.

Mangrove and harbour sediments (Table 1; Fig. 1) were collected by boat on 10 March 2005. At the mangrove sites, sediment was collected from beside or beneath tall (3-4 m) mangroves, *Avicennia marina var. resinifera*, on the seaward side of the mangrove fringe around the upper Mahurangi Harbour. Plants in these areas were exposed below mid-tide and the sediment had thick stands of pnematophors, often encrusted with wild Pacific oysters, *Crassostrea gigas*, and a light covering of mangrove leaves. The leaves were removed (hand picked) before sampling and sediment from the upper 5 cm layer was passed through a 1-mm mesh stainless steel sieve to remove large debris and shell fragments before the sample was placed in a 5-litre sample bucket and sealed.

Harbour sites were selected on the large mud flat on the true right bank of the upper Mahurangi Harbour and collected on a falling tide under calm conditions. Sediment was collected using a large bore (93 mm inside diameter) thin walled (2 mm) clear polycarbonate corer tube marked off at depths of 10, 20, and 30 cm from the cutting edge. The corer was pressed into the sediment to a depth greater than the required mark, closed at the top with a screw-on sealed cap, and then lifted out of the sediment with a hand under the core to prevent the sample falling out. The length of the cored sample was adjusted to the required mark by trimming the bottom of the core sample and discarding the excess. The remaining core sample was then placed into a 5-litre bucket, sealed and stored at 4 °C pending processesing and analysis. Three core depths (0-10 cm, 0-20 cm, and 0-30 cm) were collected at each harbour site and stored separately. For the core depth 0-10 cm, 2 core samples were combined to ensure enough sample. It was not possible to obtain a core depth of >15 cm at site H1 due to a layer of buried oysters and consequently, samples from this site was not processed.

For each soil and sediment type, including the harbour sediments, 3 separate locations (Fig.1) were sampled and duplicate samples were collected from each location. An extra quantity of soil was collected from site PPR for spike recovery tests.

3.2 Processing

Moisture content, dry matter and % organic content was determined on each sample (Table 2) using standard gravimetric techniques. One bucket of each sample pair was wet sieved to remove stones, organic debris, plant roots, and insects. To achieve this, the whole sample was placed in a 20-litre plastic bucket with about 500 ml of water (terrestrial samples only) and blended to a slurry using a proprietary plastic paint-stirrer (ring and spiral-blade type) with stainless steel shaft, driven with a variable speed drill at slow speed. There was sufficent water in the estuarine samples to enable them to be mixed without the addition of water. The open style of the paint-stirrer allowed the sample to be mixed without cutting plant roots. This procedure was time consuming, taking about 10-15 minutes to convert a dry soil into a workable slurry. This slurry was then shaken through a 1-mm mesh fine wire stainless steel sieve (30-cm diameter kitchen sieve) in small portions. The portion retained in the sieve was discarded. The sievings were combined in a large aluminium (baking) tray and dried in an air fan oven at 60 °C. While freeze drying would have been preferred, it was impractical with the size of the sample c. 0.5 – 1 kg. The dry sieved sample was crumbled into small fragments (i.e., a steel hammer and anvil were used, inside a large plastic bag, to crush the brick-like dry samples into small pieces), which were then ground into a fine powder using a high-speed food blender with a polycarbonate blending jar and stainless steel blades. The powdered sample was sieved through a 100-μm mesh stainless steel sieve and stored sealed in a wide-mouth screw-cap plastic jar. In almost all samples, the whole sample passed through the 100-μm sieve. The exception was the pasture sample, PCR, which had a small quantity of stone chips. These were discarded.

