Table No.11

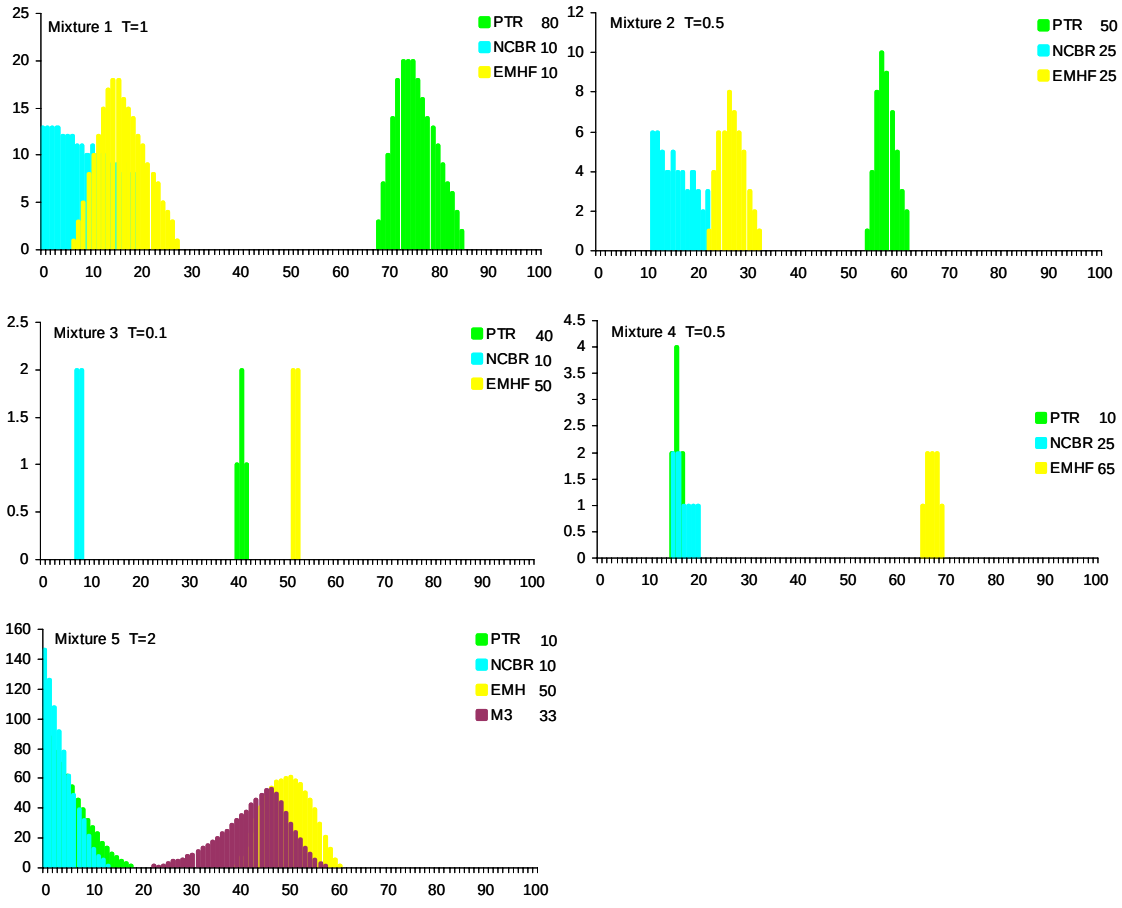
Selected mixing model predictions for the proportions of specified soil in the prepared mixtures relative to the actual mixture composition. Model outputs given ranges of feasible solutions (%) using individual and combinations of fatty acids and bulk C data from tables 4, 6, and 7A. (See Text for compound codes)

