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Sediment Source Mapping in Mahurangi Harbour

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Prepared for
Auckland Regional Council

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1 Executive Summary

Auckland Regional Council (ARC) asked NIWA to use the recently developed compound specific isotope (CSI) method to identify and apportion the sources of catchment soil contributing to the recent sediment deposited in the Harbour and to map the spatial distribution of the soil sources throughout Mahurangi Harbour from pasture, native forest and exotic pine forest. The CSI method developed in an earlier study (ARC TP 294) incorporated the conservation of mass in the modelling phase as a one-step process. This worked for test mixtures and on freshly deposited material in Mahurangi Harbour. However, to apply the CSI method to sediments where decomposition caused losses of organic matter relative to the original source material, a two-step process was required. Step one identified the sources and apportioned their contributions based on the isotopic values of the bulk carbon and extracted fatty acids and an isotopic balance in the harbour sediment. Step two scaled these proportions by the % carbon in each source to provide the conservation of mass independent of loss processes in the harbour. This change improved the method making it more robust and easier to apply. This modification was applied to the data in this study.

The sampling for this study was undertaken by ARC staff in December 2005 and the results from 77 locations have been plotted as distribution maps of each source across the whole harbour. Terrigenous soil sources investigated were pasture (catchment area 70%), native forest (catchment area 20%), and exotic pine forest (catchment area 8%). These were compared with oceanic or coastal sediment which could enter and exchange with harbour sediments via the harbour entrance.

An overview of the results showed that catchment soil entered Mahurangi Harbour via the Mahurangi River and from sub-catchments forming the side arms and local land drainage along both sides of the harbour to the sea. Soil from the different land uses was present at varying levels throughout most of the harbour. The distribution pattern of the catchment soil showed that soil entering via the Mahurangi River tended to deposit in the river delta zone around the river mouth. The data also showed that sediments of marine origin contributed to the harbour sediments and were present at varying levels for about three quarters of the distance up the harbour from the sea. The lack of sediment of marine origin in the upper harbour near the mouth of the Mahurangi River was consistent with this being a deposition zone which is slowly infilling the harbour with a river delta of terrigenous material.

Plotted by specific land use, the CSI data showed that, despite occupying only around 8% of the catchment, exotic pine forest soil accounted for a locally high proportion of recently deposited catchment soil in the river delta zone, with 45 to 80% of the soil coming from this source. This disproportional contribution of exotic pine forest soil is consistent with the results of two earlier studies which found 50 to 54% and 60 to 90% at similar locations 12 to 18 months earlier. Lower levels of soil from exotic pine forest were found along the sides of the upper harbour, also consistent with an earlier study. The proportional contribution of soil of exotic pine forest origin decreased down-

harbour from the river delta zone, and was below resolution of the method from the middle reaches of the harbour to the sea.

In terms of mass transport, however, from modelled data (Stroud & Cooper 1997, Stroud 2003), exotic pine forest was estimated to contribute about 14% of the sediment load on the whole Mahurangi Harbour. This suggests that, on average, exotic pine forest land use contributes almost twice as much soil per unit area of catchment as pasture and native forest land use.

Soil of pasture origin was found throughout the harbour except at some locations close to the harbour entrance. Pasture soil accounted for 15 to 55% of soil in the river delta zone at the head of the harbour and 10 to 30% of the sediment across much of the rest of the harbour. While part of the pasture soil entered the harbour via the Mahurangi River, the CSI method identified pasture soil entering the harbour from sub-catchments along both sides and the side arms. Although unable to quantify these inputs, this finding is consistent with earlier NIWA modelling (Stroud & Cooper 1997) which predicted that up to 70% of the total sediment load to the harbour came from the small sub-catchments along the sides of the harbour between the Mahurangi River and the harbour entrance. The CSI method also distinguished between soil from pasture on the right and left sides of the harbour, and these have been plotted separately.

Soil originating from native forest sources was also found throughout the harbour at low levels (<10%) at most locations sampled. As with pasture soil, native forest soil associated with the Mahurangi River inflow contributed less than exotic pine or pasture soil and generally accounted for <30% of the soil in the river delta zone. Native forest soil was also found to be entering the harbour via the side arms with one site, at the head of Cowen's Bay inlet, having about 40% native forest soil from the local sub-catchment.

Because catchment soils are gradually infilling the harbour and covering the oceanic/coastal sands, there is an expectation that there would be some relationship between the proportion of catchment soils and marine sand in the sediments depending on relative distance from the Mahurangi River and the harbour entrance. An unexpected find through the shallow intertidal middle reaches of the harbour was a CSI signature which was essentially marine but isotopically more highly enriched. This was probably associated with a range of biological processes and was called the "estuarine" influence. The source of this estuarine signature is uncertain and may be associated with biomass production by benthic algae, biodeposits from shellfish including farmed and wild Pacific oysters, horse mussels, and cockles, and microbial processes associated with decomposition and recycling of the organic matter in the terrigenous soil. Further study is required to resolve the source of this signature.

Towards the harbour entrance, the harbour sediments took on the isotopic signatures of oceanic sediments which were dominant throughout the lower harbour.

Interpretation of the results is based on the concept of proportional content in the sediment sampled rather than an estimate of the amount of soil from a source deposited at that location. For example, although there was 40% native forest soil in the sediment at one site at the head of Cowen's Bay, this may be associated with a few kg of soil deposited at that site. Consequently, this is a minor soil input compared with a sample from the deposition zone which may have only 10% native forest soil but the sediment input is measured in tonnes.

The CSI sediment tracing method defines where the soil in the sediment came from but does not define how much. To determine the amount of soil from a catchment land use at any location in the harbour requires knowledge of the sedimentation rate at the site sampled.

To put the soil contribution from the three land-use types into perspective, estimates of sediment loads from the half of the catchment drained by the Mahurangi River have been made using the average proportional content of each source across the river delta zone and predictions of sediment loads from models (Stroud & Cooper 1997, Stroud 2003). These estimates suggest that, for about 330 days of the year when the total sediment load on the harbour is less than 1 t d^{-1}, about 140 kg d^{-1} comes from pine forest, 42 kg d^{-1} comes from native forest, and 58 kg d^{-1} comes from pasture. The remaining 760 kg d^{-1} comes from pasture and native forest in sub-catchments along the sides of the harbour.

For the full 330 day period, pine forest would contribute a total of 46.2 t. If the same proportionality held for storm events, the sediment loads from storms with a 3-6 month return would be about 3000 t from pine forest and 22,000 t from pasture and native forest across the whole catchment. This shows that most of the sediment load on Mahurangi Harbour is delivered in a small number of storm events each year.

Based on the modelling data estimates, the bottom line is that while pine forest appears to contribute higher than expected sediment loads (about twice the average) and also produces some locally high concentrations in the upper harbour, most of the sediment load comes from pasture and native forest in the small sub-catchments along the sides of the harbour between the Mahurangi River and the harbour entrance.

The mapping of sediment sources in the Mahurangi Harbour sediments is a 'best estimate' based on the composition of surficial sediments collected around December 2005 and presents a "snap shot" of the source distribution in the harbour at that time. Weather effects and seasonal changes in land use are likely to change the relative proportions of each source at any particular location in the harbour as new material is deposited and older material is buried or reworked by in-harbour processes. Under normal conditions, changes in the general distribution patterns are likely to be small. However, if forest harvesting on steep land exposes bare soil to a storm event, the proportions of sediment from pine forestry will increase dramatically.

2 Introduction

Terrigenous soil entering the Mahurangi Harbour is affecting the macrobenthic fauna in the harbour as a result of enhanced levels of suspended solids in the water column and the deposition of that material on the harbour beds (Ellis et al. 2002; Thrush et al. 2003). Auckland Regional Council (ARC) asked NIWA to identify and apportion the sources of the soil contributing to the sediment in the Harbour. This includes mapping soil deposition in the harbour by source from exotic pine forest, pasture, and native forest.

A pilot study (Gibbs 2004) determined that it was possible to identify and apportion the soil sources contributing to a sediment deposited at a location in the harbour using the compound specific isotopic (CSI) signatures of naturally occurring biomarkers (fatty acids and resin acids) in the source soils and by comparing these with the CSI signatures of the same biomarkers in the sediment from the Harbour. The mixing model IsoSource (Phillips & Greg 2003) was used to apportion the source soils contributing to the sediment at a site in the upper Mahurangi Harbour.

A further study (Gibbs 2005a) refined the CSI method into a tool which incorporated the conservation of mass in the IsoSource modelling as a one-step process. The accuracy of the IsoSource model predictions of proportional contributions was tested using known mixtures of source soils. The results indicated that for the major soil sources, contributing more than 10% of the total sediment input, the accuracy of soil identification and apportionment was greater than 90% with some results within 3% of the actual mixture proportions. For minor sources, contributing less than 10%, the results indicated that the accuracy was reduced but was generally within 20% of the actual mixture proportions.

Tests on several sediment samples from different locations and in the upper Mahurangi Harbour indicated that there were differences in the proportional contribution of soil sources between sites and that the CSI method could be used to evaluate the spatial distribution of soil eroded from each land use type in the catchment.

However, while the mixtures tested in the method refinement study produced results in close agreement with theoretical estimates, incorporating the conservation of mass in the modelling phase did not allow for degradation of organic matter in the harbour sediment mixture. The field samples tested were all taken from the terrigenous deposition zone in the Mahurangi Harbour where, in hind-sight, degradation was also likely to be minimal. The method was not tested on more diverse samples where organic degradation occurred and oceanic sands were dominant. When subsequently tested it was found that, where sediments had lost part of their carbon content through biological processes, a two-step approach was required where the catchment sources were identified isotopically and then the feasible proportions from the IsoSource modelling were scaled by the % carbon in each source to estimate the proportional contribution of each source. This method modification did not affect the identification of the soil sources using CSIs (i.e., the isotopic value of the CSI does not change during decomposition), but has made the method more robust and independent of degradation of organic matter in the estuarine sediments. The changes to the original method are described in the methods section (Section 3.4).

This report presents the results of a spatial sampling of Mahurangi Harbour and the identification and apportionment of soil sources contributing to the sediment at each sampling site using the modified method.

3 Methods

3.1 Sampling

Surficial sediment samples were collected in November and December 2005 from 77 locations in Mahurangi Harbour (Fig. 1) by ARC staff (See Appendix 1 for sample site descriptions, sample characteristics and NZ Map Grid coordinates). The sediment samples were taken from the top 20 mm using a variety of techniques including coring and scooping from intertidal and subtidal locations. At each location, multiple samples were collected across a wide area (10-20 m^2) and combined to ensure the bulk sample (about 2 kg) was representative of that location.

With an estimated sediment accumulation rate (SAR) of around 2-4 mm y^{-1} in the main body of the harbour seawards of Hamilton's Landing (Swales et al. 1997, 2002), the top 20 mm should limit the results to sedimentation events that have occurred within the last 5 years. However, landwards of Hamilton's Landing the SAR was estimated to be ~20 mm y^{-1} which would limit the results to sedimentation events in the last year. Because of the high degree of sediment mixing in this region of the harbour, it is possible that the top 20 mm may represent an even shorter time frame. For example, recent ^{7}Be data from the Waitemata Harbour indicate sediment mixing to 20-30 mm depth with $<<$ 100 day time scale (A. Swales, NIWA, pers. comm.).

Source soils collected in March 2005 for the method refinement study (Gibbs 2005a) were augmented with additional source soil samples collected in December 2005 and March 2006. Relative locations of these samples are shown on Figure 1 (See Appendix 1 for sample descriptions and NZ Map Grid coordinates). About 2kg of surface sample (top 20 mm) was collected from an area of about 10-20 m^2 at each location to ensure the sample was representative of that site.

Each sample was sieved (1-mm mesh) to remove stones, shells, benthic macrofauna, and woody debris including twigs, root material, and leaves. Samples collected for this survey were sieved by ARC staff, sealed in new 5-litre plastic buckets and stored at 4°C pending transport to NIWA Hamilton for processing. Processing was completed within a few days of arrival at NIWA.

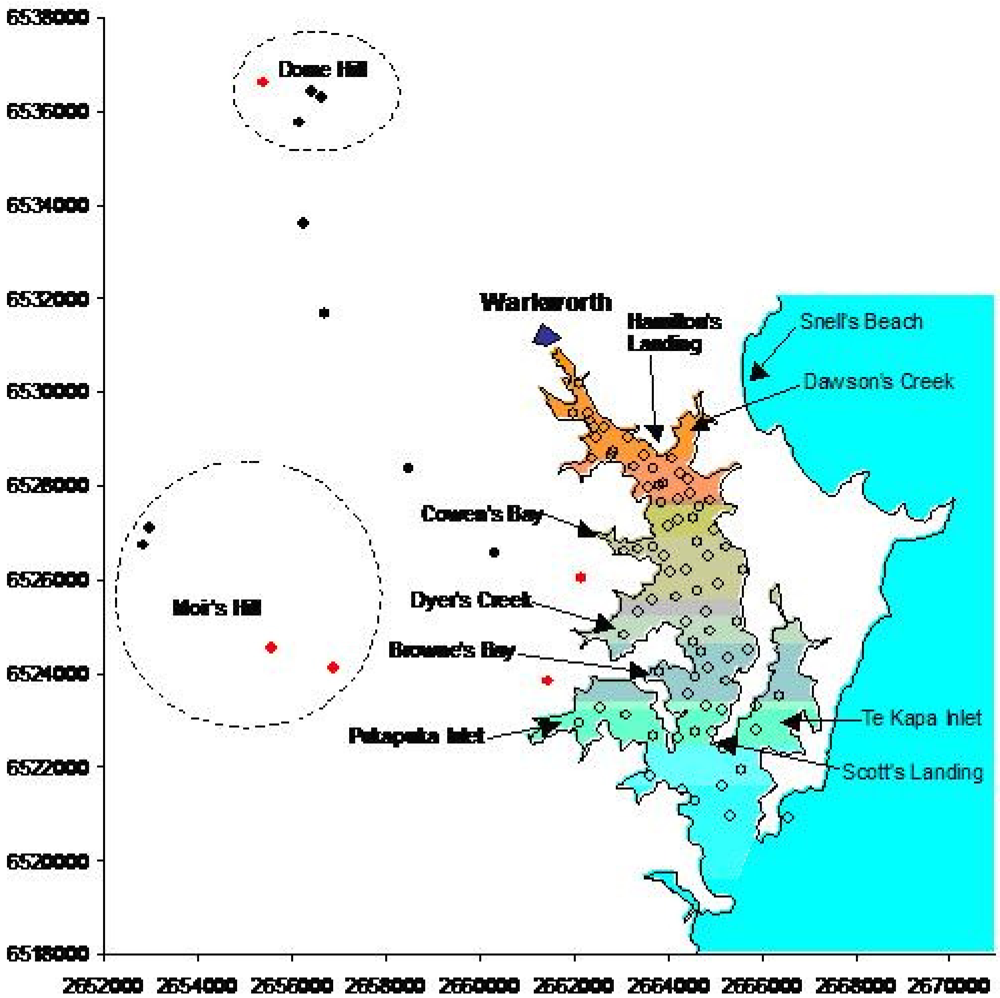
3.2 Sample analysis

The bulk sieved sample was transferred to a large aluminium baking dish and thoroughly mixed using plastic utensils. An aliquot of each sample was taken to determine moisture content by drying in an air-fan oven at 103°C and then total organic content as percent of dry weight by loss on ignition at 500°C.

For bulk ^{13}C and ^{15}N stable isotope analysis an aliquot of each sample was acidified with 1N hydrochloric acid (HCl) to remove inorganic carbonate and allowed to stand overnight. After the initial acidification, further acid was added to ensure all carbonate was removed. The acid was diluted with deionised water (Milli RQ) and decanted, and the sample rinsed again with deionised water before drying at 60 °C for 24 h.

