4 Summary and conclusions

The Northland Regional Council (NRC) commissioned NIWA to analyse and report on sediment and benthic ecological data collected as part of the 2010 LINZ Oceans 20/20 Bay of Islands (BOI) survey. These data provide: 1) detailed and robust information on the state of the environment; and 2) an opportunity to inform the future management of the catchment and the receiving coastal marine environment of the BOI system.

In this section we summarise the key findings of this study.

4.1 Catchment history

The original native-forest landcover of the Bay of Islands catchment was dominated by rimu, totara, tanekaha and kauri. Natural erosion of native-forest catchment soils occurred for thousands of years before people arrived in the Bay of Islands, as indicated by compound-specific stable-isotope (CSSI) analysis of dated sediment cores (section 3.9).

Previous paleoenvironmental studies and historical accounts show that large-scale catchment deforestation began in the Bay of Islands soon after Polynesian arrival (mid-1300s) and several centuries before European settlement began in the1820s Catchment deforestation appears to have occurred earlier than in many other locations in the North Island due to the relatively high Māori population density (section 1.5). The Waitangi and Kerikeri catchments were major population centres from the early Māori period due to the fertile volcanic soils and land cover in pre-European times was a patch-work of gardens, forest remnants and scrub (section 2.8). By the early-1800s extensive gardens of potatoes, kumara and other introduced vegetables were cultivated by Māori.

large-scale deforestation continued following European settlement even though large native-forest remnants are still found in the Waikare and Kawakawa catchments today. Wheat and maize crops were established at Okaihau (north of Lake Omapere) in the 1860s but were short lived due to the warm and humid climate. Dairying was initially established at this time on smaller farms with sheep and cattle farming occurring on larger land holdings. By the early 1900s a substantial proportion of the BOI catchment was dominated by pastoral agriculture. In the Kerikeri catchment, citrus orchards were first established in the late-1920s by George Alderton, who planted 10,000 citrus trees. Citrus production increased after World War Two as well as the introduction of other crops (e.g., kiwi fruit) from the early 1970s.

The present-day landcover of the 1294 km^2 BOI catchment is dominated by pasture (46%), with smaller areas of native forest (20%) and scrub (10%), pine forest (11%) and orchards (3%).

4.2 Sedimentation

The general approach taken in the coring study was to quantify sediment accumulation rates (SAR) along an effects gradient from major catchment outlets in the upper reaches of estuaries to the inner continental shelf.

The recent sedimentation history of the BOI system was reconstructed from historical records and dated sediment cores collected at twenty-three sites in water depths ranging from 1 m to 100 m (Fig. 2.1). Sediment cores have been dated using lead-210 (^{210}Pb), caesium-137 (^{137}Cs) and radiocarbon (^{14}C) to establish time-averaged SAR and to construct the sedimentation history of the BOI system over the last several thousand years.

Geophysical data from the Oceans 20/20 survey also provided information on seabed type and the thickness of unconsolidated sediment layers deposited over bedrock during the last ~12,000 years (Bostock et al. 2010).

The residence time of sediments in the surface-mixed layer (SML) of the seabed was evaluated at each core site using the maximum penetration depth of the short-lived berrylium-7 (^{7}Be, half-life 53 days) and ^{210}Pb SAR.

These various information strands are used to develop: (1) a conceptual understanding of sedimentation; and (2) a sedimentation budget for the BOI system over the last several thousand years.

The key results of the radioisotope analyses of the sediment cores are:

- The thickness of the active seabed layer as defined by ^{7}Be-labelled sediments is 1–5 cm. Sediments in this layer are reworked by waves and currents, and benthic fauna and are eventually removed from the SML by progressive burial. The relative contribution of physical and biological processes will vary between habitat types. The average residence time of sediments in the SML is 16 ±4.3 years (95% Confidence Interval, CI).
- Sediments in the seabed SML are composed of soils eroded by seasonal–annual storms, soils delivered within the last ~two decades and older sediments reworked within the marine–estuarine environment.
- Sediment cores from the central BOI and inner shelf preserve evidence of deep seabed erosion (~10-cm) by a large magnitude storm that most likely occurred in the early 1900s (section 3.3).
- Lead-210 (^{210}Pb) dating of sediment cores at each site yields time-averaged SAR of 1–5 mm/yr over the last 80–200 years. Fringing estuaries close to major river outlets are accumulating sediment more rapidly (<5 mm/yr) than the central Bay and inner shelf (<2.5 mm/yr). A notable exception to this general pattern is the high ^{210}Pb SAR (2.3–4.9 mm/yr) observed in Te Rawhiti Inlet. Stable-isotope data indicate that present-day sediments depositing in Te Rawhiti Inlet are most-likely derived from the Kawakawa and Waitangi Rivers. This suggests that silt discharged from these rivers during floods are transported and dispersed widely by freshwater runoff and tidal currents into the central Bay from where flood tides transport them into the Rawhiti Inlet where they accumulate, in the shelter from the ocean swell afforded by the islands of the eastern bay.
- The BOI system is infilling more slowly with sediment than other North Island estuaries. The average ^{210}Pb SAR for the entire BOI system is 2.4 mm/yr in comparison to 2.4–6.7 mm/yr in other North Island estuaries (section 3.6). This is primarily a result of the large sediment accommodation capacity of the BOI system relative to the sediment-supply rate.

- Sediment accumulation rates in the BOI system have increased by an order of magnitude following catchment deforestation. Radiocarbon dating of shell material preserved deep in the BOI sediment cores yields calibrated ages ranging from 2170 to 9409 years before present (B.P., 1950 A.D.). The long-term ^{14}C SAR of 0.23 ±0.1 mm/yr (95% CI) over the last several thousand years is an order of magnitude lower than ^{210}Pb SAR over the last 80–200 years. It should be noted that the ^{14}C SAR includes the effects Māori land-use practices since the mid-1300s. Consequently, the ^{14}C SAR values are likely to be higher than actual pre-human sedimentation rates. The order of magnitude increases in SAR following deforestation of the BOI catchment are consistent with data from other North Island estuaries.

- Comparison of the Holocene and recent sedimentation budgets indicate a major shift in the sedimentary regime of the BOI system. Annual sediment deposition in the BOI system has averaged 509,000 ±210,000 tonnes per year (t/yr, 95% CI) over the last ~150 years. This recent deposition rate compares with an average of 20,000 ±9,000 to 50,000 ±23,000 t/yr over the last several thousand years prior to catchment deforestation. The order of magnitude increase in sedimentation in the BOI system is consistent with increased soil erosion following large-scale deforestation. This is a global phenomenon (Thrush et al. 2004), although the timing and intensity of deforestation varies with location. New Zealand was the last major land mass to be colonised by humans, so that these major environmental changes have occurred in just a few hundred years.