Compound	Actual	**C**	**P**	**O**	**A**	**Ab**	**PC**	**PO**	**PA**	**PAb**	**OC**	**OA**	**OAb**	**AC**	**AAb**	**AbC**	Predicted
Soils	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	average %
Mixture 1																	
PTR	80	93-98	80-92	69-74	80-84	70-75	84-92	62-88	80-90	61-82	79-83	68-83	70-74	81-91	72-74	69-82	79.3
NCBR	10	2-6	0-8	17-19	10-13	5-10	0-6	1-21	0-8	1-21	13-18	9-21	10-13	4-15	12-13	0-19	9.8
EMHF	10	0-2	8-14	9-12	5-9	18-23	9-12	8-20	9-13	11-20	0-5	0-17	14-16	0-9	14-15	6-27	10.8
Mixture 2																	
PTR	50	66-72	0-75	22-26	48-54	52-57	39-61	39-57	38-61	40-61	38-51	25-51	39-50	56-65	51-61	54-62	49.0
NCBR	25	6-14	0-48	30-34	10-14	15-20	0-13	0-14	0-13	0-13	19-36	14-35	21-29	7-13	11-15	11-22	15.9
EMHF	25	18-22	24-82	42-46	34-38	28-31	38-50	39-49	38-50	39-50	19-36	18-54	21-36	25-35	28-35	22-32	36.0
Mixture 3																	
PTR	40	54-70	0-66	16-21	48-52	38-43	38-61	0-58	0-66	0-66	38-44	19-46	28-44	52-63	36-47	40-42	39.9
NCBR	10	0-14	0-42	21-24	4-8	6-10	0-12	0-42	0-42	0-42	15-22	5-25	6-20	0-6	4-14	7-8	13.3
EMHF	50	30-42	34-88	57-61	42-46	49-54	38-50	33-88	34-88	34-88	35-45	24-68	37-61	34-42	45-54	50-52	50.1
Mixture 4																	
PTR	10	14-41	12-40	0-3	14-18	9-14	11-41	12-37	12-42	12-42	0-27	0-27	0-21	15-31	6-19	15-17	18.4
NCBR	25	0-23	0-19	27-29	15-18	19-23	0-19	0-20	0-19	0-19	9-38	9-39	10-33	10-21	15-25	15-20	16.5
EMHF	65	59-80	58-73	69-72	61-67	64-70	58-75	60-75	58-75	58-75	48-81	47-82	54-80	56-70	64-73	62-69	66.4
Mixture 5																	
PTR	10	0-11	0-7	0-5	0-12	0-18	0-12	2-11	0-11	10-18	0-33	0-9	0-18	0-6	0-18	0-18	7.3
NCBR	10	0-46	0-7	0-16	0-18	0-13	0-10	0-10	0-11	0-6	0-38	0-21	0-13	0-16	0-13	0-13	8.4
EMH	50	52-66	68-72	28-44	44-69	39-60	65-78	61-73	60-71	50-60	31-68	27-50	39-60	57-64	39-61	39-60	55.2
M3	33	0-38	24-28	52-57	22-38	22-56	17-31	20-30	20-30	22-33	9-60	42-62	22-57	21-36	22-54	22-57	33.5

The matrix of variables used for these mixing model runs was limited to 5 compounds which were present in all samples: bulk ^{13}C (C), Palmitic acid (P), Oleic acid (O), Arachidic acid (A), and Abietic acid (Ab). Other compounds used in the pilot study i.e., Behenic acid, Lignoceric acid and Linolenic acid, were either not present at detectable levels in all samples or produced unacceptably broad ranges of feasible solutions. Consequently they were not included in the final matrix of variables. Many combinations of the selected compounds were tried in the mixing model without great improvement on the more simple approach of a matrix of one or two compound combinations (Table 11). An example of a mixing model run across all mixtures using Abietic acid + bulk ^{13}C is presented in Figure 3. These plots demonstrate the effect of the changing tolerance to accommodate variability in the analytical results between sources and the 5 mixtures. As the tolerance increases, the range of feasible solutions spreads and becomes less distinct. The peak height indicates the relative probability of each solution within the range of feasible solutions produced by the model.

Figure No.3

Mixing model predictions of feasible solutions for the 5 soil mixtures using the combination of abietic acid + bulk ^{13}C. T = tolerance set at the lowest value possible to produce valid output from the mixing model. Soil names are as per Table 1. Number behind each soil name is the actual weight (g) of soil used in the mixture.



These results (Table 11) demonstrate that, while several compounds and compound mixtures provide reasonable predictions of feasible solutions for these 5 soil mixtures (i.e., Arachidic acid, Abietic acid, Oleic acid +bulk ^{13}C, Oleic acid + Arachidic acid, Abietic acid + bulk ^{13}C), no single mixing model prediction gives a perfect result. Some solutions, especially those associated with Palmitic acid in Mixture 2 and Palmitic acid in combination with Oleic, Arachidic, and Abietic acids in Mixture 3, fall outside acceptable predictions because of the broad smearing of the feasible solutions.