It was initially intended that a portion of each sample would be water sorted to obtain the "fines" which are more likely to be transported into the harbour during a rain event. In practice, the wet sieving process had already separated the water suspended material from the heavy material that was less likely to be transported by light rainfall. On suspending a quantity of slurry in an equal volume of freshwater, shaking, and then allowing to stand overnight to separate, there was no layering of the soil that would indicate separate layers of different particle sizes. The small quantity of very fine material previously found in these soil types (see Table 2, Pilot study report) remained in suspension and settled material was mainly in the coarse silt / fine sand range of particle sizes. Consequently, without adequate separation of fine material, it was not possible to complete this experiment.

3.2.1 Mixtures and spikes

A 2-kg (dry weight) sample of pasture soil (PPR) was prepared to the processing stage after sieving the slurry but retained in the 20-litre bucket. A spike solution of resin acids

in acetone (100 ml), prepared by the analytical laboratory was added to the slurry and then stirred for about 5 minutes to ensure a thorough mixing. The spiked slurry was then re-sieved into the aluminium baking trays and dried and ground as for the other samples. The spiking procedure was done after all other samples had been processed, to prevent any possibility of cross contamination. The spike solution contained Abietic acid, Dehydroabietic acid (DHAA), pimaric acid, 7-Oxodehydroabietic acid, and Stearic acid.

Five soil mixtures were prepared by weighing portions of dry, ground sample into large plastic bags, closing the bags to leave them partially inflated, then "tumbling" the soil in the bags to facilitate mixing. The mixtures were stored in wide-mouth screw-cap plastic jars as for the other dry, ground samples.

3.3 Analysis

Portions of each sample, including the spike and soil mixtures, were analysed for the suite of resin acids, fatty acids, compound specific isotopes and bulk ^{13}C and ^{15}N stable isotopic natural abundances selected in the pilot study. Resin Acids and fatty acids were determined by R.J. Hill Laboratories, Hamilton, on an ICP Mass Spectrometer after methylation of solvent extracts and are reported as mg kg^{-1} dry weight of soil. Repeat analysis using larger sample weights was required to determine and confirm the low concentrations of resin acids in the estuarine samples.

Bulk and compound specific isotopic (CSI) compositions were measured by Iso-trace Laboratories, Dunedin. Bulk C and N isotopes were determined on a continuous flow, isotope ratio mass spectrometer (IRMS) following high temperature (1020 °C) combustion in an on-line elemental analyser. CSI compositions were determined on a GC-combustion-IRMS fitted with a B225 column, after methylation of a solvent extract of the soil. The extract was reduced to dryness then taken up in 1 ml of Hexane. Injection of 2 μl was equivalent to 1 mg of soil.

Stable isotope values are given in delta (δ) notation with the units of 'per mil' (‰). Delta values were calculated using the equation:

$$\delta^{13}C \text{ or } ^{15}N \text{ (‰)} = ((R_{sample}/R_{standard}) - 1) \times 1000$$

where R is the ratio of heavy to light isotope i.e., ^{13}C:^{12}C or ^{15}N:^{14}N. Analytical precision for $\delta^{13}C$ and $\delta^{15}N$ were 0.1 and 0.2‰, respectively. Quantification is based on % carbon (C) and nitrogen (N) content for bulk isotopes and relative peak areas for the extracted CSIs. The relationship between the bulk resin and fatty acid content and the CSI peak areas was essentially linear allowing the bulk resin and fatty acid content to be used for quantification in the mixing model.

The results obtained were applied to the multi matrix mixing model Iso-Source (Phillips & Gregg 2003) using all logical and practical combinations of soil and sediment results to determine the variability of the source fingerprint compounds and the general reliability of the overall technique. Note that the IsoSource model does not give absolute values for % composition of sources in a mixture. Rather, it produces a range of feasible solutions which are likely to include the actual % composition.

The mixing model has 4 main active parts:

- The values of the compounds (isotopes) in the mixture being investigated.
- The values of the same compounds in the sources contributing to the mixture.
- The %-step interval required (i.e., a step of 1 gives 100 steps between 0 and 100%, a step of 5 gives 20 steps between 0 and 100%, etc).
- The tolerance to be used by the model when solving equations.