- The capacity of the BOI estuaries to accommodate sediment inputs over the next century was evaluated based on measured ^{210}Pb SAR and historical rates of sea-level rise (SLR) at the Port of Auckland (1.5 mm ±0.1 mm/yr), which is the closest tie-gauge with a reliable long-term record. To a first approximation, estuary infilling occurs when SAR >SLR and in the opposite case the average depth of the estuary increases over time when SAR <SLR. The resulting net change in sediment accommodation space can be negative (infilling) or positive (increasing water depth). Long-term net changes in sediment accommodation space are in the range +0.5 to -3.5 mm/yr. The most rapid loss of accommodation space has occurred in the Waikare, Veronica and Te Rawhiti compartments. These areas are most likely to experience large-scale environmental changes, such as loss of subtidal habitats and are likely to have already lost macrobenthic communities composed of plant and animal species (e.g., sea grass, filter-feeding bivalves) most sensitive to the effects of fine sediments. This appears to be the case in the Waikare/Kawakawa Inlet whereas sensitive macrobenthic communities still occur in the Te Rawhiti Inlet, which is more remote from major river inputs (section 3.11).

4.3 Sediment sources

Present-day and past sources of terrigenous sediments deposited in the estuarine and coastal waters of the BOI system were determined using the Compound Specific Stable Isotope (CSSI) method (Gibbs 2008). The CSSI method was applied to present-day (i.e., surface) deposits as well as to the analysis of long-cores that preserve the history of sedimentation over the last several thousand years.

The CSSI method is based on the principle that organic (carbon) compounds exuded primarily by the roots of plants impart a unique isotopic signature to soils. Fatty acids (FA) have been demonstrated to be particularly suitable soil tracers, being bound to fine-sediment particles and long lived (i.e., decades–centuries, Gibbs 2008). Estuarine and coastal sediments are typically mixtures of catchment soils and reworked marine sediments from various sources. To identify the sources of sediment in a deposit, the isotopic signatures of individual sources were determined by sampling soils for each major vegetation type (e.g., native forest, pine, pasture etc.). The feasible soil sources in each sediment mixture were then evaluated using the IsoSource model (Phillip & Gregg, 2003). The output from this model is statistical information about the feasible isotopic proportion of each source (i.e., % average, standard deviation and range).

The CSSI method has not previously been applied to reconstruct historical changes in the sources of terrigenous sediment. This has been achieved in the present study by extending the CSSI method to the analysis of dated sediment cores. Importantly, this work incorporates a time-dependent correction factor that accounts for changes in the isotopic signatures of organic compounds due to deforestation and burning of fossil fuels since the early 1700s. Long-term changes in the sources of catchment sediment delivered to the BOI system were reconstructed from cores collected in the Waikare Inlet, Veronica Channel near Russell, Kerikeri Inlet, the inner Bay of Islands and the inner continental shelf near the 30-m and 100-m isobaths respectively.

In interpreting these results it is important to bear in mind that the suite of soil types detected in a dated sediment sample does not imply that these were the only vegetation types present in the catchment. What these results do indicate is the major sources of eroded soils that were eventually deposited at a site in the receiving environment.

The key results of the analysis of present-day and past sources of catchment sediments accumulating in the BOI system are:

- Soil eroded from pasture (cattle and sheep) accounts for more than 60% of the present-day sediment delivery to the BOI system. In the Kerikeri and Waitangi sub-catchments a large proportion of these eroded pasture soils are composed of subsoils. This suggests deep erosion of hillslope pasture in these sub-catchments. Production forestry (pine) also accounts for a substantial proportion of the soil deposited in the Te Puna (36%) and Kawakawa (27%) Inlets. In the Waikare sub-catchment most of the soil was eroded from kanuka scrub (70%) and native forest (26%), which reflects the large proportion of native landcover that remains in this sub-catchment today.
- The CSSI method has been extended to determine long-term changes in sources of catchment soil deposited in the BOI system over the last ≤2700 years.
- Bracken-labelled sediments are present in cores at most sites and occur hundreds to thousands of years before the arrival of people and subsequent catchment deforestation from the mid-1300s onwards. These data indicate that natural disturbance of the landscape was a feature of this environment. Likely

causes of forest disturbance include landslides during high-intensity rainstorms and/or fires.

- The effects of Māori on catchment soil erosion are not well represented in the sediment cores that were analysed. Typically the Māori period (~1300–1800 AD) occupies only a 10–20 cm-thick sediment layer in the cores. We do know from historical accounts of early Europeans that Māori had cleared large areas of native forest from the catchment. Bracken would have established on these cleared areas but this anthropogenic effect cannot be distinguished from natural catchment disturbance after 1300 AD. Only in the Kerikeri Inlet (core RAN-S18) is their some evidence of the cultivation of root crops, such as kumara. This is indicated by the presence of potato-labelled soils in single sample dated to the 1500s, which is likely to have a similar signature to kumara.
- The effects of Europeans on soil erosion over the last century are clearly evident due to the introduction of exotic plants, which over time isotopically labelled the soils. The signatures of dry-stock pasture and potato cultivation enter the sedimentary record from the mid-1800s, although the exact timing varies between core sites. In the Kerikeri Inlet, soils eroded from citrus orchards occur in the estuarine sediments from the late 1940s onwards.
- The long-term impact of soil erosion from pastoral agriculture on the BOI system is clearly shown in a core collected from 30-m water depth in the inner Bay (site KAH S-20). This core contains sediments deposited since the early 1960s and pasture soils have accounted for most of the sediment deposited at this site since the early 1980s at a rate averaging 2.4 mm/yr.

4.4 Macro-benthic communities

Benthic macro-faunal community data collected during the Oceans 20/20 BOI survey as well as monitoring data collected by NRC have been analysed to identify: (1) possible linkages between sedimentation rates and the composition of soft-sediment benthic communities; and (2) soft-sediment benthic communities at risk from sedimentation.

The macro-benthic fauna of the soft-sediment habitats of the BOI system are highly diverse and contain many taxa that are expected to be sensitive to increased terrestrial sediment inputs. In this report, we have used the known and predicted tolerance of key habitat-forming taxa, together with information on biodiversity, to determine areas that have already begun to be impacted by sediment deposition and those that would be expected to be sensitive to future deposition.