Figure No.1

Site map (NZMG coordinates) showing the locations of sediment samples in Mahurangi Harbour (open circles) and the 5 source soils (red dots) collected in the catchment around the time of the harbour sampling. Black dots indicate locations of source soils collected for the earlier study in March 2005.



The dried samples were ground to a fine powder and analysed at the Waikato University Stable Isotope Unit on a Micromass isotope ratio mass spectrometer (IRMS) after combustion in an elemental analyser at 1000 °C and separation of the gasses produced by gas chromatography (GC). Results were reported in delta (δ) notation with units of per mil (‰) calculated by the formula:

$$\delta X = (R_{sample} / R_{standard} - 1) \times 1000 \quad ‰$$

where X is ^{13}C or ^{15}N and R is the ratio of heavy to light isotope (^{13}C:^{12}C or ^{15}N:^{14}N). Standards for carbon were a reference gas (CO_2) calibrated relative to the international standard PeeDee Belemnite. For nitrogen, the reference standard was atmospheric nitrogen.

The remainder of each bulk sample was dried in an air-fan oven at 60°C. The dry sample cake was crushed and ground to a fine powder using a high powered coffee grinder. Coarse materials were removed by sieving (100 micron mesh) and reground. An aliquot of each sample was extracted in a Dionex ASE 200 Accelerated Sample Extractor. For all sediment samples from within Mahurangi Harbour, a 20-g aliquot was extracted. A 30-g aliquot of the sediment outside the harbour entrance was extracted and 10-g aliquots of the 5 new source soil samples were extracted.

Each sample aliquot was weighed into a stainless steel pressure vessel which was then closed. The extraction method used double distilled dichloromethane (DCM) as the solvent. The extraction cycle filled the sample pressure vessel with solvent which was then heated to 100°C and raised to a pressure of 2000 psi for 10 minutes. The extraction liquor was drained and flushed with clean solvent into a collection vial, and the extraction cycle was then repeated (i.e., 2 extractions of each sample). The system used a rinse cycle between each sample to prevent cross contamination. The DCM extract from each sample was reduced to near-dryness by rotary evaporation at 30°C and then transferred to a 2-mL vial (Argilent wide-mouth screw cap). The sample was allowed to evaporate to dryness at room temperature in a gentle air flow before the vials were sealed and sent to Iso-trace New Zealand Ltd for analysis of compound specific isotopes of fatty and resin acids.

3.3 Data processing and interpretation

Data from the harbour sediment samples for % organic content, % C, and bulk $\delta^{13}C$ and $\delta^{15}N$ were plotted as spatial distribution maps for Mahurangi Harbour using the contouring software package Surfer 8 (Golden Software), with Krigging as the interpolation algorithm between adjacent points. For all contour plots, to provide the contouring software with an oceanic endpoint, the position of the ocean sediment sample from outside the harbour was set as being at the centre of the entrance to the harbour. Note, the contour plots are only indicative of the spatial distribution patterns.

The bulk $\delta^{13}C$ and compound specific isotopic $\delta^{13}C$ analytical results were combined in a data matrix and evaluated relative to data for selected source soils using the mixing model, IsoSource (Phillips & Gregg 2003), and the post modelling conversion step (section 3.4). To minimize the number of sources required in each model run, the data were geographically constrained by the natural linkage between each source and the sample in the harbour (i.e., is it possible for that soil source to contribute directly to the sediment at that site in the harbour). Results were plotted as a spatial distribution map for each source soil type in Mahurangi Harbour.

3.4 Source identification and apportionment

The soil-source identification technique is based on analysis of a matrix of the CSI results from all sources compared with CSI results from the harbour sample being assessed. Initially, the CSI results are inspected by eye for patterns of commonality or difference. This is followed by exploratory data analysis, which includes scatter plots of the data, to find the most likely combination of sources influencing the sample being assessed, within the geographical constraints. These are the sources with CSI values that, when connected by straight lines, form the corners of a polygon that encloses the harbour sample CSI value. These sources are then used in the source partitioning model, IsoSource, which provides an apportionment of all feasible combinations of those sources in the harbour sample. While IsoSource has been favourably evaluated for food-web studies (Benstead et al. 2006), it is not limited to food-web studies and can also be used for any mixture where isotopic signatures are available relative to potential sources. Consequently, in the soil-source identification technique, IsoSource can be used to identify and apportion catchment soil sources contributing to the harbour sediment samples.

3.4.1 IsoSource operation

Standard linear isotope mixing models using n isotopes will allow the unique determination of at the most n + 1 sources in a mixture. With larger numbers of sources to assess, the source partitioning model, IsoSource, statistically constrains the relative proportions of the various sources in the mixture. To do this, IsoSource evaluates all combinations of each source (from 0-100%) in user-defined increments to identify source combinations that sum to the known isotopic signature of the mixture to within a prescribed small tolerance in ‰. These source combinations are collated into a distribution of the frequency and range of potential source contributions. Consequently, IsoSource does not offer a unique solution, but it does allow evaluation of the statistical constraints on the relative contributions of each source.

Essentially this process works backwards from the mixture to determine all combinations of the sources that produce feasible solutions. While each feasible solution may be the correct solution, the number of times any given proportion of each source occurs is summed to produce a frequency distribution which can be evaluated statistically to give the mean % contribution. The range of feasible solutions rather than the statistical mean should be reported where ever possible. When interpreting the model output, the total number of feasible solutions found by the model is an indication of the reliability of the result with reliability increasing as the number of feasible solutions decreases towards 1, which is a unique solution.

3.4.2 Assumptions

3.4.2.1 As used in food web studies

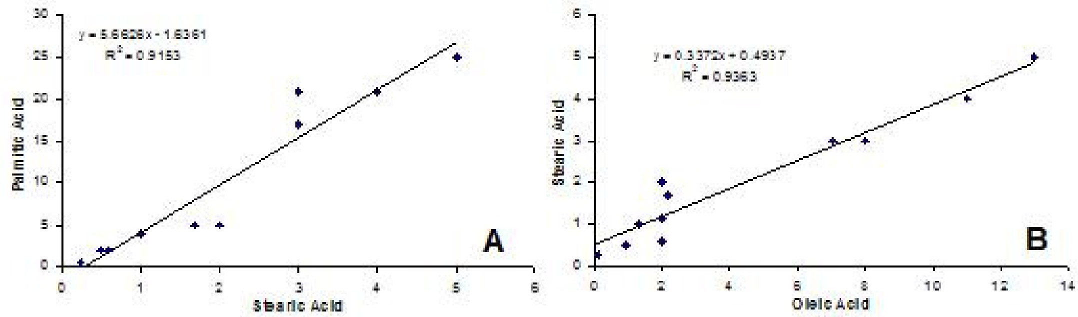
In food web studies, a fundamental and often unstated assumption of most isotopic mixing models is that the proportional contribution of a source to the mixture is similar for each element in the source (Phillips & Koch 2002). This assumption is reasonable if the elemental concentrations of each source are similar and of equal digestibility (e.g., for animals on all meat or all plant diets). Under these circumstances, there is no need to consider concentration when evaluating the mixture relative to sources and the isotopic balance will provide a range of valid feasible solutions.

If this assumption is not valid, however, a concentration dependent mixing model must be used in place of the linear mixing model in IsoSource (Phillips & Koch 2002; Newsome et al. 2004). As the concentration-dependent version of IsoSource has yet to be released, an alternative solution is to select only those elements which have similar proportions in each source for use in the model. This is the approach used in the present study.

A worked example (Fig. 2) demonstrates how the validity of the basic assumption of similar proportions was tested for CSI compounds in the present study. In Figure 2, the concentrations of the selected pairs of fatty acids in a number of soil samples were evaluated with a linear regression which gives the mean relative proportion of those fatty acids as the coefficient of "X" and the r^2 value for the relationship as an indication of how similar the proportions are of those fatty acids in each soil. The soils used include samples from Mahurangi catchment and Whangapoua catchment on the Coromandel Peninsular, to demonstrate that the similarity in proportions is not local to Mahurangi and thus this approach is valid for other regions.

Figure No.2

Relative concentrations (mg kg^{-1}) of the fatty acids Oleic acid, Palmitic acid and Stearic acid found in a range of soils from the Mahurangi and Whangapoua catchments. These plots demonstrate that these compounds occur in similar proportions in all soils and thus meet the assumptions of the mixing model (see text). The equations for the linear regression lines are included with the r^2 value.



3.4.2.2 As used in sediment tracing studies

A fundamental assumption of food web studies is that the predator – prey relationship involves the whole organism with the isotope used in the mixing model being uniformly mixed through the whole sample. This is valid where the bulk isotopes of C, N, O, H, and S are used for source apportionment. In sediment studies, however, the CSI values are only associated with the carbon content of the sample. Thus two new assumptions are made that (1) the carbon content is uniformly distributed throughout the soil and (2) the fatty acids are bound to the soil particles by an ion-exchange mechanism (Thurman 1985).

Because IsoSource uses the isotopic values of carbon and extracted fatty acids from the bulk sample, the feasible proportions produced relate to the carbon content of the soil sources. Where there is no degradation of the soil sources in the estuarine sediments (i.e., near the head of the estuary where the soils are first deposited) it is possible to include the %C as one of the elements in the IsoSource matrix and produce the feasible proportions of soil sources directly. However, where there has been loss of carbon through biological processes or winnowing from the sediments by tidal or wave action, or inadvertent loss during sampling, the one-step direct calculation of proportional contribution using IsoSource is not possible.

In this situation, IsoSource is used to identify the sources of the soils and produce feasible proportions of each contributing source based on the isotopic signature of the bulk carbon and extracted fatty acids from each source. The amount of soil from that source required to supply that proportion of carbon is calculated from the %C of the source using the equation:

$$\%source_n = \frac{\left(\%P_n / \%C_n \right)}{\sum_n^1 \left(\%P_n / \%C_n \right)} \times 100 \qquad \text{Equation 1}$$

where $\%P_n$ is the proportion of source n in the harbour at a location as estimated by IsoSource and $\%C_n$ is the % carbon in source n soil in the catchment. For simplicity, the value P used is the statistical mean feasible proportion of each source rather than the range. Because this calculation uses the %C of the sources for scaling, the proportional contribution of each source is independent of any degradation of the soil once it enters the harbour sediments.

3.4.3 Application for soil identification and apportionment

The compound specific isotopic data from the sediment extracts were combined in a large matrix of variables relative to the library of soil sources. These data were modelled using IsoSource to produce a range of feasible proportions for the contribution of source soils at each location in the harbour based on the carbon in each source soil. Where-ever possible, the bulk $\delta^{13}C$ value for each source was included as one element in IsoSource model run.

Multiple runs of multiple sources were used to identify the most likely sources contributing to the harbour sediments at the time of sampling. The model was then run with the minor sources removed and the smallest tolerance setting until the number of solutions and thus the range of feasible proportions for each source was at a minimum. This combination of sources was considered to be the most likely to be contributing to that site in the harbour, although it is possible that soil from most sources was also present but below the resolving power of the model.

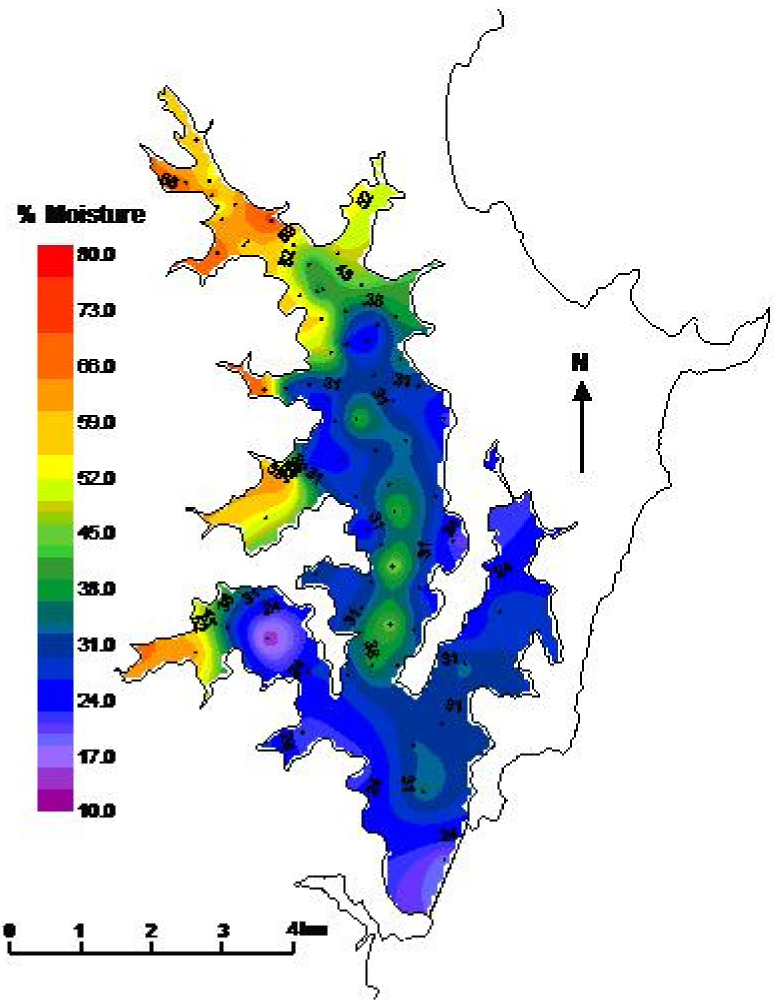
The statistical mean of the range of feasible proportions of each source at each location produced by IsoSource is then scaled to reflect the contribution of soil required to provide the proportion of carbon in each source using equation 1. The estimates of source soil proportions are presented either as contour plots showing the spatial distribution of soil contributions from different land use types as the proportion of the total sediment in the harbour, or as pie-charts showing the relative proportions of each source at specific sampling locations within the harbour.

4 Results

4.1 Moisture, Organic, and bulk isotopic content

Analytical results of % moisture, % organic, bulk isotopic C and N content of each sediment and source sample are listed in Appendix 2. Based on moisture content of the samples, the majority of the harbour sediments consist of fine silty sands with higher moisture content indicating a higher mud content around the inner harbour and inlet arms and lower moisture content indicating coarser sands in the lower harbour towards the sea (Fig. 3).