The tolerance setting defines the accuracy to which the model can define the feasible solutions. When just using bulk stable isotopes, the tolerance setting should be small (e.g., 0.1) as the source compound isotopic signatures will be in the same general range as the isotopic signature of the mixture being tested. However, when mass concentration is included, there may be larger differences between values in the source and mixture. To accommodate these large differences, the tolerance setting must be raised. Tolerance values up to 2 are likely to produce results that are acceptable in terms of % range of feasible solutions. Tolerance values of 5 may produce acceptable results or the % range of feasible solutions may be spread (smeared) across broad ranges which become increasing ambiguous and thus not acceptable. Acceptance of the model output with tolerance values above 1 is a judgement call by the user.

As the tolerance setting increases, the range of feasible solutions becomes wider and the results are less precise. For this reason, the lowest practical tolerance setting should be used for the final model run for each mixture being investigated.

4 Results

The analytical results obtained are presented in Tables 2 to 10.

4.1 Moisture, organic, C, and N

Although the terrestrial soil samples were taken in the heat of summer, there was a relatively high moisture content, especially in samples collected from beneath the forest canopy (Table 2). The Moir's Hill sites were both on the eastern side of the ridge and the native forest sites at Dome Hill were on the southern side of the hill. The flat, flood-plain pasture sites had higher moisture than the hill-side pasture sites but generally had lower moisture than the forest canopy sites. The exceptions were the Kauri native forest site and exotic pine forest sites which were generally drier than the pasture sites. The organic content of the terrestrial samples followed a similar pattern with higher organic content at the sites with higher moisture content. The high moisture and high organic content results are consistent with the location of those samples being in shaded ephemeral stream channels. The estuarine samples had lower organic content than the terrestrial samples, except for EMHF which is a subsoil comprising mostly fine clay material exposed by logging operations.

Table No. 2

Soil and sediment composition

Soil	Moisture (%)	Organic (% DW)	Carbon (%)	Nitrogen (%)	%C of Organic	%N of Organic
PTR	21.0	10.7	5.58	0.49	52.1	4.6
PCR	32.4	17.3	7.42	0.46	42.9	2.7
PPR	31.8	11.7	4.18	0.44	35.7	3.8
NDH	36.1	21.7	8.34	0.41	38.4	1.9
NMH	56.1	19.1	8.61	0.49	45.1	2.6
NCBR	24.2	14.1	6.32	0.23	44.8	1.6
EDH1	27.7	21.5	10.67	0.61	49.6	2.8
EDH2	16.5	13.9	4.39	0.33	31.6	2.4
EMH	39.3	50.7	21.10	1.10	41.6	2.2
EMHF	19.6	7.0	0.94	0.08	13.4	1.1
M1	59.2	9.4	2.32	0.22	24.7	2.3
M2	54.7	12.2	2.19	0.20	18.0	1.6
M3	60.7	13.0	3.01	0.27	23.2	2.1
H2	54.8	10.1	1.78	0.16	17.6	1.6
H3	46.6	9.3	1.35	0.12	14.5	1.3
H4	54.5	6.3	1.49	0.11	23.7	1.7

The carbon (%C) and nitrogen (%N) content of the terrestrial soil samples generally follows the pattern of the % organic content. The %C levels in the organic content (Table 2) were similar for pasture, native forest, and exotic forest top soils at an average of about 40%. The exceptions were the pasture soil PTR at 52% and the subsoil, EMHF at 13% of the organic content. In contrast, the average %N level in the organic content was about 2.5%. However, the %N levels in organic matter in the pasture samples were about 60% higher than in the native and exotic forest soils, which is consistent with the application of fertiliser to the pasture landuse type.

The %C and %N of the organic fraction of the sediments in the estuarine samples were substantially lower than in the terrestrial samples. The average C content in the mangrove organic fraction was about 22% and was slightly lower at about 19% in the organic fraction in the harbour samples. The difference between mangrove and harbour samples was more pronounced for nitrogen with average %N contents of about 2% and 1.5% in the respective organic fractions.