The key results of this analysis of soft-sediment macro-faunal data are:

- Sensitive intertidal areas are dispersed around the Bay, although those with low sensitivity are mainly concentrated in the Inlets close to major catchment sediment sources (e.g., Kawakawa, Waikare Inlets and in the upper reaches of the Te Puna and Kerikeri Inlets). Communities in these areas are dominated by mud-tolerant species including the mud crab *Austrohelice crassa*, annelids including *Nereidae* and bivalve *Theora lubrica*.

- Sensitive subtidal macrofaunal communities are mainly found within Te Rawhiti Inlet and the outer deeper areas of the Bay. Te Rawhiti Inlet and the sandy areas around Waitangi and in Veronica Channel are at highest risk, mainly driven by the higher risk associated with sedimentation. Stable-isotope analysis of sediment deposits indicates that sediments in the Te Rawhiti Inlet are primarily derived from runoff from catchment dominated by pasture and clear-felled pine forests in the Kawakawa catchment.
- Non-site specific SAR and source information make it difficult to link SAR and sediment sources to the macrobenthic communities observed at a specific site. This is not necessarily a problem that can be solved by collecting more information on SAR and sediment sources because it is difficult to interpolate subtidal SAR measurements to intertidal areas, where the properties that determine rates of sedimentation are quite different to those subtidally. This also highlights the problem of initial deposition versus resuspension and redeposition and macrofaunal effects from sedimentation versus suspended sediment. Indeed one reason why SAR from subtidal sites gave better than expected predictions for intertidal sites may have been that the subtidal deposition was higher than we would expect to see on the nearby intertidal flat. Thus it was a good proxy for the intertidal area where resuspension removes accumulated sediment but the communities are impacted both by the initial settlement of sediment and suspended sediment passing over the area.

4.5 Changes in mangrove and saltmarsh-habitats extent

Changes in the spatial extent of mangrove and saltmarsh-habitats during the time period 1978–2009 were determined from GIS analysis of aerial photographs. The total area and rate of change in the area of both habitat types (%/yr) were evaluated for each compartment of the BOI system.

The key results are:

- Mangrove and saltmarsh habitats occupy 1181 hectares (ha) and 280 ha respectively of intertidal flat in the BOI system (2009). Most of the mangrove habitat occurs in the estuaries of the eastern BOI (77%), within the Waikare and Veronica Inlets. These estuaries receive runoff from the large Kawakawa and Waitangi sub-catchments. The large areas of mangrove habitat present in these two inlets in 1978 suggests that these forests had been established decades earlier. These spatial patterns are consistent with more rapid infilling of estuaries near major river outlets and the consequent development of intertidal flats suitable for colonisation by mangroves.
- The total area of mangrove habitat increased by 10.8% (127 ha) during the period 1978–2009, while saltmarsh habitat declined by 12.3% (39 ha). Large proportions of the increase in mangrove-habitat 40%, 51 ha) and decrease in saltmarsh habitat (61% -24 ha) have occurred in the Waikare Inlet. As observed in other NZ estuaries (Morrisey et al. 2010), the loss of saltmarsh-habitat is consistent with landward expansion of mangrove into saltmarsh habitat and/or reclamations along the foreshore. Further analysis of historical

aerial photographs and/or council records could establish the relative contributions of these potential causal factors.

- The rates of mangrove-habitat expansion in the BOI system of 0.3–1.4% yr^{-1} are in the range observed in other North Island estuaries (0.2–20 % yr^{-1}) although substantially less than the average rate of 4 % yr^{-1} since the 1940s (Morrisey et al. 2010).
- Historical increases in mangrove habitat (1978–2009) has occurred most rapidly in the Te Rawhiti Inlet (1.4%), although mangrove in this compartment accounts for less than 5% of the BOI system total. Mangroves have colonised bays and small inlets that indent the eastern shoreline of Te Rawhiti, which afford shelter from wave action.
- The potential for future mangrove-habitat expansion in BOI estuaries is likely to be limited based on the low historical rate of forest expansion, deep reworking of intertidal sediments by waves (as indicated by ^{7}Be mixing depths), which will restrict seedling recruitment and the future effects of sea-level rise, which are likely to outpace tidal-flat accretion due to sedimentation.
- The findings of a study of potential future mangrove-habitat expansion in Auckland's east-coast estuaries (Swales et al. 2009) provide guidance on the likely fate of mangrove habitat in the Bay of Islands. Average SAR in BOI estuaries are typically lower than in Auckland estuaries so that even maintenance of existing mangrove habitat over the next century is only likely to occur under the historical rate of sea-level rise since 1950 (1.6 mm yr^{-1}). Large-scale loss of mangrove habitat is predicted to occur under the most likely scenarios for accelerated SLR over the next century of 5.5–8.8 mm yr^{-1}. Under these scenarios, tidal creeks would provide refuges for mangroves assuming that rapid sedimentation observed in these environments over the last 50 years continues.

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Appendix A Radioisotope dating

Radioisotopes, such as caesium-137 (^{137}Cs, ½-life 30 years) and lead-210 (^{210}Pb, ½-life 22.3 years), and plant pollen can be used to reconstruct the recent sedimentation history of an estuary.

Dating of estuarine sediments using independent methods offsets the limitations of any one approach. This is particularly important when interpreting sediment profiles from lakes and estuaries, given the confounding effects of physical and biological mixing (Robbins and Edgington, 1975; Sharma et al. 1987; Alexander et al. 1993; Valette-Silver, 1993; Benoit et al. 1999). A description of the various methods of dating sediments follows.

The S.I. unit of radioactivity used in this study is the Becquerel (Bq), which is equivalent to one radioactive disintegration per second.