Overall, the results also demonstrate that where the actual proportion of a soil is low (i.e., around 10%) the mixing model tends to link the range of feasible solutions to zero. However, while the mixing model had some difficulty apportioning two soil components in the low range (Table 11, Figure 3), the overall pattern of the results was correct and the actual % composition of the dominant soil component was generally in the range of feasible solutions produced. Results for different compounds and combinations of compounds produced similar ranges of feasible solutions for the same mixture although the absolute ranges may vary (e.g., see individual results in Table 11).

To produce a more robust evaluation of the soil mixtures, the 15 ranges of solutions were averaged to produce the "Predicted average %" (Table 11). Comparison of the "Predicted average %" with the "Actual %" shows that the major soil components were correct within 10% for all mixtures and within 2% for 3 of the 5 mixtures tested.

4.6 Mixing model procedures

With natural samples it is likely that there are many possible sources and a large array of compounds that may be used in a multiple matrix of combinations. In order to obtain a mixing model output within a reasonable amount of time (<15 minutes per run), the initial range of sources tested in each run should to be kept to the most likely. Subsequently, these can be rechecked with apparently less likely sources, by source substitution for each matrix of compounds used. The reason for this minimal approach is that the model often produces a null result (no possible solutions) with a large number of sources if the tolerance is set too low. This requires a rerun at a higher tolerance setting until a valid result produces a range of feasible solutions. As the mixing model must be manually initiated, these repeat iterations can take considerable time. Conversely, a smaller range of sources will run quickly (<2 minutes per run) and, by using a starting tolerance setting of 1, requiring fewer repeat iterations with lower or higher tolerance settings to obtain the best possible results.

Furthermore, assuming that all other constraints have been met, a broad smearing of predictions for all sources at a tolerance setting which cannot be reduced below 5 is an indication that one (or more) of the sources is not correct even though it (they) may be physically possible. Consequently, the sources should be changed until the mixing model produces a meaningful range of feasible solutions and preferably at a tolerance setting of <5. A continued failure to produce a meaningful range of feasible soulutions is an indication that a major source component is missing from the matrix of variables and further sampling is necessary to find that source.

From the individual results of the mixtures (Table 11) it is clear that a single matrix of compounds will provide an indication of the proportion of sources but will have a degree of uncertainty that prevents a precise apportioning of each source within the sample. The averaging technique applied to the mixture results improved the precision of the predictions for the dominant sources but still appeared to leave a degree of uncertainty for the low-level source components. Averaging the ranges for several different matrix compound combinations from the same range of sources is likely to improve the resolution and reduce the error, especially on the main source components.

A range of feasible results at less than 5% (especially at 0 or 0-1%) is a good indication that that source is unlikely to be present in the sample being tested.

4.7 Harbour samples

The mixing model was applied to the harbour and mangrove sediments, using the full range of catchment soils including the exposed subsoil, EMHF, from the right hand branch of the Mahurangi River catchment, and the eroded subsoil, EDH2, from the left hand branch for the catchment (Table 12). The mixing model produced consistently low ranges of feasible proportions for the source soils PCR, PPR, NMH, NCBR, EDH1, and EMH, which indicates that these soils were likely to occur in the estuarine samples only at very low levels (i.e., <5 %), if at all. In the matrix of results (Table 12), these values have been omitted for clarity but this does not mean there is none of these soils present, rather they may be present but only in very low proportions.

In the table of results, each estuarine sample, including the depth-dependent habour samples, has been assessed for the possibility of the presence of each source soil using 4 to 8 different combinations of compounds. The values presented are the average of % ranges of feasible mixing model solutions. When averaging the ranges, very broad or "smeared" ranges were not included. Averages are of the lower and upper ranges of at least 4 sets of mixing model solutions and the actual proportion of each source soil present is most likely to be within the range given.

The matrix of results (Table 12) shows a consistent pattern of feasible soil compositions which indicates that the source soils PTR, NDH, EDH2 and EMHF are likely to be present in the estuarine sediments in minor to major proportions.

Note that, whereas % ranges of 0 to a value include the possibility of none of that source soil being present, % ranges between two values indicate that that source soil is present in the estuarine sediments and most likely within the % range indicated. The smaller the % range, the more precise the estimate of that source soil proportion.