As the silts in the upper harbour and mangrove sediments are most likely to have been derived from terrestrial sediment deposition in runoff, the lower C and N content in these sediments may indicate a substantial amount of subsoil content. However, because these are estuarine sites, the lower C and N content may also reflect a considerable amount of biological uptake and biochemical processing, especially in the harbour sites where biodiversity is likely to be greater. This is consistent with the lower %N in the organic fraction of the intertidal mud flat sediments.

4.2 Resin Acids

The suite of resin acids and fatty acids measured in the pilot study was measured in these samples. The resin acid spike recovery results are presented in Table 3 and the resin and fatty acid composition of the soil samples are presented in Tables 4 and 5.

The spike recoveries of resin acids from the test soil were essentially 100% for three of the derivatives of abietic acid and the fatty acid, but 0% for the abietic acid itself. This was expected. When soils and sediments are processed under oxic conditions (i.e., in air), abietic acid rapidly oxidises and breaks down into dehydroabietic acid (DHAA). However, as DHAA was not found, this suggests that it may have been converted into some other product(s) and the extraction procedure has failed to recover the breakdown product(s) or it was lost by soil adsoption or volatilisation during the drying process. While the proportional increase in oleic acid might suggest that that this was a possible breakdown product, given the vastly different molecular structures of these two compounds (Fig. 2), this is unlikely.

From these results, the expectation would be to recover all the slow turnover components in the resin acid and fatty acid suite but not the abietic acid.

Table No.3

Resin acid recovery from the pasture soil spike. The pasture soil used was PPR. Units are in mg kg^{-1} dry weight. Spike solution added in acetone to wet soil slurry before drying and grinding.

Soil Samples	PPR	PPR +Spike	Spike added	% Recovery
Resin Acids				
Abietic acid	< 0.1	< 0.1	1.0	0
Dehydroabietic acid (DHAA)	< 0.1	1.0	1.0	100
Isopimaric acid	< 0.1	< 0.1		
Pimaric acid	< 0.1	1.0	1.0	100
Sandaracopimaric acid	< 0.1	0.2		
7-Oxodehydroabietic acid	< 0.1	1.1	1.0	110
Fatty Acids				
Myristic acid	0.5	0.5		
Palmitic acid	4.0	4.8		
Stearic acid	1.5	2.0	0.5	100
Oleic acid	0.5	1.5		
Linoleic acid	< 0.1	0.5		
Arachidic acid	1.2	0.9		
Behenic acid	4.9	4.5		
Lignoceric acid	12.0	12.0		

The concentrations of the resin and fatty acids in the soils samples obtained this study (Table 4) were much higher than found in the pilot study (Gibbs 2004;Table 4). This reflects the use of unleached soils as source materials rather than sediment from streams draining the catchment types considered.

The three exotic forest surface soil samples all had abietic acid and DHAA present in relatively high concentrations, even though the expectation from the spike recovery experiment would be for abietic acid to breakdown rapidly in air. These resin acids were not detected in the subsoil, apart from a trace of DHAA, which should have been present long after the abietic acid had gone. In contrast, the three harbour samples (0-10 cm) all had traces of abietic acid present but no DHAA. This unusual combination was also seen in one native forest sample, NCBR, where the dominant tree species was the New Zealand Kauri (*Agathis australis*) (Table 1). The conclusion from this is that the abietic acid may reflect the presence of gum in these soils and sediments, because abietic acid would be more stable in the gum medium.