^{137}Cs dating

^{137}Cs was introduced to the environment by atmospheric nuclear weapons tests in 1953, 1955–1956 and 1963–1964. Peaks in annual ^{137}Cs deposition corresponding to these dates are the usual basis for dating sediments (Wise, 1977; Ritchie and McHenry, 1989). Although direct atmospheric deposition of ^{137}Cs into estuaries is likely to have occurred, ^{137}Cs is also incorporated into catchment soils, which are subsequently eroded and deposited in estuaries (Figure A1). In New Zealand, ^{137}Cs deposition was first detected in 1953 and its annual deposition was been measured at several locations until 1985. Annual ^{137}Cs deposition can be estimated from rainfall using known linear relationships between rainfall and Strontium-90 (^{90}Sr) and measured ^{137}Cs/^{90}Sr deposition ratios (Matthews, 1989). Experience in Auckland estuaries shows that ^{137}Cs profiles measured in estuarine sediments bear no relation to the record of annual ^{137}Cs deposition (i.e., 1955–1956 and 1963–1964 ^{137}Cs-deposition peaks absent), but rather preserve a record of direct and indirect (i.e., soil erosion) atmospheric deposition since 1953 (Swales et al. 2002). The maximum depth of ^{137}Cs occurrence in sediment cores (corrected for sediment mixing) is taken to coincide with the year 1953, when ^{137}Cs deposition was first detected in New Zealand. We assume that there is a negligible delay in initial atmospheric deposition of ^{137}Cs in estuarine sediments (e.g., ^{137}Cs scavenging by suspended particles) whereas there is likely to have been a time-lag (i.e., <1 yr) in ^{137}Cs inputs to estuaries from topsoil erosion, which would coincide with the occurrence of floods.

If a surface mixed layer (SML) is evident in a core, as shown by an x-ray image and/or a tracer profile (e.g., ^{7}Be, ^{210}Pb) then ^{137}Cs is likely to have been rapidly mixed through the SML. Therefore, to calculate time-averaged sedimentation rates, the maximum depth of ^{137}Cs occurrence is reduced by the maximum depth of the SML.

Uncertainty in the maximum depth of ^{137}Cs results from: (1) the depth interval between sediment samples and (2) minimum detectable concentration of ^{137}Cs, which is primarily determined by sample size and counting time. The 1963–1964 ^{137}Cs deposition peak was about five-times than the deposition plateau that occurred between 1953 and 1972. Thus, depending on the sample size, there is uncertainty in the age of the maximum ^{137}Cs depth (i.e., 1953–1963). To reduce this uncertainty, we have maximised the sample mass that is analysed.

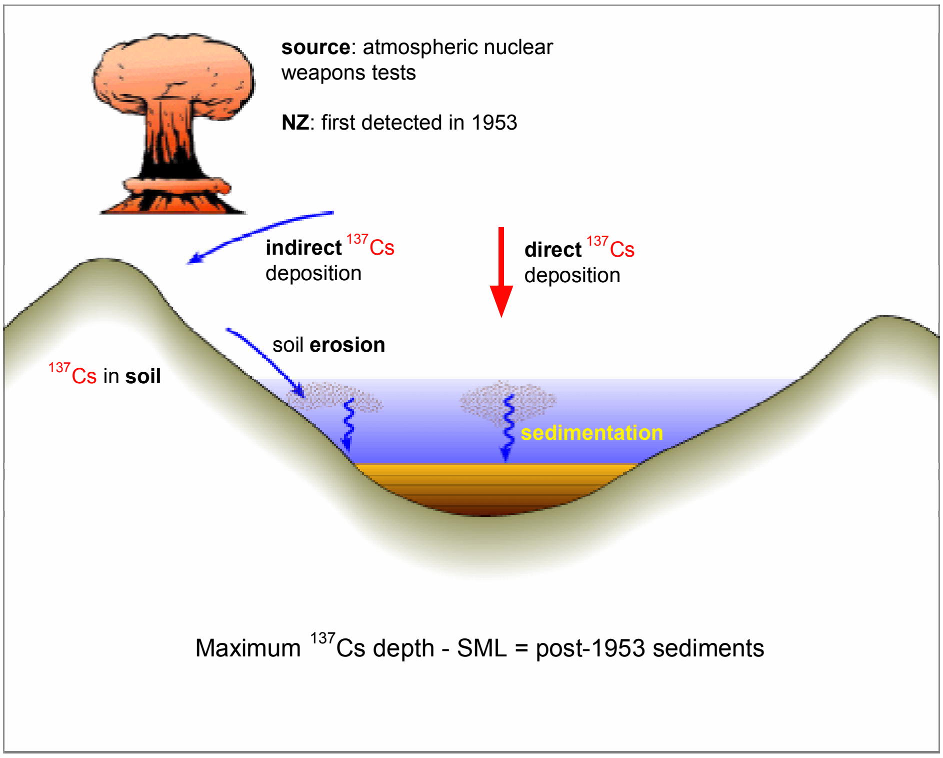

Figure A1: ^{137}Cs pathways to estuarine sediments.

^{210}Pb dating

^{210}Pb (half-life 22.3 yr) is a naturally occurring radioisotope that has been widely applied to dating recent sedimentation (i.e., last 150 yrs) in lakes, estuaries and the sea (Figure A2). ^{210}Pb is an intermediate decay product in the uranium-238 (^{228}U) decay series and has a radioactive decay constant (*k*) of 0.03114 yr^{-1}. The intermediate parent radioisotope radium-226 (^{226}Ra, half-life 1622 years) yields the inert gas radon-222 (^{222}Rn, half-life 3.83 days), which decays through several short-lived radioisotopes to produce ^{210}Pb. A proportion of the ^{222}Rn gas formed by ^{226}Ra decay in catchment soils diffuses into the atmosphere where it decays to form ^{210}Pb. This atmospheric ^{210}Pb is deposited at the earth surface by dry deposition or rainfall. The ^{210}Pb in estuarine sediments has two components: supported ^{210}Pb derived from *in situ* ^{222}Rn decay (i.e., within the sediment column) and an unsupported ^{210}Pb component derived from atmospheric fallout. This unsupported ^{210}Pb component of the total ^{210}Pb concentration in excess of the supported ^{210}Pb value is estimated from the ^{226}Ra assay (see below). Some of this atmospheric unsupported ^{210}Pb component is also incorporated into catchment soils and is subsequently eroded and deposited in estuaries. Both the direct and indirect (i.e., soil inputs) atmospheric ^{210}Pb input to receiving environments, such as estuaries, is termed the unsupported or excess ^{210}Pb.