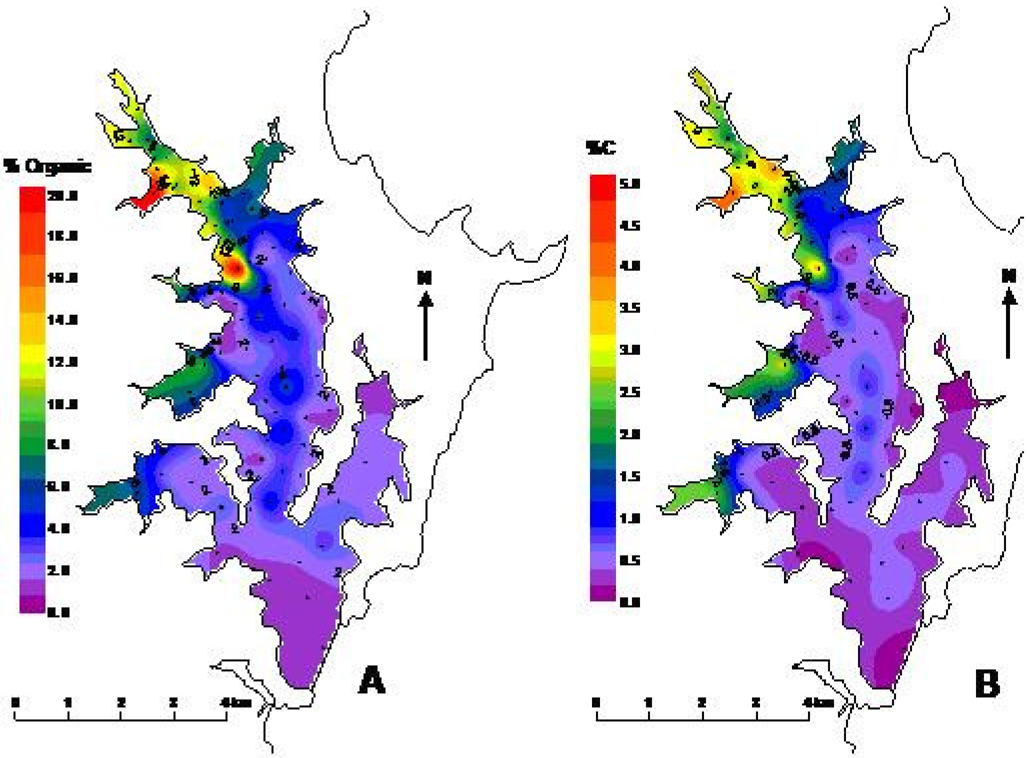
Figure No.3
Moisture content of the harbour sediment samples, with higher moisture indicating finer muddy sediments and lower moisture indicating coarser sandy sediments. Black dots indicate the position of each sample.



The distribution pattern of mud to coarse sand in the harbour sediments indicated by moisture content (Fig. 3) was matched by the distribution pattern of organic matter and carbon content (Fig. 4). These distribution patterns are consistent with terrigenous soil entering the harbour via the Mahurangi River and depositing in the upper harbour fringing mangroves and side arms, and on the upper harbour mudflats. These data also indicate that there is more organic material in the bottom of the main channel through the middle reaches of the harbour than along the shoreline on either side.

Figure No.4

Organic (A) and carbon (B) content as % of dry weight of the harbour sediment samples show highest concentrations in the upper harbour sediments and side arms, and lowest concentrations in the sandier sediments from mid-harbour towards the sea. Black dots indicate the position of each sample.



There was a strong linear relationship between the carbon and nitrogen content of the organic material in the harbour sediment samples (Fig. 5) with an average C:N ratio of 9.5:1. The C:N ratio decreased to around 5:1 in the sandy sediments closer to the harbour entrance indicating a progressive loss of carbon down the estuary.

The spatial distribution patterns of the bulk stable isotopic compositions of $\delta^{15}N$ and $\delta^{13}C$ in the organic matter in the harbour sediments are also consistent with terrigenous material entering the harbour via the Mahurangi River (Fig. 6). Terrigenous material typically has relatively depleted (more negative) $\delta^{15}N$ and $\delta^{13}C$ values compared with material from a marine source.

Figure No.5

A strong linear relationship exists between carbon and nitrogen in the organic matter in the harbour sediment. The carbon data excludes inorganic carbonate due to acidification of each sample prior to analysis. Carbon and nitrogen data are as percentages of dry organic matter.

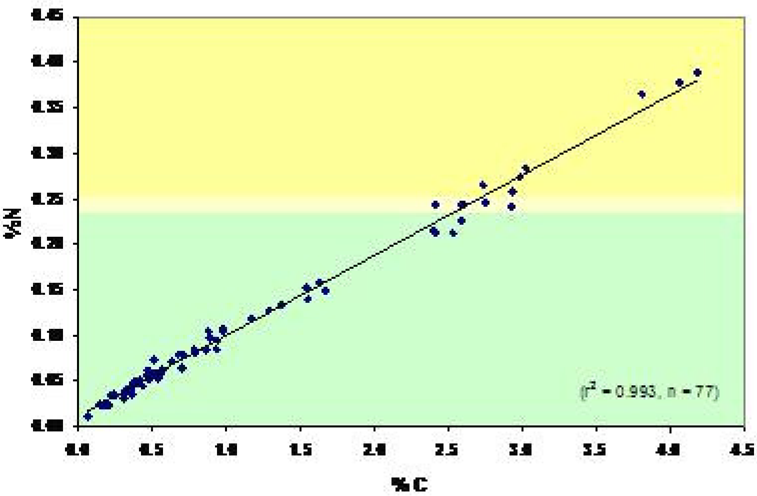
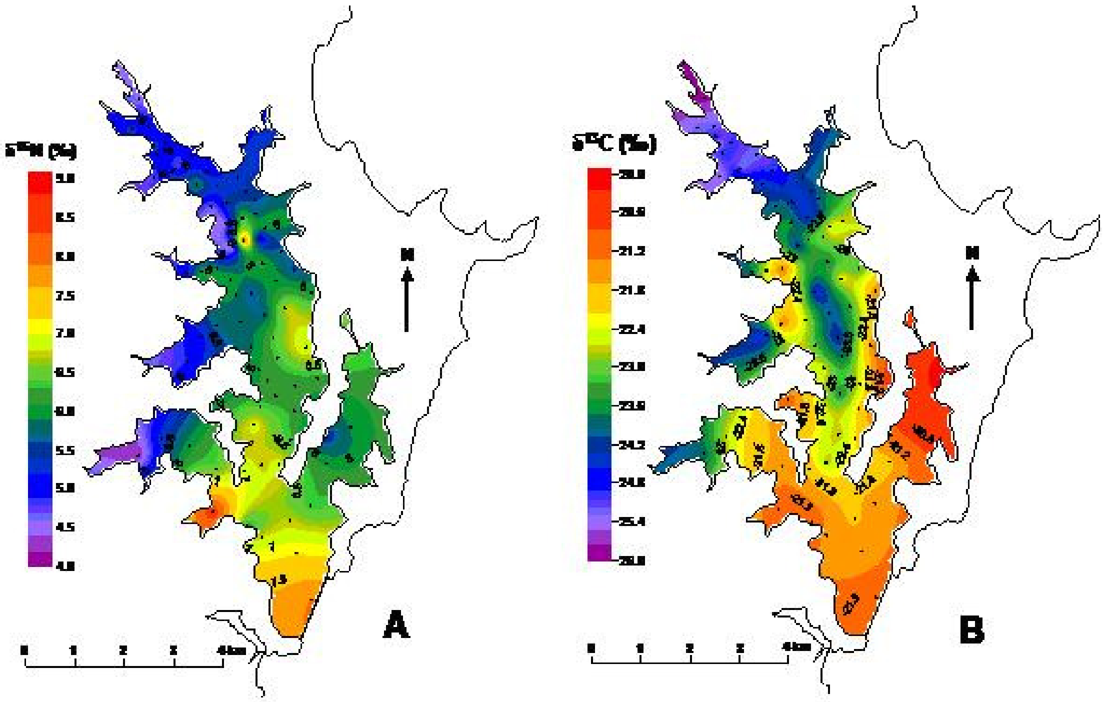


Figure No.6

Spatial distribution patterns of the bulk stable isotopic compositions of $\delta^{15}N$ (**A**) and $\delta^{13}C$ (**B**) in the organic matter in the harbour sediments. The lower values are typical of terrigenous inputs while the higher values are typical of marine environments. Black dots indicate sample positions.



Faeces and pseudofaeces from shellfish can also cause elevated $\delta^{13}C$ values and may explain part of the $\delta^{13}C$ distribution patterns obtained from the sediment samples (Fig. 6B). While there is extensive aquaculture in Mahurangi Harbour with rack farming of Pacific oysters, *Crassostrea gigas*, at the entrance to Cowen's Bay, Dyer's Creek, Browne's Bay, Pukapuka Inlet and in Te Kapa Inlet, natural shellfish beds of horse mussels, *Atrina zelandica*, and cockles, *Austrovenus stutchburyi*, occur across the bottom of the outer harbour and in the sandy inlets, and wild Pacific oysters also attach to the fringing mangroves.

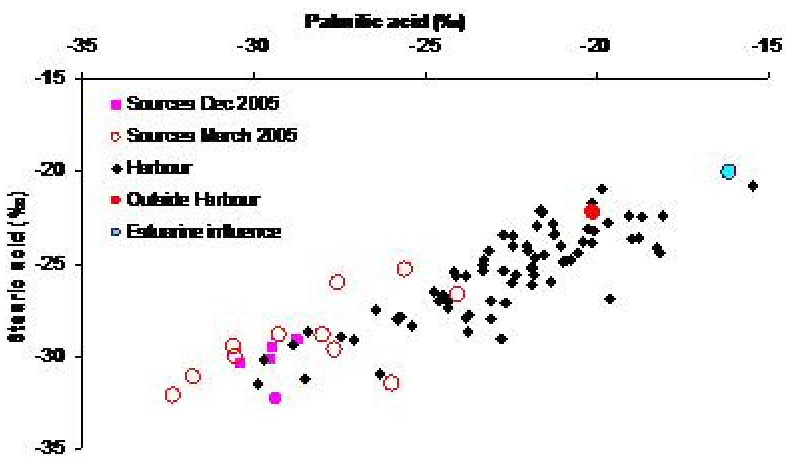
4.2 Source distribution patterns

4.2.1 Identification of sources

From the scatter plots of CSI values in the harbour samples, it was immediately apparent that an additional source was required before all data could be modelled in IsoSource. For example, the plot of end-member CSI values for Palmitic acid versus Stearic acid (Fig. 7) have the more isotopically depleted terrigenous samples at the left-hand side of the plot compared with the more isotopically enriched marine sample from outside the harbour on the right-hand side of the plot, as expected. However, while the majority of harbour sediment samples are spread between these end-member groups, there are several harbour sediment samples which are more isotopically enriched than the marine sample and thus plot further to the right.

Figure No 7

Scatter plot of CSI values (‰) of Palmitic acid vs. Stearic acid in all samples showing the terrigenous samples (pink solid squares and red open circles) towards the left-hand side of the plot, the sample from outside the harbour (red solid circle) towards the right-hand side of the plot, and the majority of harbour sediment samples (black solid diamonds) spread between these end-members. Samples which plot further to the right of the sample from outside the harbour (e.g., blue solid circle) are assumed to be associated with estuarine processes (see text).



From the requirement that all samples being assessed must lie within a polygon drawn through the end-member sources, it follows that the most enriched sample in the plot must be an end-member or very close to an end-member for the model. In this example, the most enriched sample came from location M13 (Appendix 1), in Dyers Creek and the next most enriched sample, M18, was next to it but closer to the largest Pacific oyster farm in the middle of Mahurangi Harbour. Although it is possible that the enriched signatures found are associated with biodeposits from oysters grown on racks above the harbour sediments and thus represent a pelagic food (i.e., phytoplankton), a similarly enriched signature would be expected from wild populations of oysters and other suspension feeders such as horse mussels and cockles. It is also possible that the signature is associated with benthic algae on the shallow muddy sand flats, or other estuarine processes (see discussion).

For the purposes of this study, this end-member source is referred to as the estuarine influence. During modelling these estuarine derived sediments have been distinguished from the coastal or oceanic sediments, although both have similar bulk ^{13}C isotopic values and thus combine to represent the overall marine sediment component.

Because the scaling of the isotopically derived feasible proportion data to proportion of soil source relies on the accuracy of the %C analysis and there is a possibility that some of the estuarine and oceanic sediment carbon may have been lost during sampling and subsequent sample processing (i.e., the %C content was low), time-series values for %C from the annual monitoring programme (Cummings et al. 2005) and other studies (e.g., Gibbs et al. 2005b) have been compared and used as representative values for the oceanic sediment (data from Jamieson Bay) and estuarine sediment (data from Upper Harbour) in the conversion equation.

4.2.2 Spatial distribution of source contributions in Mahurangi Harbour

The proportional contribution of source soil groups (pasture, native forest, and exotic pine forest) have been plotted as contoured spatial maps of their distribution in Mahurangi Harbour, individually and as the combined soil contribution from the catchment. These plots are compared with similar contoured distribution maps of the individual and combined marine (oceanic and estuarine) sediments in the harbour.

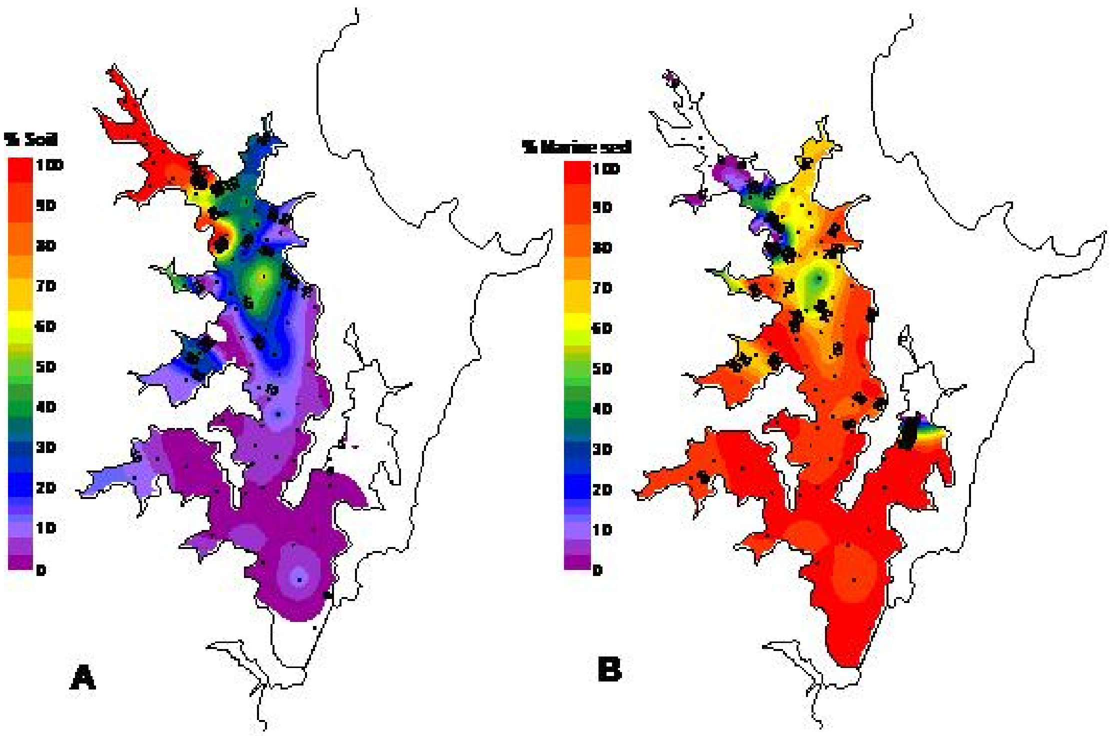
Despite potential errors arising from the use of representative %C values in the conversion equation, the plots are considered a reasonable representation of the spatial distribution of the different sources contributing to each location in Mahurangi Harbour at the time of sampling.

In these plots, the shoreline represents the interpolation boundary rather than extrapolating across narrow headlands and peninsulas.

4.2.2.1 Terrestrial soils versus marine sediments

Contour plots of the separation between sediments of terrestrial and marine origin (Fig. 8) indicate that terrestrial soils are mainly entering Mahurangi Harbour via the Mahurangi River with substantial sediment accumulation on the western (true right) side of the harbour beyond Dawson's Creek and significant amounts in the main channel as far south as Dyer's Creek. Beyond that river delta zone, terrigenous soil comprises less than 10% of the open harbour sediments although higher proportions were estimated in the side arms (Fig. 8A). Sediment with a dominant "marine" signature (Fig. 8B) extends up the harbour as far as Dawson's Creek at more than 60% of the harbour sediment, with a rapid decline in contribution above that point. While terrestrial derived material was found throughout the harbour, the sediment with a "marine" signature was below the level of discrimination of the method in the upper harbour near the river inflow, which is consistent with infilling and burial by soils eroded from the catchment.