Table No.12

Proportion of source soils in harbour and mangrove sediments in the upper Mahurangi Harbour as determined by the mixing model. Values are presented as % ranges of feasible soil compositions. All % ranges are an average of at least 4 mixing model runs (See text). Source soil results in the % range of <5% have been omitted for clarity (See text).

Soils	PTR	PCR	PPR	NDH	NMH	NCBR	EDH1	EDH2	EMH	EMHF
Sites										
H2 0-10	0-15			12-35				10-22		62-86
H2 0-20	0-12			10-32				0-32		65-85
H2 0-30	0-10			20-40				2-28		64-86
H3 0-10	4-18			0-6				0-17		63-92
H3 0-20	4-18			0-14				2-22		72-92
H3 0-30	2-14			0-6				0-15		71-94
H4 0-10	0-10			0-10				0-19		74-89
H4 0-20	4-8			2-7				0-32		82-91
H4 0-30	0-10			1-18				0-32		64-89
M1	13-34			6-13				0-10		28-68
M2	8-27			2-13				0-10		44-78
M3	19-35			21-48				0-23		33-61

4.7.1 Sources of sediment in the upper Mahurangi Harbour

Overall, these results are comparable with the pilot study results which indicated that, of the three source soil types, the exotic pine forest soil component of the upper 2-cm layer of the harbour sediment was in the order of 50-54%, with native forest and pasture contibuting 32-44% and 6-14%, respectively. In this study, the results indicate the presence of all three soil types as sources but with a higher proportion of exotic forest subsoil and less native soil in these samples. The other difference between this and the pilot study is that the present results restrict the source of these soils to specific regions within the Mahurangi catchment.

Although three pasture soil types were sampled, only one, the rolling hill-side pasture PTR (Photo 1, section 8), showed any consistent appearance as a component of the estuarine sediments. This is consistent with the low-lying flood-plain soils (Photos 2-4, section 8) being more likely to be deposition zones of hill-side runoff than being eroded by rainfall events. The enriched $\delta^{13}C$ value and higher %C content of the soil PTR, relative to the other pasture soils, also indicated that this soil type was consistently used for grass or grain and may have been exposed to erosion periodically when cultivated for planting. This soil also had a lower $\delta^{15}N$ value than the other pasture soils, which would be expected if urea fertiliser has been used to promote grass growth.

The three native forest soil types were all hill-side and widely spaced across the catchment. However, the results consistently identified soil from the native forest on the south-facing slopes of Dome Hill (Photos 5 & 6, section 8) as most likely to be present in all the estuarine samples. This may be explained by examining the three sites sampled. At Moir's Hill (Photos 7 & 8, section 8) and Cowan Bay Road (Photos 9 & 10, section 8) sites the native forest was undisturbed with a dense canopy to reduce rainfall intensity and a high proportion of fine surface roots which would be able to contain most of any soil movement within the native forest. At Dome Hill, the native forest was more open allowing higher rainfall intensity at ground level and appeared to have less fine root structure to retain soil eroded during rainfall events. While the left branch of the Mahurangi River flows through the native forest and is likely to pick up sediment directly from the forest, the slopes below the sampling site NDH comprised old cut-over exotic forest which had a thick regrowth of grass and wild ginger on the slopes but bare well-weathered ephemeral gulleys which could direct the run-off from the native forest into the river.

Only two areas of exotic pine forest were sampled and the results indicate that both areas contributed to the sediment in the harbour. However, at both areas the surface soils were of little or no magnitude while the subsoils tended to be major sources of sediment. At Dome Hill, although both EDH1 and EDH2 were on slopes above the Mahurangi River left branch, the undisturbed EDH1 site (Photos 11, section 8) appeared to contribute little or no soil to the estuarine sediments. In contrast, there was a consistent presence of eroded subsoil from the EDH2 site (Photos 12, section 8) which had been cut and left with a cover of desiccated pine litter that afforded no

mechanism for retaining any soil movement during rainfall events. The Dome Hill site had been extensively logged and was revegetating with grass and wild ginger.