The concentration profile of unsupported ^{210}Pb in sediments is the basis for ^{210}Pb dating. In the absence of atmospheric (unsupported) ^{210}Pb fallout, the ^{226}Ra and ^{210}Pb in estuary sediments would be in radioactive equilibrium, which results from the substantially longer ^{226}Ra half-life. Thus, the ^{210}Pb concentration profile would be uniform with depth. However, what is typically observed is a reduction in ^{210}Pb concentration with depth in the sediment column. This is due to the addition of unsupported ^{210}Pb directly or indirectly from the atmosphere that is deposited with sediment particles on the bed. This unsupported ^{210}Pb component decays with age (k = 0.03114 yr^{-1}) as it is buried through sedimentation. In the absence of sediment mixing, the unsupported ^{210}Pb concentration decays exponentially with depth and time in the sediment column. The validity of ^{210}Pb dating rests on how accurately the ^{210}Pb delivery processes to the estuary are modelled, and in particular the rates of ^{210}Pb and sediment inputs (i.e., constant versus time variable)

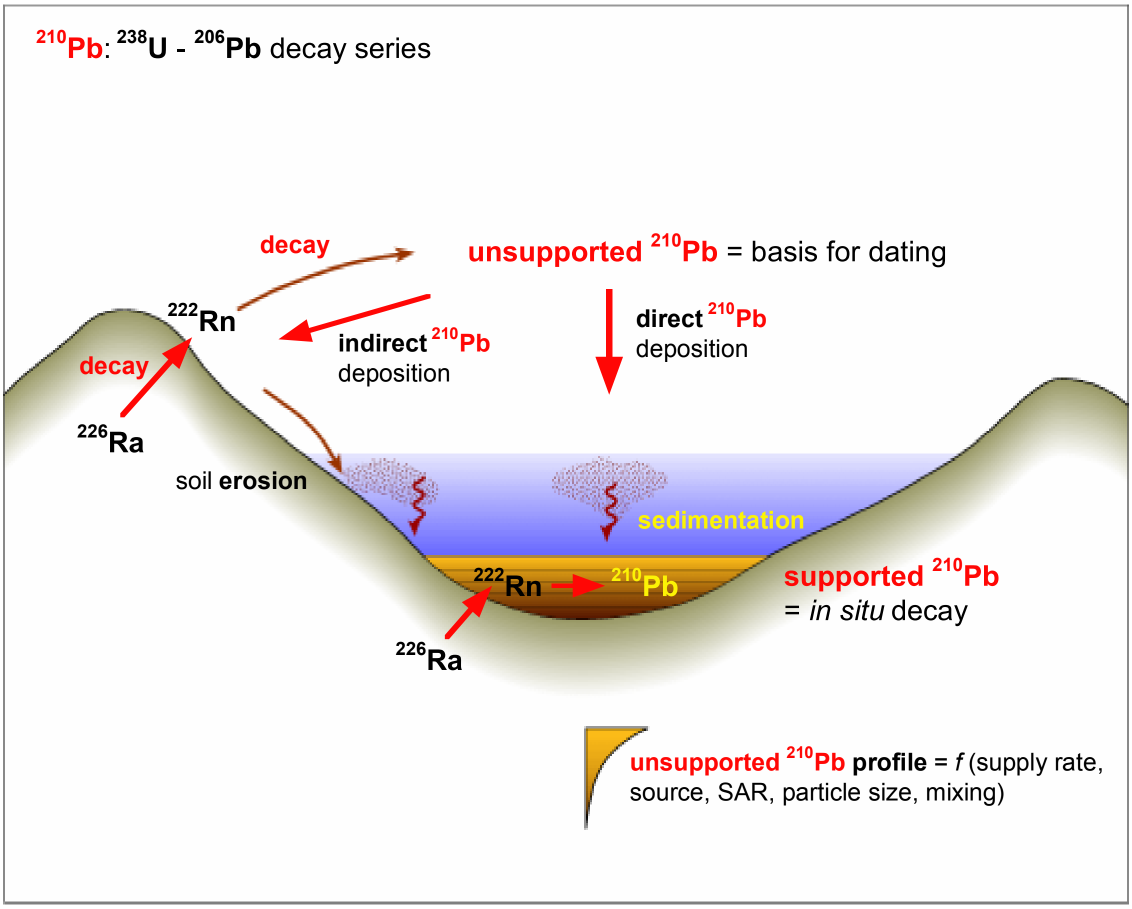

Figure A2: **^{210}Pb pathways to estuarine sediments.**

Sediment accumulation rates (SAR)

Sedimentation rates calculated from cores are **net average sediment accumulation rates (SAR), which are usually expressed as mm yr^{-1}**. These SAR are net values because cores integrate the effects of all processes, which influence sedimentation at a given location. At short time scales (i.e., seconds–months), sediment may be deposited and then subsequently resuspended by tidal currents and/or waves. Thus, over the long term, sedimentation rates derived from cores represent net or cumulative effect of potentially many cycles of sediment deposition and resuspension. However, less disrupted sedimentation histories are found in depositional environments where sediment mixing due to physical processes (e.g., resuspension) and bioturbation is limited. The effects of bioturbation on sediment profiles and dating resolution reduce as SAR increase (Valette-Silver, 1993).

Net sedimentation rates also mask the fact that sedimentation is an episodic process, which largely occurs during catchment floods, rather than the continuous gradual process that is implied. In large estuarine embayments, such as the Firth, mudflat sedimentation is also driven by wave-driven resuspension events. Sediment eroded from the mudflat is subsequently re-deposited elsewhere in the estuary.

Although sedimentation rates are usually expressed as a sediment thickness deposited per unit time (i.e., mm yr^{-1}) this statistic does not account for changes in dry sediment mass with depth in the sediment column due to compaction. Typically, sediment density (ρ = g cm^{-3}) increases with depth and therefore some workers prefer to calculate dry mass accumulation rates per unit area per unit time (g cm^{-2} yr^{-1}). These data can be used to estimate the total mass of sedimentation in an estuary (tonnes yr^{-1}) (e.g., Swales et al. 1997). However, the effects of compaction can be offset by changes in bulk sediment density reflecting layering of low-density mud and higher-density sand deposits. Furthermore, the significance of a SAR expressed as mm yr^{-1} is more readily grasped than a dry-mass sedimentation rate in g cm^{-3} yr^{-1}. For example, the rate of estuary aging due to sedimentation (mm yr^{-1}) can be directly compared with the local rate of sea level rise.

The equations used to estimate time-averaged SAR from the excess ^{210}Pb and ^{137}Cs profiles are described below.