Figure No 8
Contour plots of % contribution of A) catchment derived soil and B) sediment with a dominant "marine" signature in Mahurangi Harbour sediments as at December 2005.



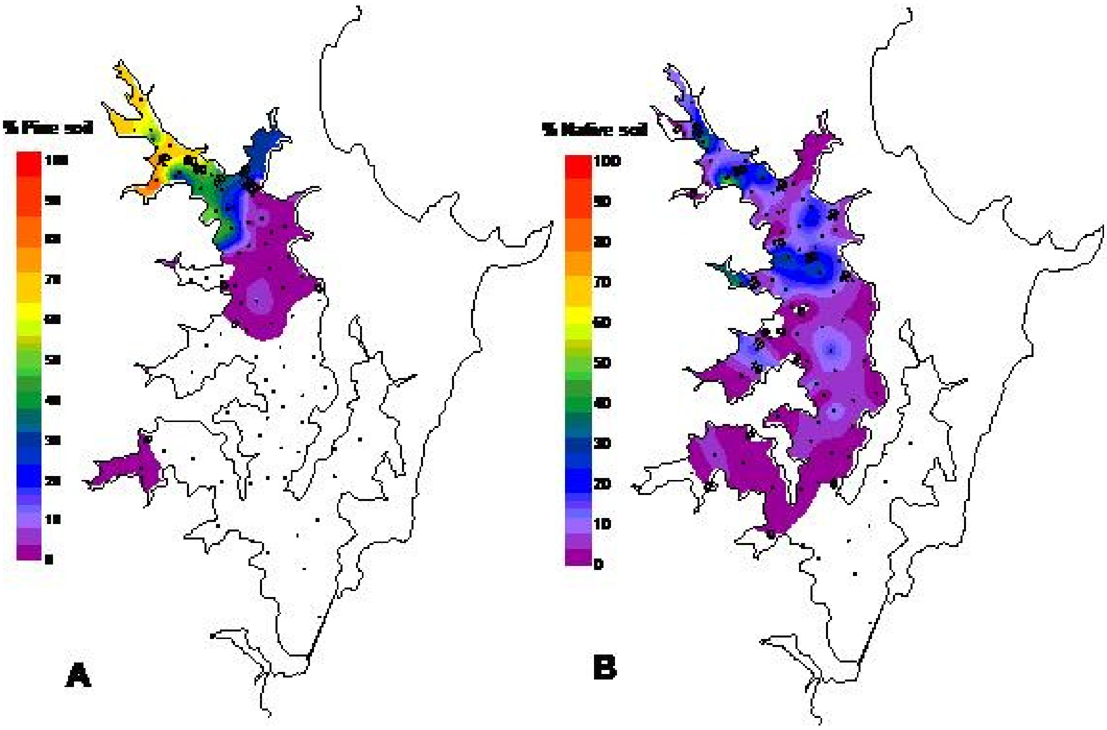
4.2.2.2 Forest soils: native versus exotic pine

Of significance, soils from exotic pine and native forest from the true left side of the Mahurangi catchment (i.e., Dome Hill area) did not feature strongly in any model output on this occasion, although pasture soils did (see below). This may reflect the time of sampling and the depth of the sample collected relative to the extent of land vulnerable to erosion at that time, or just *in situ* mixing, rather than being an indication that there was minimal soil erosion from the Dome Hill area. For example, with SARs of~20 mm y^{-1} landwards of Hamilton's landing (Swales et al. 1997, 2002) and regrowth reducing sediment runoff from the Dome Hill area relative to the potentially high sediment production from recent clear-fell harvesting on Moir's Hill area, the expectation would be for the top 20 mm of sediment in the river delta zone to be dominated by the more productive sediment source within the last year.

The majority of exotic pine and native forest soils came from the true right side of the Mahurangi catchment (i.e., Moir's Hill area) with the subsoils featuring more than the surface soils from the pine forest. The pine signature at the head of Pukapuka Inlet (Fig. 9A) is consistent with a local area of exotic pine forest near the inlet.

Figure No 9

Contour plots of % soil contributions from A) exotic pine and B) native forest to Mahurangi Harbour sediments as at December 2005.



In contrast to the extensive influence at low proportions (mostly <10%) of soil from native forest land (Fig. 9B), the exotic pine forest signature (Fig. 9A) was present at high proportions (>45%) in the upper harbour, with some sites having up to 80% of the surface sediments derived from exotic pine forest at the time of sampling. The spatial distribution of the exotic pine forest soil around the Mahurangi River mouth and down the right-hand side of the harbour to the end of the river delta zone opposite Dawson's Creek is consistent with the flocculation and sedimentation of the clay material and reduction in stormwater current speeds seawards of Hamilton's Landing due to increase in cross-sectional area (Swales et al. 1997).

The rapid fall in proportional contribution of exotic pine forest soil downstream of the river delta zone may indicate that terrigenous material is being transformed by estuarine recycling processes (see discussion). This implies that the contribution of native forest soil beyond the extent of the exotic pine soil contribution reflects additional inputs from the side arms as demonstrated by a higher proportion of native forest soil contribution at the inner end of the Cowen's Bay arm than at the entrance to that bay (Fig. 9B). Cowen's Bay sub-catchment has large areas of native forest as reserves and the gullies.

The input of soil from the sides and side arms of the harbour is consistent with earlier NIWA modelling (Stroud & Cooper 1997) which found that about 50% of the catchment draining via the Mahurangi River contributed only about 30% of the sediment load to the harbour while the remaining 70% came from the other half of the catchment comprised of smaller sub-catchments closer to the harbour mouth.

4.2.2.3 Pasture soils: overall and local sources

Pasture soil contributions to the sediments in Mahurangi Harbour (Fig. 10) were similar in distribution extent to the native forest soil contributions (Fig. 9B). While the proportional contributions were also low (mostly <10%), they were generally slightly higher than the native forest soil contributions especially in the upper harbour. As with the native forest soil contributions, the distribution of pasture soil contributions beyond the extent of the exotic pine forest soil (Fig. 9A) is consistent with additional inputs from the side arms.

Because of the spread of source soils collected from pasture and the differences in the CSI values from the different pasture areas, it was possible to separate the overall pasture soil source contribution proportions into the contributions from the true right and true left of the Mahurangi catchment (Fig. 11). Separated and plotted in this way it is apparent that pasture sediment is entering the Mahurangi Harbour from both the left and right branches of the Mahurangi River and from local sub-catchments on the left and right sides of the harbour.

For example the CSI value of the pasture soil, ML0, taken from a farm above Pukapuka inlet matched the CSI values of the sediment trapped in the roots of the fringing mangroves at the head of Pukapuka Inlet. It is more likely that this represents trapping of local catchment runoff rather than advection of sediment from the Mahurangi River, where the CSI signature if the ML0 source soil was not found. A small amount of exotic pine CSI signature was also found at the head of Pukapuka Inlet consistent with a small local area of pine forest around part of the head of the inlet (Fig. 9A).

More reference source soils would be required to refine the separation of soil from individual sub-catchments around the harbour.

Figure No 10

Contour plot of the contribution of pasture soils from all sources to Mahurangi Harbour as at December 2005.

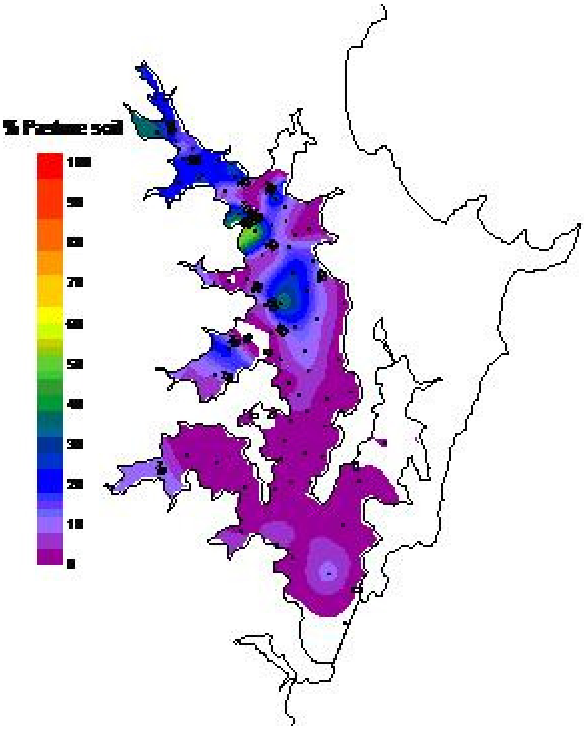
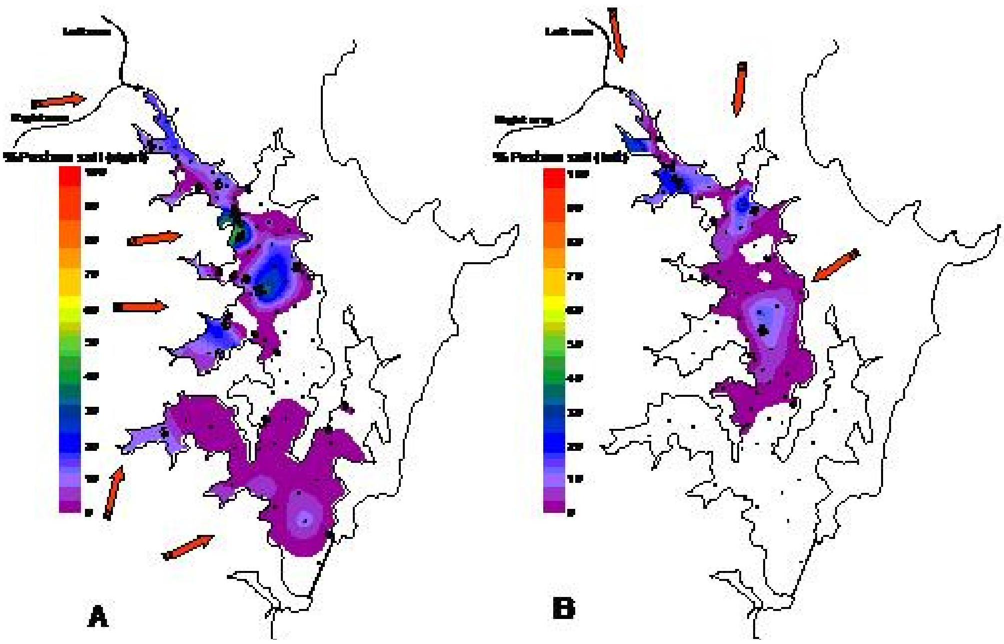


Figure No 11

Contour plots of pasture soil contributions separated into sources from sub-catchments on A) the true right and B) the true left sides of Mahurangi Harbour as at December 2005. Stylised arrows indicate the general areas contributing soil to the harbour and are not indicative of specific sources.



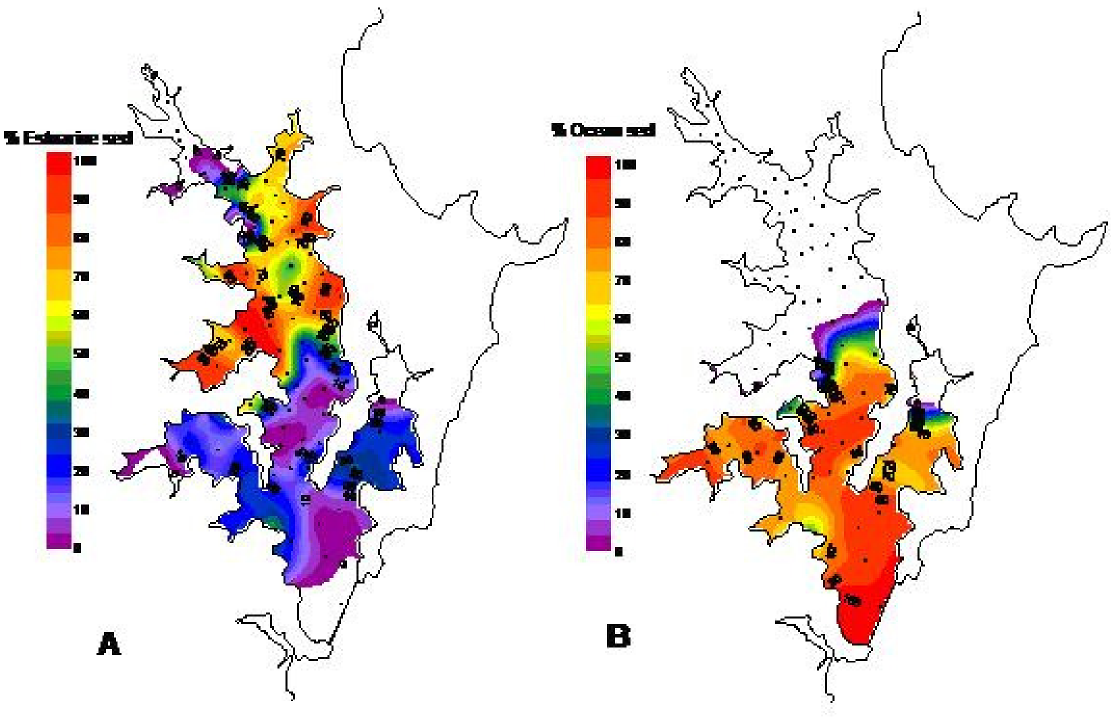
4.2.2.4 Marine sediments: estuarine versus oceanic (coastal)

While the distribution of sediment with a dominant "marine" signature extended into the Mahurangi Harbour as far as Dawson's Creek (Fig. 8B), this sediment includes terrigenous material which has been recycled within the harbour (i.e., the estuarine influence) as well as coastal sands and sediment advected into the harbour by tidal action. Although the bulk ^{13}C isotopic signature of these materials suggest that they are all essentially coastal or oceanic sediments, it is possible to discriminate between sediments which have been dominated by the estuarine processes inside the harbour and those that either retain their oceanic signatures or have recently been deposited in the harbour from coastal waters (Fig. 12).

Of significance, the proportion of sediment dominated by estuarine processes is largely confined to the middle reaches of the Mahurangi Harbour (Fig. 12A) adjacent to the largest area of Pacific oyster farming in the harbour. The signature being detected may be that of marine phytoplankton in the biodeposits of the oysters. However, while the expectation would be for the highest amount of this material to occur in the sediments near the largest oyster farms, as seen at the entrance to Dyer's Creek, this material does not correlate to the same extent with oyster farms further down the harbour in Browne's Bay, Pukapuka Inlet, and Te Kapa Inlet, and alternative explanations are required (see discussion).

Figure No 12

Contour plots of marine sediment proportions separated into A) estuarine influenced sediments and B) oceanic sediments which are linked to material from coastal waters outside Mahurangi Harbour as at December 2005.



The apparent proportion of sediment dominated by estuarine processes reduces seawards from Dyer's Creek towards the harbour entrance. This reduction may be influenced by wave suspension and tidal dispersion of the estuarine sediments and exchange with oceanic or coastal sediments.

The spatial distribution of oceanic or coastal sediments was confined to the lower Mahurangi Harbour (Fig. 12B). This distribution pattern may indicate the limit of intrusion of oceanic and coastal sediments into the harbour, or it may reflect the overwhelming influence of the estuarine sediments which are masking the oceanic signature as these move down the harbour.

4.2.3 Relative proportions of source contributions in Mahurangi Harbour

While the spatial plots indicate where the various sources may accumulate within Mahurangi Harbour, comparative plots, using pie charts, showed the relative proportions[1] of each general type of source contributing to the sediment at selected locations within the harbour (Fig. 13)..