Another interesting feature of the resin acid / fatty acid matrix of results is the lack of resin acids in the mangrove samples and the pasture samples. The traces of resin acids in sample PCR may indicate deposition of the exotic forest sediment on these fields during past storm / flood events, as there is pine forest on the surrounding hills. The presence of the resin acid pair, pimaric and sandaracopimaric acids, is only a valid indication of resin acid-producing trees when the pimaric acid content is very much greater than the sandaracopimaric acid (i.e., typical ratio > 5:1 and up to 10:1). The high sandaracopimaric acid content in the NCBR sample looks spurious but may be a function of some difference in the presence of Kauri resin.

A requirement of the mixing model technique is that the sources and sinks must all have the same compound present to enable an accurate assessment. The standard resin acid analysis procedure and the resin acid / fatty acid matrix of results (Table 4) show that while many soils have traces or higher concentrations of resin and fatty acids, the limiting factor is the subsoil, EMHF, where 5 compounds were below detection level. These compounds do not meet the mixing model requirements and cannot be used. The presence of the abietic acid from gum is a direct link with the exotic forest and Kauri forest soils while the presence of pimaric and sandaracopimaric acids in one of the harbour sites in the expected ratio points to the exotic forest rather than the native kauri forest being a sediment source at that site.

Figure No. 2

Molecular structure of abietic acid and its initial breakdown product, dehydroabietic acid (DHAA), relative to oleic acid showing the key differences between the "ring-based" structure of resin acids and the "straight chain" structure of fatty acids. (Intersections and ends of thin grey lines without symbols are carbon atoms with enough hydrogen atoms to complete 4 'bonds' per carbon atom. Two parallel lines indicate double bonds).

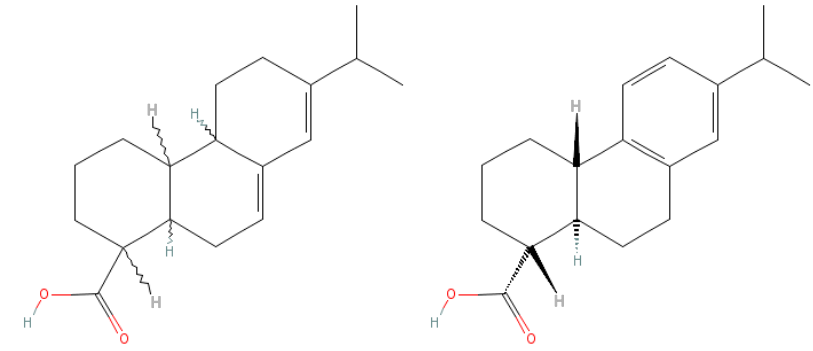


Table No. 4

Resin acid and fatty acid composition matrix of soil samples. (Values given in mg kg^{-1} dry weight; missing value less than detection limit)

Soil Samples	PTR	PCR	PPR	NDH	NMH	NCBR	EDH1	EDH2	EMH	EMHF	M1	M2	M3	H2	H3	H4
Resin Acids																
Abietic acid	0.01	0.12				7.87	8.88	3.14	6.50	0.07	0.05	0.08	0.06	0.12	0.22	0.04
Dehydroabietic acid	0.04	0.4	0.08	0.02	0.2	0.4	11.7	6.01	17.0	0.17	0.08	0.05	0.05	0.11	0.06	0.03
Isopimaric acid		0.78	0.03	0.69	0.6	0.12	1.74	1.18	4.3		0.02	0.06	0.03	0.03	0.05	0.02
Pimaric acid						2.05	10.0	3.4	2.3	0.04	0.07	0.13		1.35		
Sandaracopimaric acid	0.1	0.24	0.03	0.29	0.8	5.08	1.2	0.5	0.9		0.11	0.13	0.12	0.14	0.16	0.08
7-Oxodehydroabietic acid	0.04	0.03				0.81	2.7	1.6	3.2	0.02	0.03	0.03	0.03	0.03	0.03	0.02
Fatty Acids																
Myristic acid	1.2	1.2	0.5	1.3	4.5	1.8	4.3	0.8	23.0		5.2	1.9	2.3	0.5	0.5	
Palmitic acid	22.0	15.0	4.0	15.0	33.0	34.0	32.0	7.0	76.0	1.2	15.8	10.0	10.0	3.1	2.7	1.0
Stearic acid	5.4	6.0	1.5	3.7	9.0	7.0	14.0	2.6	20.0	0.6	3.5	2.2	2.5	0.8		
Oleic acid	4.8	2.2	0.5	3.1	7.0	9.0	15.0	2.5	23.0		1.9	1.4	1.7	0.7		
Linoleic acid	1.2	0.6		0.9	1.7	2.6	1.6	0.6	6.5				0.5			
Arachidic acid	7.6	7.0	1.2	2.7	3.6	15.0	16.0	4.0	22.0	0.7	1.1	0.9	1.2	0.5	0.3	0.3
Behenic acid	17.0	28.0	4.9	13.0	12.0	48.0	57.0	15.0	46.0	3.7	3.6	2.4	3.3	2.2	1.7	1.4
Lignoceric acid	40.0	110.0	12.0	20.0	30.0	60.0	130.0	40.0	50.0	11.0	12.0	8.0	9.0	6.0	7.0	5.0