Dome Hill has a relatively small area of exotic forest clearing compared with Moir's Hill and adjacent areas where there has been extensive logging operations in recent years. Consequently, it is not surprising that the largest component of exotic forest soil in the estuarine samples came from this area of the catchment. Here again there was discrimination with the surface soil type, EMH, (Photos 13, section 8) contributing little to the composition of the estuarine samples while the subsoil type, EMHF, (Photos 14 & 16, section 8) was clearly a substantial source of sediment run off. Again, examination of the sample sites shows that beneath the canopy of the undisturbed pines the surface soil is held together with an extensive mat of fine roots and leaf litter to reduce the impact of rain-drops and retain any soil movement within the forest. Conversely, the subsoil type exposed by logging had no protection from rain impact or any mechanism of preventing soil movement to the stream at the bottom of the hill. At this particular site the hawser used to haul logs up the hill to the skidder pads had scoured the surface soil completely, leaving a well defined "channel" down which the water-borne soil could flow to the stream. The hauler line appeared to cross the stream at the bottom (Photos 16, section 8).

It must be noted here that while the soil sample sites,EMH, EMHF, and NMH lie outside the catchment area of the Mahurangi River (Fig. 1), they are representative of the soil types in other parts of the Moir's Hill exotic forest which are in the Mahurangi River right branch catchment. Access to the forest within the Mahurangi River catchment on Moir's Hill was not permitted at the time of sampling. While it is possible that there is a spatial isotopic difference between the sites sampled and those about 2 km away in the adjacent Mahurangi River catchment, the difference is likely to be small and unlikely to cause a substantial change in the apportioning of source soils in the estuary sediments.

4.7.2 Depth distribution of sedimentation in the upper Mahurangi Harbour

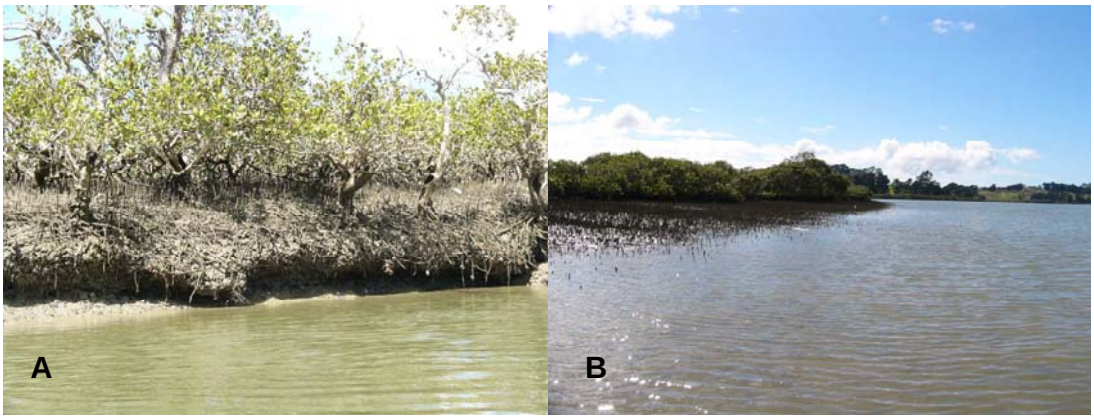
In contrast to the pilot study, where only the upper 2 cm of harbour sediment (representing the last 5 years sedimentation or thereabouts based on the coring work by Swales et al. (2002) using ^{210}Pb dating) was collected, in this study the harbour sediments were cored to depths of 10 cm, 20 cm and 30 cm. These depths encompass longer periods of time during which riverine-sediment has deposited and were collected to determine whether the 2-cm core was appropriate for spatial surveys or whether deeper coring was necessary.

Rather than taking a 30-cm core and sectioning it for depth layers, the technique used was to take a 0-10 cm, a 0-20 cm, and a 0-30 cm core from each location on the harbour mudflats. As each whole core was mixed and analysed as a composite whole rather than taking depth-defined sections of each core, the expectation would be for a slight gradient with increasing depth of sample. There were surprisingly small differences in the source soil proportions between the three core depths at site H2 (Table 12), while at sites H3 and H4 the differences appeared to be more pronounced with an almost step-wise change between 0-10 cm and 0-20 cm depths. As the 0-10

cm sediment is included in the 0-20 cm sediment, this implies a difference in the source material in depth layer between 10 cm and 20 cm deep, or a substantial amount of reworking of the sediments at the locations chosen.

From previous work by Swales et al. (2002), sedimentation rates should be in the order of up to 4.5 mm y^{-1} on the intertidal zone and slightly less at around 3.5 mm y^{-1} subtidally. However, in discussion with Swales it would appear that the central mudflats are relatively mobile with the shape of the channel periodically changing in the upper estuary. In places, mud banks erode exposing the root zones of mangroves and depositing those sediments elsewhere in the harbour.