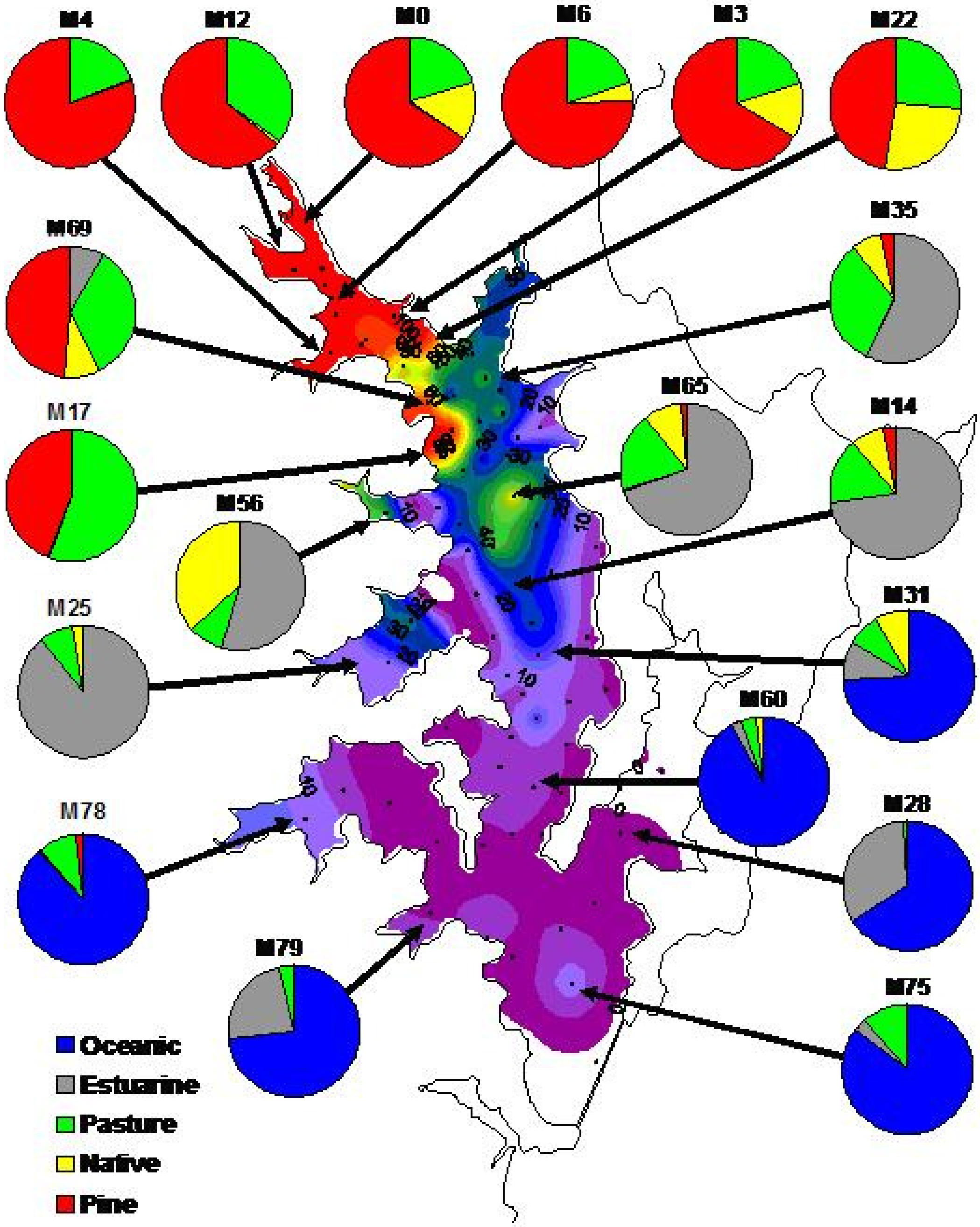
Sediments in the upper Mahurangi Harbour appeared to be entirely derived from the catchment soils (base map, Fig. 13) and most of the surficial sediment in that part of the harbour was derived from exotic pine forest (Fig.13). At most sampling locations in the upper harbour, the pine forest soil component was more than 45% of the harbour sediment, with some sites having up to 80% pine forest soil. The down-harbour extent of the pine forest soil dominance coincided with the seawards edge of the river delta zone which has a large deposition zone on the true right of the estuarine channel. Soil derived from pasture was also a major component (20-55%) in the upper harbour sediments while the native forest soil component rarely exceeded 30%. Whereas the pine forest soil component became minimal down-harbour from the river delta zone, the pasture soil component was present throughout the harbour at up to 20% of the harbour sediments.

This distribution pattern is consistent with earlier modelling (Stroud & Cooper 1997) where the Mahurangi River drainage basin half of the catchment contributed about 30% of the total sediment to the harbour. Assuming 30% of the total sediment load entering the harbour via the Mahurangi River, the up to 80% pine forest soil content of the river delta zone represents <25% of the sediment load on the harbour as a whole. This implies that pasture and native forest land-uses contribute the remaining 75% of the sediment with most of that entering the harbour from the small sub-catchments along the sides of the harbour towards the harbour entrance.

[1] Values used are calculated from the statistical means of the range of feasible proportions produced by the IsoSource model corrected for concentration. The range from the IsoSource model is not given.

Figure No 13

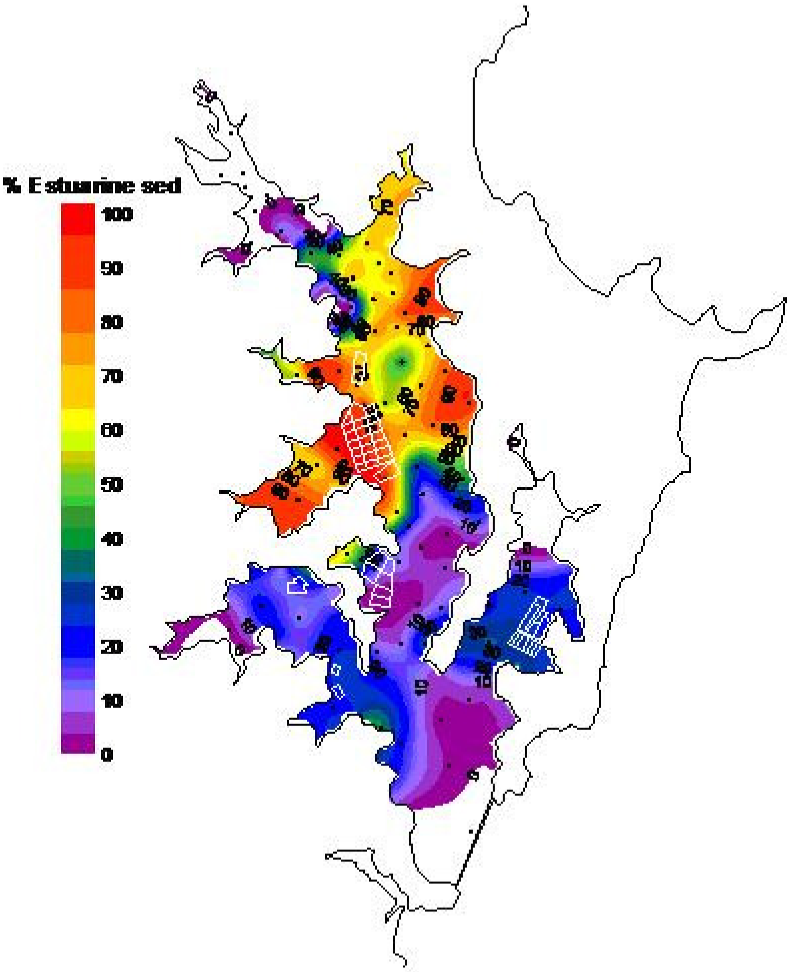
Comparative contribution of the each general source to the sediments at selected locations in Mahurangi Harbour as at December 2005. The Base map used is the spatial distribution of terrigenous soil (Fig. 8A).



Sediment influenced by 'estuarine' processes was the dominant component of the sediments throughout the middle reaches of the harbour and, as previously noted, the largest proportional contributions (up to 100%) coincided with the presence of oyster farms near Dyer's Creek, but not further down the harbour (Fig. 14).

Figure No 14

Positions of oyster farms (white boxes) relative to the spatial distribution of sediment influenced by estuarine processes in Mahurangi Harbour as at December 2005.



Pasture and native-forest soils were the major catchment components of the sediments through the middle reaches with soil inputs from the side arms as well as transport down the main channel. For example the sediment at the head of Cowen' Bay had almost 40% native forest soil, consistent with the large blocks of native forest reserve in this catchment, but no exotic pine forest soil, even though low levels of exotic pine forest were present in the sediments of the main channel down-harbour from Cowen's Bay. This indicates that sediment moving down the main channel of the harbour was unlikely to be deposited in that side arm and is consistent with the earlier modelling (Stroud & Cooper 1997).

Pasture soil was also found at the head of most side arms consistent with local inputs rather than deposition from the main channel. Further confirmation of the local soil inputs was found in Pukapuka Inlet where a small amount of exotic pine forest soil was found adjacent to an area of exotic pine forest at the head of that inlet.

In the lower harbour, the sediments were dominated by oceanic or coastal sediments. These sediments also had low levels of pasture and native forest soil present with about 10% pasture soil in the sediments in the bottom of the deep trench near the harbour entrance. Although not the largest sediment component, estuarine influenced sediment was a major component of the sediments (up to 30%) near the oyster farms at the entrance to Pukapuka Inlet and adjacent to the oyster farm in Te Kapa Inlet.

A summary of the proportional contribution of soil sources (Table 1) based on the mean feasible proportions estimated from the IsoSource model corrected for concentration (Appendix Table A3c for full data) is divided into upper, middle, and lower harbour, i.e., the river delta and deposition zone landwards of Dawson's Creek to landwards side of the entrance to Cowen's Bay is called upper harbour, from there seawards to Grant's Island and the landwards side of the entrance to Browne's Bay is called middle harbour, and from there to the sea is called lower harbour. This summary shows that while there is a large degree of variability between locations across the sediments in the channel and side arms in these divisions (ranges), there is an overall consistency with the mean proportions of terrigenous sources decreasing down harbour while the mean proportions of oceanic sediment increased towards the sea from the middle harbour division. The estuarine influenced sediment had highest proportions in the middle harbour division with less in the upper and lower harbour divisions.

Table No. 1

Summary of the proportional contribution (%) of soil sources to the sediments in the upper middle, and lower harbour, including side arms and embayments. These data are means (range) values across the whole harbour in each division. Upper harbour is the Mahurangi River delta zone and is essentially the input from the half of the catchment drained by the river.

Harbour division	Pasture	Native	Pine	Estuarine*	Oceanic
Upper Harbour	19.1	14.3	46.4	20.3	<1
	(<1 to 55.6)	0.2 to 51.4)	(1.7 to 80.4)	(<1 to 77.4)	<1
Middle Harbour	8.3	10.6	1.3	77.9	1.9
	(<1 to 40.6)	(<1 to 37.0)	(<1 to 9.0)	(23.2 to 100)	(<1 to 47.6)
Lower Harbour	2.3	1.6	0.1	18.0	77.7
	(<1 to 11.4)	(<1 to 12)	(<1 to 1.7)	(<1 to 61.3)	(38.2 to 100)

5 Discussion

The CSI method for tracing sediment sources has been developed over a number of years. The initial concept for using the isotopic signatures of organic biomarkers was based on the forensic application of stable isotopes in other fields. These include archaeology where CSI values of fatty acids and other naturally occurring biomarkers extracted from soil horizons have been used to evaluate early climate and land use, and palaeodietary studies where CSI values of fatty acids extracted from pottery shards have been used to determine whether early humans in certain areas were nomadic hunter-gatherers or crop-raising farmers resident in that area, and whether their diet included meat, grain and fish.

Since this CSI method was first tested, a number of other workers have also been investigating organic biomarkers. A recent study (Banowetz et al. 2006) found that the use of fatty acids as biomarkers for soils from different crop-lands held promise for identifying the sources of soil in surface waters. The limitation was that the fatty acids where decomposed within 1 to 2 weeks and then the signal was lost. In contrast to using just the fatty acids, the CSIs of the fatty acids can be detected to a much lower concentration. Decomposition of a fatty acid produces new compounds which are not included in the analysis of the original fatty acid and thus the CSI value does not change even though the concentration of the fatty acid decreases.

As demonstrated by the archaeological studies, fatty acids bound to soil can be stable for many thousands of years. In the aquatic environment, this longevity may be reduced but by how much is unknown.

5.1 Method improvement

The fact of decomposition affects the conservation of mass when calculating the proportion of soil from a source. The original method for determining and apportioning sources of catchment soil in harbour sediments (Gibbs 2005a) incorporated a conservation of mass constraint using %C in the IsoSource modelling as a single step. This worked for laboratory prepared mixtures and for sediments in the deposition zone close to the Mahurangi River mouth where catchment soils were recently deposited. However, applied to sediments further away from the river mouth, IsoSource could not accommodate the loss of carbon through dilution, dispersion and decomposition processes. Because loss of carbon through these processes does not change the isotopic signatures of the organic compounds used as tracers, excluding the mass constraint from the IsoSource modelling did not prevent identification of the soil sources by the isotopic balance in the sediment mixture. However, removing the mass constraint from the modelling step means that the source apportionment was now based only on the carbon in each source soil. To determine the proportion of source soil required to contribute that amount of isotope to the sediment mixture, the IsoSource results were scaled according to the relative proportion of carbon in each soil source (Equation 1).

Because the %C of the sediment is not required for the isotopic balance or the scaling of the sources, this refinement improves the method by making it independent of dilution or decomposition processes in the harbour sediments.

5.2 Source soil distribution

The data from this study show that terrigenous material from the catchment is entering the Mahurangi Harbour via the Mahurangi River and the side arms. Material entering via the Mahurangi River appears to accumulate in the upper harbour upstream of Hamilton's Landing on the left bank and downstream as far as Cowen's Bay on the right bank. This deposition pattern is consistent with a river delta zone where the inflow velocity decreases as the cross-sectional area of the estuary increases and freshwater mixes with estuarine water and flocculation would most likely occur. Within this delta zone, material of marine origin was not found and the sediment was comprised entirely of soil which came from pasture, native forest, and exotic pine forest land use within the catchment.

The CSI method indicated that the highest proportion of this soil, 45 - 80%, originated from exotic pine forest while 15 – 55% of soil originated from pasture. Up to 40% of the soil originated from native forest sources at a few locations but, generally <10% of the soil came from this source.

Downstream from the river delta zone, the expectation would be for the terrigenous soils to be gradually dispersed and re-distributed down the harbour as they are resuspended by wave and tidal action. Some of this material could become permanently incorporated into the sediments throughout the harbour without change, during sediment reworking by tidal currents, bioturbation, and trapping by mangroves, and some could be transported out of the harbour on the ebb tide and during flood events. The remainder is likely to be influenced by estuarine processes including ingestion and excretion by suspension feeders, or be degraded and transformed by microbial processes of decomposition and biological uptake of the nutrients released.

Consistent with these general processes, downstream of the river delta zone the harbour sediments took on the isotopic characteristics of marine sediments but with CSI signatures that indicated a greater estuarine influence in the middle reaches of the harbour, compared with CSI signatures that reflected oceanic or coastal influences closer to the harbour entrance.

The source of this estuarine influence in the middle reaches of the harbour is not certain. While the strongest influence coincided with the oyster farms around the entrance to Dyer's Creek (Fig. 14) and thus might have been attributed to biodeposits from the oysters, the influence also extended to areas without oyster farms and conversely only occurred at lower levels (<30%) around oyster farms further down the harbour. Although this does not exclude shellfish (i.e., oyster, cockle, horse mussel) biodeposits from being part of the source, it suggests that this CSI signature may be coming from biological production within the harbour.