Estimating SAR using ^{210}Pb profiles

The rate of decrease in excess ^{210}Pb activity with depth can be used to calculate a net sediment accumulation rate. The excess ^{210}Pb activity at time zero (C_0, Bq kg^{-2}), declines exponentially with age (*t*):

$$C_{\mathrm{t}} = C_0 e^{-kt}$$

Assuming that within a finite time period, sedimentation (*S*) is constant then $t = z/S$ can be substituted into the above equation and by re-arrangement:

$$\frac{\ln\left[\frac{C_t}{C_0}\right]}{z} = -k/S$$

Because excess ^{210}Pb$_{us}$ activity decays exponentially and assuming that sediment age increases with depth, a vertical profile of natural log(*C*) should yield a straight line of slope $b = -k/S$. A linear regression model is fitted to natural-log transformed excess ^{210}Pb data to calculate *b*. The SAR over the depth of the fitted data is given by:

$$S = -(k)/b$$

An advantage of the ^{210}Pb-dating method is that the SAR is based on the excess ^{210}Pb profile rather than a single layer or horizon, as is the case for ^{137}Cs were the maximum penetration depth of this radioisotope is used for dating. Furthermore, if the ^{137}Cs tracer is present at the bottom of the core then the estimated SAR represents a minimum value.

Estimating SAR using ^{137}Cs profiles

The ^{137}Cs profiles will also be used to estimate time-averaged SAR based on the maximum depth of ^{137}Cs in the sediment column, corrected for surface mixing. The ^{137}Cs SAR is calculated as:

$$S = (M - L)/T - T_0$$

where S is the ^{137}Cs SAR, M is the maximum depth of the ^{137}Cs profile, L is the depth of the surface mixed layer (SML) indicated by the ^{7}Be profile and/or x-ray images, *T* is the year cores were collected and T_0 is the year (1953) ^{137}Cs deposition was first detected in New Zealand.

Sediment mixing

Biological and physical processes, such as the burrowing and feeding activities of animals and/or sediment resuspension by waves (Figure a3), mix the upper sediment column (Bromley, 1996). As a result, sediment profiles are modified and this limits the temporal resolution of dating. Various mathematical models have been proposed to take into account the effects of bioturbation on ^{210}Pb concentration profiles (e.g., Guinasso and Schink, 1975).

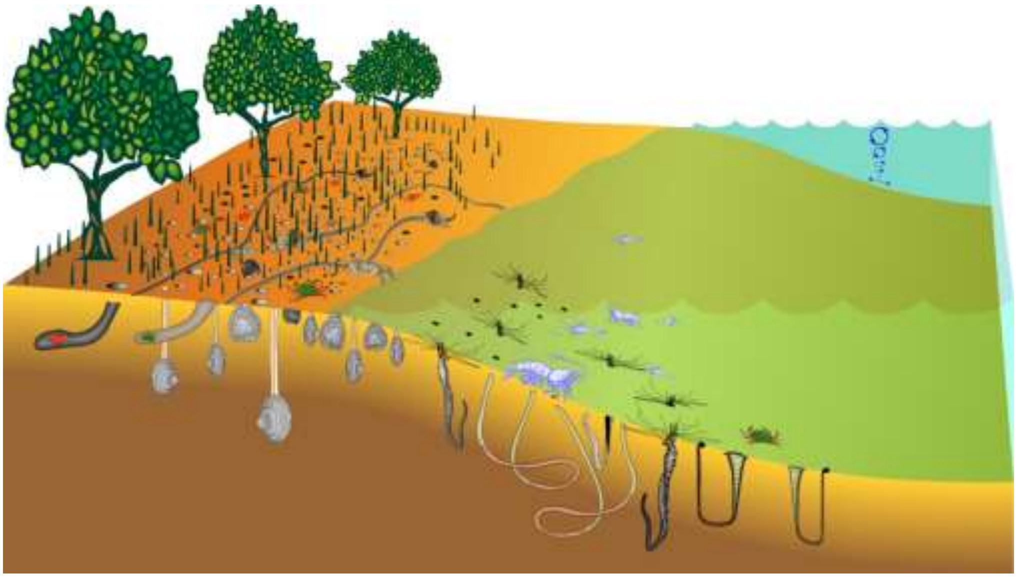

Figure A3: **Biological and physical processes, such as the burrowing and feeding activities of animals and/or sediment resuspension by waves, mix the upper sediment column. As a result, sediment profiles are modified and limit the temporal resolution of dating. The surface mixed layer (SML) is the yellow zone.**

Biological mixing has been modelled as a one-dimensional particle-diffusion process (Goldberg and Kiode, 1962) and this approach is based on the assumption that the sum effect of ‘random’ biological mixing is integrated over time. In estuarine sediments exposed to bioturbation, the depth profile of unsupported ^{210}Pb typically shows a two-layer form, with a surface layer of relatively constant unsupported ^{210}Pb concentration overlying a zone of exponential decrease. In applying these types of models, the assumption is made that the mixing rate (i.e., diffusion co-efficient) and mixing depth (i.e., surface-mixed layer, SML) are uniform in time. The validity of this assumption usually cannot be tested, but changes in bioturbation process could be expected to follow changes in benthic community composition.

Appendix B Compound Specific Stable Isotopes

Introduction to stable isotopes

In this section we describe how stable isotopes are used to identify the sources of catchment sediments deposited in lakes, estuaries and coastal waters and explain how isotopic data are interpreted.

Stable isotopes are non-radioactive and are a natural phenomenon in many elements. In the NIWA Compound Specific Stable Isotope (CSSI) method, carbon (C) stable isotopes are used to determine the provenance of sediments (Gibbs 2008). About 98.9% of all carbon atoms have an atomic weight (mass) of 12. The remaining ~1.1% of C atoms have an extra neutron in the atomic structure, giving it an atomic weight (mass) of 13. These are the two stable isotopes of carbon. Naturally occurring carbon also contains an extremely small fraction (about two trillionths) of radioactive carbon-14 (^{14}C). Radiocarbon dating is also used in the present study to determine long-term sedimentation rates.

To distinguish between the two stable isotopes of carbon, they are referred to as light (^{12}C) and heavy (^{13}C) isotopes. Both of these stable isotopes of carbon have the same chemical properties and react in the same way. However, because ^{13}C has the extra neutron in its atom, it is slightly larger than the ^{12}C atom. This causes molecules with the ^{13}C atoms in their structure to react slightly slower than those with ^{12}C atoms, and to pass through cell walls in plants or animals at a slower rate than molecules with ^{12}C atoms. Consequently, more of the ^{12}C isotope passes through the cell wall than the ^{13}C isotope, which results in more ^{12}C on one side of the cell wall than the other. This effect is called isotopic fractionation and the difference can be measured using a mass spectrometer. Because the fractionation due to passage through one cell-wall step is constant, the amount of fractionation can be used to determine chemical and biological pathways and processes in an ecosystem. Each cell wall transfer or "step" is positive and results in enrichment of the ^{13}C content.