Figure 4.
A) Bank erosion exposing mangrove roots down to a layer of oyster shell. B) Mangrove progradation expanding out into the estuary where sediment is depositing.



A core (H1), taken from the site previously used for the pilot study, struck a layer of Pacific Oyster shell at a depth of about 15 cm which prevented obtaining a 30-cm deep core and hence that site was not used for the comparison of deep cores. At a deposition rate of 4.5 mm y^{-1}, the 15 cm sediment layer should represent about 33 years sedimentation, which would be consistent with the arrival of the Pacific Oysters (*Crassostrea gigas*) in Mahurangi Harbour in the mid 1970s. However, as Pacific Oysters usually form rafts above the soft sediments (see examples in Manukau Harbour and elsewhere), their burial must have been associated with a flood event or higher than normal sedimentation rates.

Sedimentation rates in Mahurangi are likely to be highly variable with predicted estimates from < 1 t d^{-1} to in excess of 30,000 t d^{-1} and modelled annual average sediment loads are likely to be in the order of 377 to 423 t km^{-2} $year^{-1}$ (Stroud 2003). As undisturbed forest, native or exotic, is unlikely to deliver that quantity of sediment, the proportion of exotic forest sub-soil exposed during logging operations is the most likely source and entirely consistent with the proportions suggested by the mixing model (Table 12). The other major potential source would be pasture, where the top-soil is exposed during regrassing or planting of crops. Farming operations of this type provide short-term periods only of bare soil exposed to erosion compared with the long-term exposure of clear-felled exotic forest.

Sediment reworking in the harbour could effectively sort terrigenous sediment by density, winnowing the lighter more organic material out and leaving the heavier sediment behind. However, because of the possibility of sediment reworking by tidal currents, as well as bioturbation, there can be no firm conclusions about the use of deeper cores for any future spatial survey of the harbour, based on these results.

It would seem reasonable to limit the sediment used in any spatial survey to the upper 2 cm, especially in the middle regions of the estuary, and to avoid areas where scouring and strong tidal currents can rework the sediment. Different core depths may be needed in different parts of the estuary and the appropriate depths may only be known once sampling begins. In most locations it is unlikely that cores deeper than 2 cm would be needed.

4.7.3 Spatial distribution of sedimentation in the upper Mahurangi Harbour

Because sediment cores were taken on both sides of the upper harbour mangroves and along the length of the central mudflat in the upper harbour, the results (Table 12) may also be interpreted in terms of spatial deposition. The most obvious feature of the results is the markedly higher proportion of pasture soil and lower proportion of exotic forest subsoil in the mangrove samples than in the harbour samples. Because this pattern is consistent across all sites, it may indicate selective deposition possibly based on the organic content of the source soils and hence their potential density. Table 2 in the pilot study showed that the sediment in the mangroves had a much higher proportion of fines than sediment from the central mud flats in the harbour. Based on the grain size of the source soils (Table 2, pilot study) the expectation would be for a high exotic forest proportion in the mangrove sediments. However, in this study the isotopic evidence suggests that, while exotic forest subsoils are present, there is a higher proportion of pasture and native forest soils in the mangrove sediments than in the harbour sediments. The subsoils with high clay but low organic content are likely to flocculate and aggregate into larger, heavier (denser) particles that may preferentially settle from the inflow water onto the central mudflats. Conversely, the pasture and native forest top-soil, with a higher organic content are likely to be less dense (more buoyant) and thus stay in the freshwater layer longer, allowing more of this material to be carried into the fringing mangroves as the freshwater plume spreads across the estuary surface.

This scenario is speculative, requiring further work to prove, but provides one possible explanation for the results obtained. While there are likely to be other explanations, at present there is insufficient data to obtain any other meaningful information about spatial deposition.

5 Discussion

The purpose of this study was to expand on the pilot study to perfect the method for determining the proportions of source soils in the sediments of Mahurangi Harbour using a multiple matrix of variables (compounds) and a mixing model (IsoSource), and to document the procedural steps of the process. From the pilot study, specific questions were raised as concerns (see Introduction) and these have been answered as follows:

- Were the selected chemical signatures of the sediments affected by leaching or biodegradation i.e., is the signature [relatively] stable in the aquatic environment?