For example, the area of highest estuarine influence is also an area of shallow intertidal muddy sand flats. Such areas can support a high level of benthic algal production using atmospheric CO_2 and the nutrients released from the sediments (Gibbs et al. 2005b) and excreted by macro-benthos, including shellfish. Organic carbon from the soil can also be processed through the benthic foodweb into new biomass (van Oevelen et al. 2006) which will have a new isotopic signature. As algae are plants, and the CSI method assumes that all plants produce a similar range of fatty acids but with different isotopic values according to the way they grow, it is feasible that benthic algae are producing the isotopically enriched fatty acids measured. There may be other explanations also and it would require further study to resolve this issue.

For the purposes of this study, however, the estuarine influence can be considered to be an indication of sediment "originating" from the middle reaches of the harbour rather than coming directly from the catchment or coastal waters. However, the caveat is that biological production within the harbour implies recycling of the sediment nutrients and thus these may include the breakdown of organic matter originating from either the catchment or the coastal waters.

For most of its history the harbour filled with clay-rich mud ("Mahurangi Mud" - Swales et al. 1997). It is only since catchment deforestation that this has been capped by sandy mud about 0.4 m thick seawards of Hamilton's Landing and up to 3 m or more thick upstream of Hamilton's Landing. This means that the bulk of the sediment in the harbour is most likely catchment soil that has been recycled within the estuary. As recycling takes time and the SAR seawards of Hamilton's Landing was estimated to be about 2–4 mm y^{-1}, it is consistent to see low levels of present day catchment soils mixed in with the older recycled soils through the main body of the harbour.

The apparent reduction in the amount of recent catchment soil in the sediments down the harbour is likely to be a function of dilution with older recycled sediments, exchange with coastal sediments, and decomposition. The rate of breakdown and the residence time of sediment within this zone of the harbour is unknown. Since only surficial sediments were analysed all of these factors will be dependent on the period of time since the last substantial catchment soil erosion event prior to sampling and the vertical mixing rate of sediment through bioturbation at the sampling location.

5.3 Sediment proportion interpretation

The proportions of source soils estimated in the harbour sediments at each location do not indicate the rate of deposition of each source. Consequently, these relative proportions are not an indication of how much sediment is entering the harbour from the side arms versus the Mahurangi River. For example, the relatively high proportion (40%) of native forest soil in the sediment at the head of Cowen's Bay does not imply that this is the major source of native forest sediment as there may have been only a few kg of soil deposited in this arm. In contrast, the relatively low proportion (~10%) of native forest soil in the sediments near the Mahurangi River inflow may have been associated with several tonnes of catchment soil delivered by the river and thus constitutes a much larger input of soil from that land use in the catchment at that time.

To convert the source proportions into the mass of soil from each source requires knowledge of the mass of sediment deposited at each location within a specified period of time.

5.4 Relative proportions of main sources

Given that the Mahurangi catchment has three main land use types, pasture (70%), native forest (20%) and exotic pine forest (8%), a reasonable expectation might be to see catchment soil in the harbour sediments in similar relative proportions to these catchment areas[2]. Because these proportions were not seen indicates that factors other than % area of the catchment are more important in controlling soil erosion and runoff. Such factors will include local intensity of rainfall, the slope of the land, and the amount of stable vegetative cover relative to bare land at the time of rainfall events (Phillips et al. 2005; Marden & Rowan 1995; Marden et al. 2006).

The catchment soil entering the Mahurangi Harbour via the Mahurangi River tends to accumulate in the sediments of the river delta and should reflect the relative proportions of soil being lost from the catchment before estuarine processes rework them and disperse or redistribute them further down the harbour. This and the previous two studies (Gibbs 2004, 2005a) have consistently found that exotic pine forest soil is the largest contributor of soil to the sediments in the river delta zone of the upper harbour. The pilot study (Gibbs 2004) found around 50-54% of the soil was of exotic pine forest origin at one site on the open mudflat opposite Hamilton's Landing. The method refinement study (Gibbs 2005a) found variable proportions ranging from 60% to 90% in the same area and 30% to 80% within the root trapping-zone of the fringing mangroves on both sides of the harbour in that area. In this study, the amount of soil derived from exotic pine forest in the river delta zone ranged from 30% to 80% spatially across these mudflats, with 45% to 80% on the right bank from the river mouth to the downstream end of the river delta zone.

The consistency of these findings with earlier estimates lends credibility to the levels found and highlights the disproportionately large contribution of soil to the harbour from the small area of exotic pine forest in the catchment.

The modelling by Stroud and Cooper (1997) indicates that about half of the total Mahurangi Harbour catchment is drained via the Mahurangi River and contributes about 30% of the total sediment load to the harbour. The remaining half of the catchment consists of small sub-catchments along both sides of the Harbour from the river to the sea. In combination these contribute up to 70% of the sediment load to the harbour.

Assuming that the modelled 30% sediment load from the Mahurangi River half of the harbour catchment is correct, then pine forest is contributing up to 25% of the total sediment load on the whole harbour from about 8% of the catchment area.

It is not within the scope of this study to determine why there is a disproportionately large proportion exotic pine forest soil being delivered to the harbour via the Mahurangi

[2] Relative proportions of catchment land use are approximations only

River. However, studies by other workers (e.g., Phillips et al. 2005; Marden et al. 2006) suggest that this may be associated with forestry practice during harvesting of production forest. For example, the majority of the pine plantations in the Mahurangi catchment are located around Dome Hill to the north, and Moir's Hill to the west, on the left and right branches of the Mahurangi River respectively. Whereas soil from Dome Hill was present in the harbour sediments adjacent to Hamilton's Landing in an earlier study (Gibbs 2005a), the proportional contribution was minimal on this occasion and the majority of the pine forest soil appeared to come from Moir's Hill. This is consistent with recent forestry logging operations on Moir's Hill about 2 weeks before the harbour sediment sampling began.

5.5 Sediment load estimates

The calculations in this section rely on the outputs of computer models from other workers. They are included in this report to put the proportional contribution of different sediment sources into a catchment based context.

From the average daily sediment loads on the harbour between 1994 and 2002 (Table 2, Stroud 2003), for about 330 days of the year the predicted sediment load on the harbour from the whole catchment was <1 t d^{-1}. For a 1 t d^{-1} sediment load, using the 30% sediment load factor from the Mahurangi River catchment and assuming the upper harbour catchment division (Table 1) represents the average proportions of source soils entering the harbour via the Mahurangi River, this suggests an average sediment load of about 140 kg d^{-1} from pine forest, about 42 kg d^{-1} from native forest, and about 58 kg d^{-1} from pasture on the upper harbour. The remaining 760 kg d^{-1} come from pasture and native forest from the sub-catchments along the sides of the harbour.

The average sediment load on the whole harbour of 140 kg d^{-1} from pine forest is 14% of the average daily sediment load from the whole catchment under low flow conditions and is much closer to the areal proportion of catchment under pine forest cultivation (~8%). However, while this may be close to the areal proportion of pine forest in the catchment, that sediment is mostly deposited on the river delta in the upper harbour where is it is a locally disproportionately large part of the sediment. This sediment load equates to 46.2 t over the 330 days of low flow.

Under storm events, the sediment load from pine forest will increase, as will the sediment loads from the other land use areas. Events with a return time of 0.25 and 0.5 times per year (Stroud 2003) would occur on average for 3.3 and 1.8 days per year and deliver 3000 and 6000 t d^{-1} of sediment, respectively. A proportional increase from all catchments during such events would see the soil contribution from pine forest increase more than 60-fold to a total of about 3000 t and the combined total sediment load from native forest and pasture would be around 22000 t from the whole catchment.

This demonstrates that the majority of the sediment is deposited from a few events during the year. It also implies the high level of turbidity throughout the harbour is associated with wind-wave mixing across the shallow and intertidal zones.

The concept of a proportional increase in sediment load from all catchments during a storm event is unlikely and relative sediment loadings will change dependent on factors such as local rainfall intensity, soil moisture, land slope, and the proportion of bare soil exposed through tillage, cropping or harvest. Clear felling of pine forest at harvest can produce very large sediment loads during storm events and the clear felled areas can continue to produce high sediment loads for several years after harvest (Phillips et al. 2005; Marden et al. 2006).

Further studies of sediment transport from different land-use sub-catchments would be required to quantify the actual sediment loads from each source during storm events.

6 Conclusions

- Soil eroded from the Mahurangi catchment is being deposited in the harbour via the Mahurangi River inflow and from the smaller sub-catchments along the sides of the harbour between the Mahurangi River and the harbour entrance.
- The major sources of sediment are pasture, native forest, and exotic pine forest.
- The CSI sediment tracing technique determined that there was a disproportionately large contribution of exotic pine forest soil in the sediments (up to 80%) in the river delta zone in the upper harbour.
- Evaluation of these proportions relative to the modelled sediment loads show that, under normal weather conditions, the estimated sediment load from pine forest was about 14% of the total sediment load on the harbour from a land use area of about 8% of the catchment. This is almost twice the average.
- Modelling (Stroud 2003) showed that there were, on average, 330 days per year of normal weather which produced <1 t d^{-1} of sediment. Extrapolating from this with average proportions of source soil contributions, these "normal" conditions were estimated to produce about 46.2 t and 283.8 t of sediment from pine forest and pasture plus native forest, respectively.
- The sediment load from storm events with a return period of 3 and 6 months was estimated to be about 3000 t and 22,000 t from pine forest and pasture plus native forest, respectively. This assumes a linear proportionality for sediment loads from each land use type with increasing rainfall.
- This shows that most of the sediment load on Mahurangi Harbour is delivered in a small number of storm events each year.
- If forest harvesting on steep land exposes bare soil to a storm event, it is likely that the proportions of sediment from pine forestry will increase dramatically.

Based on the modelling data estimates, the bottom line is that, while pine forest appears to contribute higher than expected sediment loads (about twice the average) and also produces some locally high concentrations in the upper harbour, most of the sediment load comes from pasture and native forest in the small sub-catchments along the sides of the harbour between the Mahurangi River and the harbour entrance.

The mapping of recent sediment sources in the Mahurangi Harbour sediments is a 'best estimate' based on the composition of surficial sediments collected around December 2005 and presents a "snap shot" of the source distribution in the harbour at that time. Storm events, including floods, and seasonal changes in land use are likely to change the relative proportions of each source at any particular location in the harbour.

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9 Appendix 1

Table No. A1a

Site information for harbour samples. Key: **Flats**: **SO** (Sandflat open), **MO** (Mudflat open), **S** (Sticky), **G** (Gloopy), **C** (Channel edge), **SB** (Shellbank), **PM** (Prostrate mangroves). **Channel**: **IT** (Intertidal), **ST** (Subtidal). Hardness = approximate penetration depth (cm). All samples collected between 29 November and 20 December 2005.

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M0	2662119	6530148	Furthest north	Channel			Channel centre, primary sample
M1	2662656	6529237	Mid mangrove	PM	3cm		150m from channel, 50m from side channel, 1cm thick fresh deposition layer
M2	2662840	6528716	Inside corner of channel bank	Channel		Few small *Theora lubrica* and thin tube worms	5m from north bank inside of channel bend
M3	2663173	6529001	Mangroves by Hamilton's Landing	PM, S	1-2cm		Part farmland, part native40m from side channel, 300m from main channel
M4	2662407	6528556	Mid mangrove	PM, above root mat very gloopy	2cm		300m from main channel, 100m from side channel, 1cm fresh deposition, farmland to west and north
M6	2662479	6529022	Mangrove flats	Mangroves, sticky mud, firm in mangroves	1-2cm		Surrounded by farm
M7	2662339	6529369	Mid mangrove, 30m from channel	Mangroves	Hard		Inland from point in mangroves, 10m into sample lower mangrove forest
M8	2662414	6529212	Mid channel, shelving	Channel, G	Soft	Cockles	20m from north bank, gentle shelving channel bank on inside of channel bend
M9	2662779	6528656	Channel edge flat	Flats, S	30-40cm		Channel edge flats, sticky
M10	2663371	6525326	Approx. 40m from large mangrove fringe, Dyers Creek	PM	2cm		
M11	2662303	6529566	Channel edge, waist deep	C	Soft		Inside bend of channel, dotted mangroves poking through opposite , part of channel marker
M12	2661970	6529545	Mid mangrove	Mangroves	Hard		30m from lower channel

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M13	2663659	6525555	Taken at Dyers MarEco site	MO	0.5cm	*Macomona,* Cockles, *Nucula,* Chiton, *Zeacumantus*	Very sandy
M14	2664645	6525765	Middle of channel, NE of Dyers Creek	Channel	6-7cm	Worms, *Theora lubrica*, isopods, worm tubes	Shell hash, sediments fluffy, large holes
M15	2665058	6525908	500m north of Grant's Island	Channel	8cm	A few *Nucula*	Lots of shell hash
M16	2664200	6527728	Harbour surrounded by water north of Cowan's Bay	Channel, G	6cm		Southwest of port channel marker, mid harbour, shell hash
M17	2663868	6527620	Middle of prostrate mangroves, 100m approx. from inner edge of larger ones, off north head of bay north of Cowans	PM	4cm		Brown surface
M18	2664164	6525639	100m inside farm in middle of Dyers	Channel	12cm	*Theora lubrica, Cominella adspersum*, tube worms, juv. *Macomona*, polychaetes.	
M19	2663280	6528405	Under large mangroves on channel edge	Large mangroves, no mat, S	1cm	Oysters	Under large mangroves, south side of channel, mud ripples
M22	2663485	6528668	Mangroves by Hamilton's Landing	PM, S	1cm		All native, 15m in from side channel, 125m from main channel
M24	2664530	6524661	Bays in between Dyeres and Brownes	ST flats	5cm	Tube worms, polychaetes	Gloopy
M25	2663098	6524819	Upper Dyers, near the most inland mangrove edge	C	15cm	Crab	Very sticky and claggy
M26	2664060	6526176	Bradley Point	Channel	7cm	1 *Nucula,* tube worms	Pseudo faeces
M27	2665894	6523295	Tekapa Inlet, MarEco site	SO/MO	1-2cm	Lots of *Austrovenus, Cominella, Nucula, Macomona*, some small worms	
M28	2665885	6522759	Tekapa Inlet mouth	Channel	8cm	Worm casts, polychaetes, baby scallops, olive shells	

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M29	2663694	6528386	True left edge of channel	C	Soft, 8cm	Oyster beds	Channel edge, gentle slope, below pneumatophores zone
M30	2665243	6523829	South of Grant's Island, East of channel	Channel	7-8cm	*Austrovenus, Nucula*, olive shell, polychaetes	Shell hash
M31	2664902	6524909	Mid-channel, west of Grant's Island	Channel	7-8cm	Some worm cases, worms, polychaetes, possibly *Atrina*	Shell hash
M32	2665240	6526676	Directly east of Cowans	Channel	16cm	*Nucula, Theora lubrica,* tube worms, polychaetes, unidentified spp. (bottled)	Gloopy, no shell hash
M33	2664109	6528552	Waist deep in middle of gut	MO at low tide	Soft, 7cm		Fine sediment, surrounded by native bush and mangroves
M35	2664270	6528257	South of Dawson's mouth	MO, IT	18cm	*Alphius* holes, dog cockle?, tube worms, *Theora lubrica*	
M36	2664874	6524137	Mid-channel, just north of Brownes Bay	Channel	7-8cm	Crab, polychaetes, *Nucula*	
M37	2664570	6523913	Northern mouth point of Brownes Bay	Channel	8-9cm	Lots of *Atrina* on bottom, crab, worms, worm casts	Shell hash
M38	2664939	6522734	North of Scott's Landing	Channel (bay)	10cm	*Atrina*	In boat mooring area, 50m from land, fine, soft sediment
M39	2663688	6522649	Near mouth of Pukapuka inlet	Channel	3-4cm	*Nucula, Cominella, Macomona,* polychaetes, tube worm casts	Some shell hash, gloopy and gritty
M40	2664005	6527143	Just north of Cowans Bay mouth	PM (very)	2cm	*Halicae, Amphibola, Alphius*	Thick and sticky, dense, surface cracked, high clay content
M41	2664225	6527270	Harbour off mangrove point	Channel, G, gritty, sandy, lumpy	6cm		Large depositional area at head of harbour, high in moisture, 1.5m water depth, 100m off mangroves, near end of oyster farms
M42	2664655	6527536	Harbour off hill with 2 horses	Channel, G, gritty, sandy, lumpy	6cm	Tube worms	Large depositional area at head of harbour, 1.5m water depth, 250m off mangroves, shell hash
M43	2663953	6526482	Taken at MarEco, Cowans Bay southern mouth	Channel	8cm	1 *Nucula,* tube worms, unknown crab	Shell hash