The amount of fractionation is very small (about one thousandth of a percent of the total molecules for each step) and the numbers become very cumbersome to use. A convention has been developed where the difference in mass is reported as a ratio of heavy-to-light isotope. This ratio is called "delta notation" and uses the symbol "δ" before the heavy isotope symbol to indicate the ratio i.e., δ^{13}C. The units are expressed as "per mil" which uses the symbol "‰". The delta value of a sample is calculated using the equation:

$$\delta^{13}C = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right]1000$$

where *R* is the molar ratio of the heavy to light isotope ^{13}C/^{12}C. The international reference standard for carbon was a limestone, Pee Dee Belemnite (PDB), which has a ^{13}C/^{12}C ratio of 0.0112372 and a δ^{13}C value of 0 ‰. As all of this primary standard has been consumed, secondary standards calibrated to the PDB standard are used. Relative to this standard most organic materials have a negative δ^{13}C value.

Atmospheric CO_2, which is taken up by plants in the process of photosynthesis, presently has a δ^{13}C value of about -8.5. In turn, the δ^{13}C signatures of organic compounds produced by plants partly depends on their photosynthetic pathway, primarily either C_3 or C_4. During photosynthesis, carbon passes through a series of reactions or trophic steps along the C_3 or

C_4 pathways. At each trophic step, isotopic fractionation occurs and organic matter in the plant (i.e., the destination pool) is depleted by 1 ‰. The C_3 pathway is longer than the C_4 pathway so that organic compounds produced by C_3 plants have a more depleted $\delta^{13}C$ signature. There is also variation in the actual amount of fractionation between plant species having the same photosynthetic pathway. This results in a range of $\delta^{13}C$ values, although typical bulk values for C_3 and C_4 plants vary around -26 ‰ and -12 ‰ respectively. The rate of fractionation also varies between the various types of organic compounds produced by plants. Thus, by these processes a range of organic compounds each with unique $\delta^{13}C$ signatures are produced by plants that can potentially be used as natural tracers or biomarkers.

The instruments used to measure stable isotopes are called “isotope ratio mass spectrometers” (IRMS) and they report delta values directly. However, because they have to measure the amount of ^{12}C in the sample, and the bulk of the sample C will be ^{12}C, the instrument also gives the percent C (%C) in the sample.

When analysing the stable isotopes in a sample, the $\delta^{13}C$ value obtained is referred to as the bulk $\delta^{13}C$ value. This value indicates the type of organic material in the sample and the level of biological processing that has occurred. (Biological processing requires passage through a cell wall, such as in digestion and excretion processes and bacterial decomposition.) The bulk $\delta^{13}C$ value can be used as an indicator of the likely source land cover of the sediment. For example, fresh soil from forests has a high organic content with %C in the range 5% to 20% and a low bulk $\delta^{13}C$ value in the range -28‰ to -40‰. As biological processing occurs, bacterial decomposition converts some of the organic carbon to carbon dioxide (CO_2) gas which is lost to the atmosphere. This reduces the %C value and, because microbial decomposition has many steps, the bulk $\delta^{13}C$ value increases by ~1‰ for each step. Pasture land cover and marine sediments typically have bulk $\delta^{13}C$ values in the range -24‰ to -26‰ and -20‰ to -22‰, respectively. Waste water and dairy farm effluent have bulk $\delta^{13}C$ values more enriched than -20‰. Consequently, a dairy farm where animal waste has been spread on the ground as fertilizer, will have bulk $\delta^{13}C$ values higher (more enriched) than pasture used for sheep and beef grazing.

In addition to the bulk $\delta^{13}C$ value, organic carbon compounds in the sediment can be extracted and the $\delta^{13}C$ values of the carbon in each different compound can be measured. These values are referred to as compound-specific stable isotope (CSSI) values. A forensic technique recently developed to determine the provenance of sediment uses both bulk $\delta^{13}C$ values and CSSI values from each sediment sample in a deposit for comparison with signatures from a range of potential soil sources for different land cover types. This method is called the CSSI technique (Gibbs, 2008).

The CSSI technique is based on the concepts that:

1. land cover is primarily defined by the plant community growing on the land, and
2. all plants produce the same range of organic compounds but with slightly different CSSI values because of differences in the way each plant species grows and also because each land cover type has a characteristic composition of plant types that contribute to the CSSI signature.

The compounds commonly used for CSSI analysis of sediment sources are natural plant fatty acids which bind to the soil particles as labels called biomarkers. While the amount of a biomarker may decline over time, the CSSI value of the biomarker does not change. The CSSI values for the range of biomarkers in a soil provides positive identification of the source of the soil by land cover type.

The sediment at any location in an estuary or harbour can be derived from many sources including river inflows, coastal sediments and harbour sediment deposits that have been mobilised by tidal currents and wind-waves. The contribution of each sediment source to the sediment mixture at the sampling location will be different. To separate and apportion the contribution of each source to the sample, a mixing model is used. The CSSI technique uses the mixing model IsoSource (Phillips & Gregg, 2003). The IsoSource mixing model is described in more detail in a following section.

While the information on stable isotopes above has focused on carbon, these descriptions also apply to nitrogen (N), which also has two stable isotopes, ^{14}N and ^{15}N. The bulk N content (%N) and bulk isotopic values of N, δ^{15}N, also provide information on land cover in the catchment but, because the microbial processes of nitrification and denitrification can cause additional fractionation after the sediment has been deposited, bulk δ^{15}N cannot be used to identify sediment sources. The fractionation step for N is around +3.5‰ with bulk δ^{15}N values for forest soils in the range +2‰ to +5‰. Microbial decomposition processes result in bulk δ^{15}N values in the range 6‰ to 12‰ while waste water and dairy effluent can produce bulk δ^{15}N values up to 20‰. However, the use of synthetic fertilizers such as urea, which has δ^{15}N values of -5‰, can result in bulk δ^{15}N values <0‰.

Analyses

An aliquot of each dry sediment sample was acidified with 1 N hydrochloric acid to remove inorganic carbonate before analysing for bulk organic C and N stable isotopes. About 50 mg of each acidified sample was combusted in a helium gas stream in a Fisons N1500 Elemental Analyser coupled via a ConFlo-II interface to a Thermo-Finnegan Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS).