The analytical results show no major distortions of the CSI signatures between the source soils and the estuarine sediments. The soil preparation included a washing stage which does not appear to have altered any isotopic signatures. If the compound being analysed broke down or decayed, then it would become a new chemical not included in the analysis of the original compound and thus it would not affect the isotopic signature i.e., the signature is relatively stable in the aquatic environment.

- Were the proportions of selected chemical signatures in the sediments uniform with particle size i.e., is the proportion of a chemical signature higher in the fines, which are more easily transported by water into the harbour?

It was found that once suspended in freshwater, the source soils produced fine suspensions which would be easily transported by water into the harbour. As there was essentially no apparent particle size gradient except for aggregation of particles, there should be no signature difference between fines and aggregations of the fines.

- Does the mixing model accurately apportion the amount of sediment from each source in a mixture of those sediments?

Yes. Tests using artificial mixtures showed predicted proportions were generally within 10% of the actual proportions and for the higher proportions, the error was often less than 3%. Greatest uncertainty occurred where the source soil was present in low concentrations.

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

The depth of coring required to integrate sedimentation over the last 5 years was estimated by Swales et al. (2002) to be in the order of 2 cm. The results from the harbour depth-dependent samples were inconclusive and indicate considerable reworking towards the outer edges of the main mudflat in the upper harbour. It is likely that different sampling depths will be required in different locations but few should exceed 2 cm.

5.1 Method evaluation

While the preparation of the source samples was slightly different from that used in the pilot study, oven drying at 60 °C rather than freeze drying, the end result was essentially the same, i.e., a dry soil ground to a fine powder which was ready for analysis.

The resin acid results produced by the standard methods used by commercial laboratories for routine analyses of soils was not adequate to meet the requirements of this study either in sensitivity or quantification. Consequently, while it is appropriate to use the commercial laboratory for this work, the analytical method used needs to be modified to meet these requirements. Hill Laboratories in Hamilton have developed an appropriate in-house method which is capable of producing results to the sensitivity and quantification required. While details of the actual method used remain the property of Hill Laboratories, the basic method includes solvent extraction of the resin and fatty acids, and derivatisation followed by GCMS analysis. [GCMS = gas chromatography mass spectrometry]. Spike recoveries on a soil were essentially 100% for the compounds tested with the exception of abietic acid which was not recovered.

The CSI results were produced by Iso-trace (NZ) Ltd., using a similar technique of solvent extraction and methylation, followed by analysis on a GC-combustion-isotope ratio mass spectrometer. For methylated resin and fatty acid separations, the GC column used was a DB225. About 5 g of source soil was extracted and each analysis used the equivalent of 1 mg of original soil. Internal standards were used for qualitative identification of the naturally occurring but derivatised resin and fatty acids.

While this method development has focused on the use of resin and fatty acids for apportioning soil sources in the sediments of the estuary, several recent publications in the literature have used CSIs of n-alkanes to track the sources of carbon and anthropogenic contaminants in aquatic environments (Mead et al. 2005; Schwarzbauer et al. 2005) and paleoecology (Glaser & Zech 2005). Reanalysis of 3 sample extracts using a DB5 column in place of the DB225 column required for the resin and fatty acids, demonstrated that there are 14 n-alkanes in the chain length of 17 to 30 carbon atoms which might also be useful in discriminating between soil sources where resin and fatty acids are indistinct. [Results not presented].

Spatial surveys using bulk ^{15}N isotopic composition and conventional components of estuarine plants have been used for spatial mapping of land-derived nutrients in coral reefs and seagrass beds (Umezawa et al. 2002; Yamamuro et al. 2003; Fourqurean et al. 2005). However, as nitrogen may be transformed during recycling within the sediments and therefore undergo isotopic fractionation independent of the source origin, ^{15}N isotopic composition cannot be used to apportion source soils in estuarine sediments.

The analysis of the prepared soil mixtures demonstrated that it was possible to obtain good precision on the estimate of source soil contribution to the mixture where the source soil was a major component of the mixture. However, where the source soil was a low or very minor component of the mixture, the results were less certain although most likely to be within 10 units of the actual % composition. If this is a major

concern, the use of CSIs of the n-alkanes may improve resolution at these lower levels. It is unknown whether this would provide significant improvement as this additional data has not been tested. However, as the range of variables in the multiple matrix increases, the probability is for better resolution. The downside is that the mixing model runs may become extensive and time consuming for little gain in accuracy.