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M44	2664609	6526820	Middle of harbour channel opposite Cowans mouth	Channel	7cm	*Alpheus* holes, *Nucula* worms	Soft, muddy, shell hash, sandy with mud on surface
M45	2664823	6525291	Just NW of Grant's Island	Channel	12cm	*Theora lubrica,* some crab holes?	Very fluffy and gloopy
M46	2663696	6526691	Centre of mouth of Cowans Bay	Intertidal sandflat	0.5cm	*Austravenus*, *Macamona* shells?	Lots of shell hash, sandy sediment
M47	2663370	6526645	Middle of Cowans Bay	Intertidal mudflat	9cm	*Alpheus* and *Helice* holes, worms	Some shell hash, sediment very soft
M48	2665485	6525118	Inshore from Grant's Island	SO	4cm	Loads of worms*, Nucula*	
M49	2664985	6257056	Eastern side of channel, NE of Cowans	Channel	22cm	Flounder tracks, *Alphius* holes, tube worms, *Theora lubrica*	
M50	2664926	6527655	Harbour off hill with 2 horses, but closer	Channel, G	8cm	Tube worms	100m from mangrove gut
M51	2664240	6522608	West of Scott's Landing	Channel	3cm	Shell hash, olive shells, worm casts, *Atrina*	Gritty
M52	2664584	6522737	Mid harbour, 200m north of Scott's Landing	Channel	3cm	Very little life, shell hash, worm casts	Muddy sand
M53	2664468	6527825	Harbour off hill further north	Channel, G	6cm	Tube worms	150m offshore, 100m from port channel marker
M54	2665592	6526218	MarEco MH2	Channel	1cm	*Macamona liliana, Nucula* (many)*, Zeacumantus*, juv. *Nucula*	Shell hash
M55	2664528	6527319	Mid -channel, north of Cowans Bay	Channel	7cm	*Alphius* holes, *Cominella, Nucula*	Gloopy, shell hash
M56	2663071	6526618	Mangroves Cowans Bay	Larger PM	5cm		Loose fibrous mat, thicker layer above root mat
M57	2664364	6525118	South mouth poing of Dyers Creek	ST flats	20cm	*Cominella, Theora lubrica*	
M58	2665270	6524341	SE of Grant's Is., by the mooring	Channel	10cm	*Boccocardia,* tube worm casts, olive shell	
M59	2664442	6523554	Brownes Bay mouth, 30m from oyster forms	Channel	7cm	Worm casts, lots of polychaetes & worms, *Atrina* & sponges on surface	Shell hash

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M60	2664842	6523316	Mid harbour 400m north of Scott's Landing	Channel	3cm	Sponges, tube worms, worm casts, shell hash	Muddy sand
M61	2665172	6523240	South of Burton Wells rescue	Channel		No *Atrina,* seaweed	Shell hash, soft sediment, hole
M62	2666384	6523496	Tekapa, deep in inlet	Channel	6cm	A few worms, polychaetes, worm casts	Gloopy
M63	2663799	6524028	Brownes Bay upper, 10m from mangrove edge	Flats	7cm		Shell hash, gloopy
M64	2664436	6528103	HL Mar Eco site	Mudflat open	12cm	Lots of *Alpheus* holes, lots of worms	
M65	2664877	6526470	Middle of harbour channel opposite southern head of Cowans Bay	Channel	2.5cm	Lots of *Nucula,* worms	shell hash
M66	2664365	6526209	Between southern head of Cowans and M65 in channel	Channel	19cm	*Alpheus, Theora lubrica,* 1 large worm	Surface undulated, little shell hash
M67	2664706	6524434	Just around the point N of Brownes Bay, but N of 36 & 37	Channel		Worms, *Theora lubrica*, worm casts, polychaetes	
M68	2665718	6524491	In the bay under the large white mansion	Flats	2cm	*Nucula*, worm casts	Shell hash
M69	2663570	6527958	Mid mangrove	PM, S	1cm		PM some south, pasture to west, pine
M70	2663806	6528011	Harbour opposite Dawson's Creek	Channel, G	6cm	Tiny cockles, worms	Large depositional area at head of harbour, 1.5m water depth
M71	2663894	6528037	Harbour opposite Dawson's Creek, closer to true left	Channel, G	6cm		Large depositional area at head of harbour, 1.5m water depth
M73	2666563	6520898	Open coast reference site	Channel	Hard, solid sand		Black sand, shell hash
M74	2665166	6521611	Just south of Casnell Island	Channel	6cm	Horse mussel bed (*Atrina*), worm casts, tube worms	Sandy, shell hash

Sample code	Easting	Northing	Sublocation	Habitat description	Hardness (cm)	Organisms	Comments
M75	2665300	6520946	Mid bay Te Kapa	Channel, sandy mud	3cm, excess water mixed in	Heart urchin, tube worms, polychaete, small fragile bivalue, worm casts	Sandy, gritty, shell hash
M76	2663117	6523118	Middle of Pukapuka inlet	Channel	3cm	*Nucula,* polychaetes, *Cominella* sp., *Macomona*	Gloopy
M77	2662554	6523273	Upper Pukapuka, near channel	Channel	7-8cm	*Austrovenus,* some flounder tracks, tube worms	Very soft, a little shell hash
M78	2662101	6522924	Mid mangroves, top of Pukapuka Inlet	PM	2cm	*Amphibola, Helice crassa*	Fibrous mat, 40-50m from mangrove edge
M79	2663606	6521791	Middle of bay south of Pukapuka	Zostera 0.6m	3cm	*Zostera, Nucula, Macamona* shells	Shell hash
M80	2664293	6521508	MarEco site near houses and moorings		Hard, 0.5cm	*Atrina, Cominella, Echinocardium*, tube worms	Fine sand, just subtidal, knee deep
M81	2664592	6521269	Just in behind headland at southern mooring area		2cm	*Patiriella, Atrina,* tube worms, orange sponges, *Echinocardium*	Fine sand, 2m deep
M82	2665568	6521908	East of Casnell Island	Channel	6cm	*Atrina,* worm casts, bubble shells, *Zeacumantus*	Sandy, shell hash

Table No. A1b

Site information for source soil samples collected in December 2005. Source soils listed also include samples collected in March 2005 for an earlier study

Sample	Easting	Northing	Sublocation	Habitat description	Hardness	Comments
Dec-05						
ML0	2661448	6523830	Perkinson's Farm	Long grass, not heavily grazed, flowers,	Hard	80m from stream surrounded by scrub
ML1	2662167	6526053	Rodney District Council Bush	Ephemeral streambed, in native bush		
ML3	2655580	6524525	Moirs Hill Rd	Forestry, not felled, trees 3-5m tall, valley near staging	Hard and sl. Moist	Lots of turned soil at staging. Lots of undergrowth, grasses, etc about 1.8m tall.
ML4	2656916	6524139	Moirs Hill Rd	Forestry, clear felled within last 2 weeks.	Hard and dry	About 50m from top of catchment, were mature trees, crew working about 300m away, samples taken from cutting on hillside, about 150mm below surface.
ML7	2655412	6536609	Dome Hill	Emphemeral streambed, in native bush	Claggy	Lots of supplejack and Taniwha weed
Mar-05						
PTR	2658490	6528350	Thompson Rd	Rolling hill-side pasture	Firm black loam	Regrowth after hay cropping
PCR	2656710	6531670	Carran Rd	Flat flood-plain near stream	Hard stoney black loam	Stock grazed area
PPR	2656250	6533580	Phillips Rd	Flat flood-plain near stream	sandy clay loam	Stock grazing area
NDH	2656410	6536390	Dome Hill	Ephemeral streambed in steep native forest	Hard and dry	Nikau, Rimu, Titoke plus small native understorey (above cutover pine)
NMH	2652870	6526740	Moir's Hill	Ephemeral streambed in steep native forest	Soft and moist	Nikau, Rimu, Titoke, Taraire plus small native understorey. (In pine forest block)
NCBR	2660310	6526590	Cowan Bay Rd	Steep native forest	Hard and dry	Kauri, Rimu, Tanekaha, Titoke with Kanuka edge (Block by pastured land)
EDH1	2656640	6536280	Dome Hill (far)	Steep undisturbed production forest	Hard and dry	Tall pines with native understorey, on ridge above clearfelled pine. Wild ginger rampant in clearfelled area

Sample	Easting	Northing	Sublocation	Habitat description	Hardness	Comments
Dec-05						
EDH2	2656200	6535750	Dome Hill (near)	Moderate slope clearfelled production forest	Hard and dry	Recent clearfelled pine with pine debris lying on dry ground (ginger present)
EMH	2652970	6527110	Moir's Hill	Steep undisturbed production forest	Hard and dry	Tall pines about to be cut, native understorey (surface soil only)
EMHF	2652970	6527090	Moir's Hill frit	Steep cut face by active logging	crumbly dry clay	Subsoil exposed by log-hauler. Clearfelled previous week.

10 Appendix 2

Table No A2a

Analytical data for Mahurangi Harbour samples collected between 29 November and 20 December 2005.

Sample code	Moisture (%)	Organic (% DW)	Carbon (%)	Nitrogen (%)	%C of Organic	%N of Organic	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
M0	55.5	11.5	2.5	0.2	22.1	1.8	-25.9	4.5
M1	62.4	9.4	2.7	0.2	29.2	2.6	-25.0	5.0
M2	59.5	10.1	2.6	0.2	25.6	2.2	-25.3	4.8
M3	72.7	12.3	4.1	0.4	32.9	3.1	-25.2	5.0
M4	67.9	23.2	4.2	0.4	18.0	1.7	-25.5	4.8
M6	61.5	14.5	3.0	0.3	20.9	2.0	-24.9	5.1
M7	66.3	10.1	3.0	0.3	29.5	2.7	-24.9	5.0
M8	46.6	6.6	1.5	0.1	23.5	2.1	-25.4	5.3
M9	58.0	9.5	2.6	0.2	27.4	2.6	-24.7	5.3
M10	63.6	8.8	2.9	0.2	33.3	2.8	-24.6	5.1
M11	52.4	6.6	1.7	0.1	25.3	2.2	-25.2	5.0
M12	65.6	10.4	2.9	0.3	28.0	2.5	-25.2	5.3
M13	26.3	1.3	0.2	0.0	16.4	1.8	-21.3	5.7
M14	29.9	2.9	0.6	0.1	19.1	2.0	-24.1	5.7
M15	33.9	4.0	0.6	0.1	14.2	1.5	-23.4	6.8
M16	36.0	4.5	0.9	0.1	19.1	1.9	-24.6	6.4
M17	55.8	8.0	1.6	0.2	20.3	2.0	-23.6	4.5
M18	25.4	2.1	0.4	0.0	17.1	2.0	-22.6	5.9
M19	54.3	10.3	2.7	0.3	26.6	2.6	-24.3	6.0
M22	49.7	14.4	2.4	0.2	16.8	1.5	-25.0	5.0
M24	23.5	2.8	0.3	0.0	11.0	1.2	-22.5	6.1
M25	51.4	6.9	1.5	0.2	22.1	2.2	-23.8	4.9
M26	27.3	2.3	0.4	0.0	17.1	2.0	-22.6	5.9
M27	22.5	1.5	0.2	0.0	14.0	2.2	-21.0	5.4
M28	33.0	2.4	0.5	0.1	18.9	2.3	-21.8	6.1
M29	40.0	5.1	0.9	0.1	18.5	1.8	-24.6	5.2
M30	26.8	2.6	0.4	0.0	13.6	1.6	-22.0	6.3
M31	41.4	6.0	0.9	0.1	14.8	1.6	-24.0	6.4
M32	30.3	2.4	0.5	0.1	22.6	2.4	-23.2	5.6
M33	48.6	5.9	1.3	0.1	22.0	2.2	-24.1	5.4
M35	46.4	7.2	1.4	0.1	19.1	1.8	-24.3	5.4
M36	47.5	4.7	1.0	0.1	20.7	2.3	-23.6	6.2
M37	30.0	3.6	0.5	0.1	13.7	1.5	-22.7	6.4
M38	32.9	2.6	0.5	0.1	18.4	2.2	-22.3	6.9
M39	26.9	3.0	0.3	0.0	10.5	1.0	-21.5	6.4

Sample code	Moisture (%)	Organic (% DW)	Carbon (%)	Nitrogen (%)	%C of Organic	%N of Organic	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
M40	47.8	23.9	3.8	0.4	15.9	1.5	-24.4	4.3
M41	25.1	2.1	0.4	0.0	17.5	1.7	-23.1	8.3
M42	26.7	2.6	0.4	0.1	14.9	2.0	-22.4	6.1
M43	25.4	1.5	0.4	0.0	24.1	2.9	-22.6	6.1
M44	30.3	3.2	0.4	0.0	13.5	1.4	-23.5	6.2
M45	34.3	3.1	0.7	0.1	22.7	2.1	-24.4	6.4
M46	28.2	1.8	0.2	0.0	10.4	1.3	-21.1	5.9
M47	30.3	3.0	0.5	0.1	15.7	1.7	-22.5	6.2
M48	29.3	2.4	0.4	0.0	15.6	1.9	-21.4	7.0
M49	35.8	2.8	0.7	0.1	24.0	2.8	-23.0	5.6
M50	37.8	4.7	0.7	0.1	15.2	1.7	-22.7	6.1
M51	29.0	1.9	0.4	0.1	22.2	2.7	-21.8	7.0
M52	38.2	4.5	0.6	0.1	13.8	1.6	-22.8	6.7
M53	35.1	3.3	0.8	0.1	23.6	2.4	-24.1	5.6
M54	21.7	1.2	0.2	0.0	12.5	2.0	-21.3	6.1
M55	24.6	2.0	0.3	0.0	16.4	2.0	-22.9	4.6
M56	66.3	5.7	2.4	0.2	42.3	4.3	-23.7	5.0
M57	29.4	2.6	0.5	0.1	20.4	2.0	-23.1	5.8
M58	31.9	1.4	0.5	0.1	35.2	4.2	-22.5	6.1
M59	31.4	1.1	0.5	0.1	41.7	5.0	-22.3	6.9
M60	45.3	3.7	0.9	0.1	23.6	2.8	-22.8	6.5
M61	31.6	1.8	0.5	0.1	25.2	3.1	-22.1	6.4
M62	29.5	2.4	0.5	0.1	19.8	2.6	-20.5	6.0
M63	31.2	2.1	0.5	0.1	23.6	2.8	-21.0	6.0
M64	44.7	5.8	1.0	0.1	16.8	1.8	-23.9	5.6
M65	27.9	2.6	0.3	0.0	9.9	1.3	-22.4	6.0
M66	41.3	5.4	0.9	0.1	17.3	1.6	-24.7	5.5
M67	32.2	2.7	0.5	0.1	19.9	2.2	-23.0	6.1
M68	20.8	1.6	0.2	0.0	10.6	1.5	-20.8	6.2
M69	52.2	10.7	2.6	0.2	24.1	2.3	-24.0	4.6
M70	36.6	4.4	0.8	0.1	17.7	1.9	-24.0	5.2
M71	39.6	5.8	1.2	0.1	20.2	2.0	-24.3	5.4
M73	18.7	1.0	0.1	0.0	6.0	1.1	-21.1	7.9
M74	32.7	1.7	0.5	0.1	27.6	3.6	-21.8	6.7
M75	34.6	0.9	0.5	0.1	55.4	7.9	-21.5	7.2
M76	12.8	1.5	0.3	0.0	16.6	2.2	-21.9	6.0
M77	30.0	2.6	0.5	0.1	18.3	2.2	-22.6	5.3
M78	62.6	6.3	2.4	0.2	38.0	3.4	-23.9	4.2
M79	21.1	1.3	0.2	0.0	12.4	1.8	-20.9	8.7
M80	21.4	1.5	0.1	0.0	9.9	1.6	-21.0	6.2
M81	22.4	1.1	0.2	0.0	22.6	3.3	-21.5	6.8
M82	29.8	3.0	0.4	0.0	12.3	1.6	-21.5	6.3

Table No A2b

Analytical data for source soil samples collected form Mahurangi catchment in December 2005.