Results of the depth-dependent sample analyses from the harbour sites are presented in Table 5.

Table No.5

Resin acid and fatty acid composition matrix of the 3 depth-dependent harbour samples. (Values given in mg kg^{-1} dry weight, missing values less than detection limit)

Harbour sites	H2	H2	H2	H3	H3	H3	H4	H4	H4
Core depth (cm)	0-10	0-20	0-30	0-10	0-20	0-30	0-10	0-20	0-30
Resin Acids									
Abietic acid	0.12	0.26	0.226	0.22		0.08	0.04	0.16	0.24
Dehydroabietic acid (DHAA)	0.11	0.08	0.06	0.06		0.03	0.03	0.03	
Isopimaric acid	0.03	0.03	0.04	0.05	0.06	0.05	0.02	0.09	0.02
Pimaric acid	1.35	0.08							
Sandaracopimaric acid	0.14	0.24	0.26	0.16	0.31	0.2	0.08	0.42	0.26
7-Oxodehydroabietic acid	0.03	0.03	0.03	0.03			0.02	0.02	
Fatty Acids									
Myristic acid	0.5	0.4	0.4	0.5					
Palmitic acid	3.1	2.0	2.0	2.7	0.9	1.3	1.0	1.6	
Stearic acid	0.8								
Oleic acid	0.7								
Linoleic acid									
Arachidic acid	0.5	0.3	0.3	0.3	0.2	0.3		0.3	
Behenic acid	2.2	1.6	1.7	1.7	0.9	1.5	1.0	1.4	0.5
Lignoceric acid	6.0	6.0	7.0	7.0	3.0	6.0	4.0	5.0	

In these samples, the cross-sectional area of the core remained the same while the volume of sediment increased by a factor of 2 and 3 with each depth sample. If the the sediments were evenly mixed through their depth, the expectation would be for no major difference in results between shallow and deep cores at a location. While some compounds showed little difference between core depths, other compounds were often not detected in one or more depths, or were present at highest concentrations in the 0-10 cm depth range. At site H4, four of the compounds found in the 0-10 cm samples from the other sites were below detection level while they were measured in the 0-20 cm core. Also, other compounds were present at higher concentrations in the 0-20 cm core than the 0-10 cm core at this site. This may imply an active surface layer which is being depleted of these compounds or a time dependent deposition of sediment in the harbour.

Only four of the fatty acids identified from Table 4 as being present in all samples (i.e., palmitic acid, arachidic acid, behenic acid, and lignoceric acid) were also present in all harbour samples to a depth of 20 cm. Below that depth at site H4, palmitic acid, arachidic acid, and lignoceric acid were not found.

The depth-dependent resin acid results (Table 5) are comparable with the pilot study results which looked at the surface 0-2 cm layer only in the harbour sample.