As the method is at present, it provides a relatively rapid and robust assessment of the most likely sources of major soil components in the estuarine sediments and indicates which sources are likely to be absent or to be present in very low proportions. The exact proportions of the minor soil components may not be an issue.

The method appears to discriminate between source soils of the same type from different parts of the catchment and that discrimination is reasonable based on field observations. It was assumed that soils in adjacent valleys of the same area (i.e., Moir's Hill) had similar CSI signatures when evaluating the source of soils in the natural estuarine samples. However, small local differences may have influenced the precision of the mixing model results with some compound combinations.

The method also allows some degree of spatial discrimination across the intertidal sediments of the estuary. The difference in the proportions of source soils beneath the mangroves on the exposed mudflats indicates a potential mechanism of soil sorting within the estuary and also indicates that there is likely to be a spatial pattern of sediment deposition along the length of the estuary.

5.2 Method summary

The following is a summary of the method developed for the sediment tracking technique, assuming that the source soils already obtained can be used as reference material:

- Collect 2-cm deep estuarine sediment samples using a large-bore (60-100 mm diameter) core tube and record the GPS coordinates of each sample location. (Several cores will need to be combined from each location to ensure there is enough material for analysis after drying.) Decant overlying water if taking subsurface cores. Manually remove obvious large debris such as stones, wood, shell, leaves, etc.,and place sediment in a 5-litre clean, sealable, plastic bucket, and seal. Store chilled to 4°C until processing as soon as practical.
- Process by mixing the sediment completely using a mechanical paddle, such as a drill-powered plastic paint stirrer at low speed, and take a subsample of the mixed sediment for moisture and % organic content assay. If the sediment is too thick to stir, after taking the subsample for moisture content, add sufficient water to aid mixing and subsequent sieving.
- Sieve the remaining sediment through a 1-mm fine wire stainless steel mesh into a clean (acetone rinsed) large aluminium oven tray. Discard sievings.

- Dry sediment, either by freeze drying or in a fan convection air oven at 60°C for 24 hours or until dry.
- Grind the dry sediment to a fine powder and sieve through a 100 µm mesh into a wide-mouth PET screw-cap jar for storage. Grinding may require the dry sediment cake to be broken into small pieces using a hammer and anvil (suitably cleaned) before grinding in a blender (coffee grinder – food blender) or ball mill (if available).
- Divide the sample into appropriate size aliquots (e.g., 50 – 100 g) for analysis and retain the remainder as a backup sample.
- Specify low level detection limits for resin acids (i.e., DL < 0.01 mg kg^{-1} dry weight) and compound specific isotopes.
- Specify resin and fatty acid analysis for the CSI samples as well as bulk ^{13}C and ^{15}N analyses. Include a reference sample soil for comparison with previous isotopic results. Specify internal standards that do not interfere with compound results required from the analysis.
- Collate the complete set of results before attempting to use the mixing model on the multiple matrix of variables. Variables which are not present in all samples should be moved to a sub matrix which can be used for a smaller number of samples as additional confirmation of results.
- If there are problems of sensitivity or missing compounds that are likely to compromise the use of the mixing model, request an analysis of the n-alkane components from the CSI samples to make the mixing model results more robust.
- Select logical source soils which encompass the range of the sediment sample results for each variable and apply the mixing model to a number of alternative variable combinations including individual compounds and mixtures, but also including an element of mass for quantification.
- Start the mixing model runs using a tolerance T of 1 and either reduce or increase the value of T in each subsequent model run until valid results are obtained for the lowest value of T. Discard results where T = 5 and the results are smeared across a broad range (>30%).
- Repeat this procedure for each variable or combination of variables and each sample until an array of results is produced.
- Average the upper and lower % values of all valid ranges of source soil in each sediment sample to produce a mean % range of feasible proportions of the source soils in the sediment samples.

The array of results may then be used as required.

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8 Photo gallery

The following photos show specific sampling sites and locations referred to in the text.

Photo 1

PTR. Rolling hill-side pasture, above Thompson Road.

Photo 2

PPR. Low-lying flood-plain pasture below Phillips Road.

Photo 3

PCR. Low-lying flood-plain pasture by Carran Rd

Photo 4

View south across flood-plain pasture at Carran Rd.