Sample code	Moisture (%)	Organic (% DW)	Carbon (%)	Nitrogen (%)	%C of Organic	%N of Organic	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
ML0	29.0	15.4	5.8	0.6	37.8	3.6	-27.1	3.9
ML1	42.0	8.1	2.2	0.1	27.0	1.8	-27.7	1.2
ML3	29.2	8.7	3.0	0.2	34.5	2.3	-27.4	4.0
ML4	28.2	12.6	2.8	0.2	22.2	1.4	-26.5	6.5
ML7	41.0	9.4	2.6	0.2	27.4	2.0	-27.8	0.4

11 Appendix 3

Table No A3a

Analytical data for sources used in the IsoSource modelling and the subsequent scaling to soil contribution. The CSIs used were Oleic acid, Palmitic acid, Stearic acid, and Pentadecanoic acid plus the bulk $\delta^{13}C$ value of the sample. Missing data indicates that compound was not found in the sample above analytical detection limit. * Representative values (see section 4.2.1)

Sample Code	Location Type, general area	%C (%)	$\delta^{13}C$ (‰)	Oleic (‰)	Palmitic (‰)	Penta-dec (‰)	Stearic (‰)
Dec-05							
ML0	**Pasture**, Pukapuka Inlet	5.81	-27.10	-29.12	-29.37		-32.30
ML1	**Native**, Cowen's Bay	2.19	-27.69	-28.17	-30.37	-29.25	-30.40
ML3	**Pine** (young trees), Moir's Hill	3.01	-27.42	-27.68	-29.47	-30.31	-30.25
ML4	**Pine** (clear felled), Moir's Hill	2.79	-26.52	-28.25	-28.71	-28.47	-29.10
ML7	**Native**, Dome Hill	2.59	-27.81	-28.16	-29.46	-29.84	-29.60
M13	**Estuarine**, Dyer's Creek	1.07*	-21.32	-18.05	-16.12	-13.94	-20.07
M73	**Oceanic**, outside harbour	0.58*	-21.07	-22.35	-21.59	-18.67	-22.26
Mar-05							
PTR	**Pasture,** right branch	5.58	-22.20	-21.59	-24.03	-21.29	-26.68
PCR	**Pasture,** Left branch	7.42	-25.50	-23.39	-25.98	-28.72	-31.49
PPR	**Pasture,** Dome Hill	4.18	-26.90	-24.87	-27.97	-35.95	-28.85
NDH	**Native,** Dome Hill	8.34	-28.00	-28.67	-30.55	-30.30	-30.04
NMH	**Native,** Moir's Hill	8.61	-28.20	-28.34	-30.55	-27.66	-29.48
NCBR	**Native**, Cowen's Bay	6.32	-25.07	-27.83	-25.57	-26.91	-25.36
EDH1	**Pine** (mature trees), Dome Hill	10.67	-27.70	-28.28	-31.74	-32.28	-31.12
EDH2	**Pine** (clear felled), Dome Hill	4.39	-24.14		-27.55	-31.19	-26.05
EMH	**Pine** (mature trees), Moir's Hill	3.01	-28.70	-29.54	-32.35	-29.99	-32.11
EMHF	**Pine** (clear felled), Moir's Hill	2.79	-26.17	-25.04	-27.64		-29.64

Table No A3b

Analytical data for harbour sediment samples used in the IsoSource modelling. The CSIs used were Oleic acid, Palmitic acid, Stearic acid, and Pentadecanoic acid plus the bulk $\delta^{13}C$ value of the sample. Missing data indicates that compound was not found in the sample above analytical detection limit.

Sample Code	$\delta^{13}C$ (‰)	Oleic (‰)	Palmitic (‰)	Penta-dec (‰)	Stearic (‰)
M0	-25.86	-27.11	-29.69	-25.99	-30.19
M1	-24.95	-27.41	-28.83	-21.29	-29.42
M2	-25.28	-24.55	-27.07	-21.81	-29.12
M3	-25.22	-27.01	-28.70	-21.80	
M4	-25.54	-30.21	-29.90	-21.66	-31.46
M6	-24.89	-27.20	-26.3	-19.23	-30.88
M7	-24.90	-26.94	-26.46	-20.06	-27.50
M8	-25.37	-25.25	-28.40	-23.39	-28.64
M9	-24.66	-24.19	-22.70	-16.11	-23.45
M10	-24.55	-25.70	-25.38	-20.87	-28.39
M11	-25.22	-24.98	-24.49	-21.15	-26.66
M12	-25.20	-27.00	-28.51	-23.08	-31.17
M13	-21.32	-18.04	-16.12	-13.94	-20.07
M14	-24.11	-22.82	-23.04	-16.39	-27.90
M15	-23.36	-23.07	-19.60	-12.71	-26.89
M16	-24.56	-24.10	-22.66	-16.59	-27.12
M17	-23.64		-25.72		-27.87
M18	-22.58	-21.99	-18.14	-14.60	-24.44
M19	-24.33	-23.48	-21.87	-19.85	-26.14
M22	-24.99	-26.47	-27.42	-20.57	-28.91
M24	-22.49	-22.90	-20.14	-18.23	-23.84
M25	-23.80	-22.21	-20.92	-15.67	-24.89
M26	-22.60	-20.45	-18.24	-14.28	-24.16
M27	-20.99	-21.04	-19.64	-16.91	-22.78
M28	-21.78	-21.62	-20.57		-24.38
M29	-24.58	-24.27	-23.28	-17.68	-25.42
M30	-21.98	-23.64	-21.92	-17.14	-25.23
M31	-23.95	-24.16	-24.09	-21.18	-25.65
M32	-23.21	-21.99	-21.31	-16.97	-22.90
M33	-24.06	-22.39	-20.75	-16.93	-24.81
M35	-24.26	-23.48	-22.76	-19.01	-29.02
M36	-23.55	-25.08	-24.56	-22.29	-27.06
M37	-22.68	-23.61	-22.39	-19.78	-25.56
M38	-22.27	-21.99	-21.00	-15.87	-24.84
M39	-21.52	-21.78	-20.16	-15.90	-21.73
M40	-24.38	-25.22	-23.72		-28.63
M41	-23.13	-22.71	-21.55	-17.64	-24.51
M42	-22.43	-22.19	-18.96	-17.70	-23.65
M43	-22.60	-23.30	-22.01	-18.40	-24.36
M44	-23.51	-24.70	-24.15	-19.03	-25.44
M45	-24.41	-24.65	-24.33	-19.95	-27.39
M46	-21.11	-21.77	-18.78	-17.33	-23.61

Sample Code	$\delta^{13}C$ (‰)	Oleic (‰)	Palmitic (‰)	Penta-dec (‰)	Stearic (‰)
M47	-22.48	-20.72			-21.63
M48	-21.38	-22.39	-19.09	-14.49	-22.39
M49	-23.03	-23.32	-22.71		-25.43
M50	-22.66	-21.32	-18.10	-17.21	-22.44
M51	-21.79	-22.34	-21.23	-14.73	-23.44
M52	-22.76	-23.72	-23.28	-20.04	-25.08
M53	-24.05	-24.45	-23.79	-16.51	-27.92
M54	-21.33	-20.18	-18.05	-17.01	-22.42
M55	-22.92	-23.28	-22.47	-17.93	-24.03
M56	-23.72	-25.34	-23.70		-27.76
M57	-23.14	-20.41	-18.70	-12.03	-22.47
M58	-22.53	-24.50	-23.79	-17.83	-25.68
M59	-22.25	-24.45	-23.26	-19.09	-24.74
M60	-22.78	-24.48	-24.32	-21.77	-27.02
M61	-22.13	-22.94	-21.74	-17.31	-22.92
M62	-20.53	-23.20	-19.87	-18.06	-20.99
M63	-21.01	-19.36	-15.44		-20.80
M64	-23.90	-24.04	-21.35	-18.70	-25.98
M65	-22.44	-22.33	-22.02	-15.64	-24.02
M66	-24.73	-22.93	-24.74	-19.73	-26.48
M67	-22.97	-22.10	-22.44	-18.30	-26.08
M68	-20.80	-22.35	-21.61	-20.19	-22.19
M69	-23.96	-23.59	-23.03	-19.15	-27.07
M70	-23.99	-21.82	-20.10	-16.01	-23.23
M71	-24.34	-22.86	-21.82	-15.38	-24.67
M73	-21.07	-22.34	-21.58	-18.67	-22.26
M74	-21.75	-22.23	-22.48	-17.81	-23.46
M75	-21.54		-23.12	-19.45	-24.35
M76	-21.90	-22.34	-21.86	-19.73	-25.21
M77	-22.63	-23.38	-21.82	-19.10	-25.57
M78	-23.90	-26.44	-25.83	-20.54	-28.05
M79	-20.94		-20.26	-17.40	-23.10
M80	-20.95		-20.39	-17.29	-23.90
M81	-21.47		-21.83		
M82	-21.46	-24.24	-21.06	-16.94	-24.04

Table No A3c

Proportional (mean %) composition of harbour sediments by major land use type including the estuarine and oceanic separation of the marine sediment source component. Pasture sources are given as total pasture and as pasture from the true left and right banks of the harbour and catchment. (Values are the calculated from the statistical mean proportions of the feasible solutions from the IsoSource model output corrected for concentration. There is a range associated with each value).

Sample Code	Pasture L (Left)	Pasture-R (Right)	Pasture (Total)	Native	Pine	Estuarine	Oceanic
M0	16.4	3.9	20.3	14.07	65.6	0	0
M1	15.6	0.2	15.8	13.3	71	0	0
M2	2.4	20.7	23.1	22.1	40.2	14.6	0
M3	10.2	10	20.2	13.2	66.7	0	0
M4	6.3	13.2	19.5	0.2	80.4	0	0
M6	0	19.9	19.9	4.8	75.4	0	0
M7	13.7	5	18.7	44.4	36.9	0	0
M8	5.1	2.7	7.8	30.9	61.4	0	0
M9	0	25.4	25.4	51.4	23.2	0	0
M10	20.6	0	20.6	16.3	0	63.2	0
M11	17	0	17	24.7	58.4	0	0
M12	10.6	24.8	35.4	0.6	64	0	0
M13	0	0	0	0	0	100	0
M14	1.1	15.2	16.3	8.2	2.8	72.8	0
M15	0	10.7	10.7	4	0	85.3	0
M16	0	15.2	15.2	14.2	2.3	68.3	0
M17	48.1	7.5	55.6	0.3	44.1	0	0
M18	0.2	0.1	0.3	6.7	0.2	92.8	0
M19	7.4	0	7.4	6.1	40.7	45.9	0
M22	14.4	11.8	26.2	26.3	47.6	0	0
M24	0	0.2	0.2	9.4	0	67	23.4
M25	8.1	0	8.1	2.9	0	89.1	0
M26	1.1	4.6	5.7	0.4	0.7	93.2	0
M27	0	0	0	0	0	21.1	78.9
M28	1.4	0	1.4	0	0	33	67
M29	0.2	0	0.2	12.9	33.1	53.8	0
M30	0	0.4	0.4	3.2	0	7.1	89.4
M31	0	8.1	8.1	8.2	0	9.7	74
M32	1.6	4.2	5.8	6	4.1	84.1	0
M33	0	0	0	2.6	29.9	67.5	0
M35	0	32	32	7.5	3.3	57.2	0
M36	0	4.2	4.2	12	0	3.8	79.9
M37	0	0.8	0.8	5.2	0	13.3	80.8
M38	2.7	0	2.7	0.1	0	30.4	66.7
M39	0.1	0	0.1	1.4	0	23.9	74.6
M40	0.2	4.8	5	32.4	2.6	60.1	0
M41	2.1	0	2.1	8.5	7.2	80.2	0
M42	0.5	0.3	0.8	8.1	0.6	90.5	0
M43	11.8	0.3	12.1	13.2	2.2	72.6	0
M44	24.4	0.4	24.8	30.9	3.9	40.4	0

Sample Code	Pasture L (Left)	Pasture-R (Right)	Pasture (Total)	Native	Pine	Estuarine	Oceanic
M45	0	12.2	12.2	17	0	23.2	47.6
M46	0	2.9	2.9	5.6	0	91.5	0
M47	0	0.2	0.2	5.8	0	93.6	0
M48	0	0.3	0.3	3.6	0	46.3	49.8
M49	14.4	0.4	14.8	15.1	3.1	67	0
M50	0.4	0.3	0.7	5.4	0.5	93.5	0
M51	0.6	0	0.6	1.2	0	14.2	84.1
M52	3.9	0	3.9	0.1	0	7.3	88.8
M53	7.1	3.4	10.5	24	8.6	56.9	0
M54	0	2.3	2.3	2.4	0	95.2	0
M55	15.7	0	15.7	16.2	0.7	67.4	0
M56	8.7	0	8.7	37	0	54.4	0
M57	4	0	4	0.7	0	95.3	0
M58	0	1.1	1.1	6	0	1	80.1
M59	0	0.7	0.7	4.6	0	2.1	92.7
M60	4.2	0	4.2	1.6	0	2.2	92.1
M61	0.6	0	0.6	2.5	0	13.2	83.8
M62	0.1	0	0.1	0	0	25.9	74
M63	0	0.2	0.2	0.3	0	61.3	38.2
M64	0	10.8	10.8	18	1.7	69.6	0
M65	19.4	0	19.4	9.8	1	69.9	0
M66	39.3	1.3	40.6	0	9	50.4	0
M67	0	6	6	0.4	0	18.4	75.3
M68	0	1.6	1.6	1.9	0	16.4	80.1
M69	34.1	0	34.1	8.9	48.6	8.4	0
M70	0.1	0	0.1	6.1	16.5	77.4	0
M71	0	0.6	0.6	6.2	26.6	66.7	0
M73	0	0	0	0	0	0	100
M74	4.4	0	4.4	0	0	0.3	95.3
M75	11.4	0	11.4	0	0	3	85.6
M76	1.5	0	1.5	0.1	0	10.4	88.1
M77	0.3	0	0.3	5.8	0	22.7	71.2
M78	10	0	10	0	1.7	0.5	87.8
M79	3.7	0	3.7	0.1	0	23.2	73.1
M80	7.8	0	7.8	0	0	41.4	48.7
M80	0.1	0	0.1	0	0	20	79.9
M82	0.8	0	0.8	0	0	5.1	94.1