For δ^{13}C, CF-IRMS measurements typically have a precision of ± 0.1 ‰ or better and the instrument also provides the proportion of organic C and N (%) in each sample.

Aliquots (20 to 40 g) of the non-acidified dry sediment were extracted with hot dichloromethane (100 ºC) under high pressure (2000 psi) in a Dionex Accelerated Solvent Extractor (ASE 2000) to extract the fatty acids bound to the sediment particles. The fatty acids were methylated using 5% boron trifluoride catalyst in methanol to produce fatty acid methyl esters (FAMEs). These FAMEs were analysed by gas chromatography (GC)-combustion-IRMS to produce compound-specific stable isotope δ^{13}C values i.e., CSSI values. Method details and data interpretation protocols were described previously by Gibbs (2008).

Data processing and presentation

The bulk δ^{13}C values, %C and suite of CSSI values for the extracted FAMEs were assembled into a matrix table and modelled using IsoSource to estimate the number (*n*) of isotopically feasible proportions of the main sediment sources at each sampling location. In successive model iterations, potential sources were added or removed to find an isotopic balance where the confidence level was high (lowest n value) and uncertainty was low. The isotopically feasible proportions of each soil source are then converted to soil proportions using the %C of each soil on a proportional basis. That is to that the higher the %C in the soil, the less of that soil source is required to obtain the isotopic balance. In general, soil proportions less than 5% were considered possible but potentially not present. Soil proportions >5% were considered to be present within the range of the mean ± SD.

The per cent-soil proportions for the major river inflows were then plotted as spatial distribution maps of the BOI system using the contouring programme "Surfer-V8" (Golden Software), using linear kriging. Because of the paucity of data, the contour plots produced by linear kriging are indicative rather than definitive.

CSSI Method

The CSSI method applies the concept of using the $\delta^{13}C$ signatures of organic compounds produced by plants to distinguish between soils that develop under different land-cover types. With the exception of monocultures (e.g., wheat field), the $\delta^{13}C$ signatures of each land-cover type reflects the combined signatures of the major plant species that are present. For example, the isotopic signature of the Bay's lowland native forest will be dominated by kauri, rimu, totara and tānekaha. A monoculture, such as pine forest, by comparison will impart an isotopic signature that largely reflects the pine species, as well as, potentially, any understory plants.

The application of the CSSI method for sediment-source determination involves the collection of sediment samples from potential sub-catchment and/or land cover sources as well as sampling of sediment deposits in the receiving environment. These sediment deposits are composed of mixtures of terrigenous sediments, with the contribution of each source potentially varying both temporally and spatially. The sampling of catchment soils provides a library of isotopic signatures of potential sources that is used to model the most likely sources of sediments deposited at any given location and/or time.

Straight-chain Fatty Acids (FA) with carbon-chain lengths of 12 to 24 atoms (C12:0 to C24:0) have been found to be particularly suitable for sediment-source determination as they are bound to fine sediment particles and long-lived (i.e., decades). In the present study, five types of FA were used to evaluate the present-day and historical sources of terrigenous sediments deposited in the Bay: Myristic Acid (C14:0); Palmitic (C16:0); Stearic (C18:0); Arachidic (C20:0) and Behenic (C22:0). Although breakdown of these FA to other compounds eventually occurs, the signature of a remaining FA in the mixture does not change.

The stable isotope compositions of N and C and the CSSI of carbon in the suite of fatty acid (FA) biomarkers are extracted from catchment soils and marine sediments. It is the FA signatures of the soils and marine sediments that are used in this study to determine sediment sources. Gibbs (2008) describes the CSSI method in detail.

In the present study, the CSSI method has also been extended to reconstruct the changes in sediment sources over time that are preserved in the sediment cores collected from the BOI system. We refer to this new method as the CSSI dating technique. To achieve this, the changes in the isotopic signatures of plants due to the "Suess Effect" needed to be incorporated into the CSSI method. The so-called Suess Effect refers to the change in the isotopic signatures of plants and animals due to the release of “old carbon” into the atmosphere associated with the burning of fossil fuels and deforestation since 1700. Consequently, the stable-isotope signatures of the FA tracers being produced by plants will have also changed over time and the CSSI signatures of sediment core samples of different ages are corrected for this effect to allow direct comparison with modern values for each soil source in the soil library. The methods used to correct the isotopic signatures of soil sources over the last ~300 years are described below.

Correction of CSSI signatures of old sediments for the Suess effect

The reconstruction of changes in sources of terrigenous sediment deposited in the BOI system is derived from dated cores using the FA isotope signatures preserved in the sediments. Before the feasible sources of these sediments could be evaluated using the IsoSource package, the isotope (i.e., input) data required correction for the effects of the release of “old carbon” into the biosphere over the last 300 years, associated with the burning of fossil fuels and deforestation.

Specifically, the release of old carbon with a depleted δ^{13}C signature has resulted in a decline in δ^{13}C in atmospheric CO_2 ($\delta^{13}CO_2$). The changing abundance of carbon isotopes in a carbon reservoir associated with human activities is termed the Suess effect (Keeling 1979). This depletion in atmospheric $\delta^{13}CO_2$ is of the order of 2 ‰ since 1700 and has accelerated substantially since the 1940s (Verburg 2007). Thus, the δ^{13}C signatures of plant biomarkers, such as Fatty Acids have also changed due to the Suess effect. Consequently, the isotopic signatures of estuarine sediments (i.e., the mixture) deposited in the past must be corrected to match the isotopic signatures of present-day source soils.

Figure B1 presents the atmospheric δ^{13}C curve reconstructed by Verburg (2007) using data collected in earlier studies and includes measurements of material dating back to 1570 AD. These data indicate that the atmospheric δ^{13}C signature was stable until 1700 AD, with subsequent depletion of δ^{13}C due to release of fossil carbon.

In the present study, we use this atmospheric δ^{13}C curve to correct the isotopic values of the FA in sediment samples of varying ages taken from cores to equivalent modern values. This is required because the δ^{13}C values of the FA from the potential catchment sources are modern (i.e., 2010 AD), and are therefore depleted due to the Suess effect. For example, the δ^{13}C value of a Fatty Acid derived from a kauri tree growing today will be depleted by -2.15 ‰ in comparison to a kauri that grew prior to 1700 AD (Fig. 8.1). It can be seen that the isotopic correction for the period since 1700 is variable depending of age. Examples of this correction process for isotopic data for sediments taken from core RAN-5B are presented in Table B2.

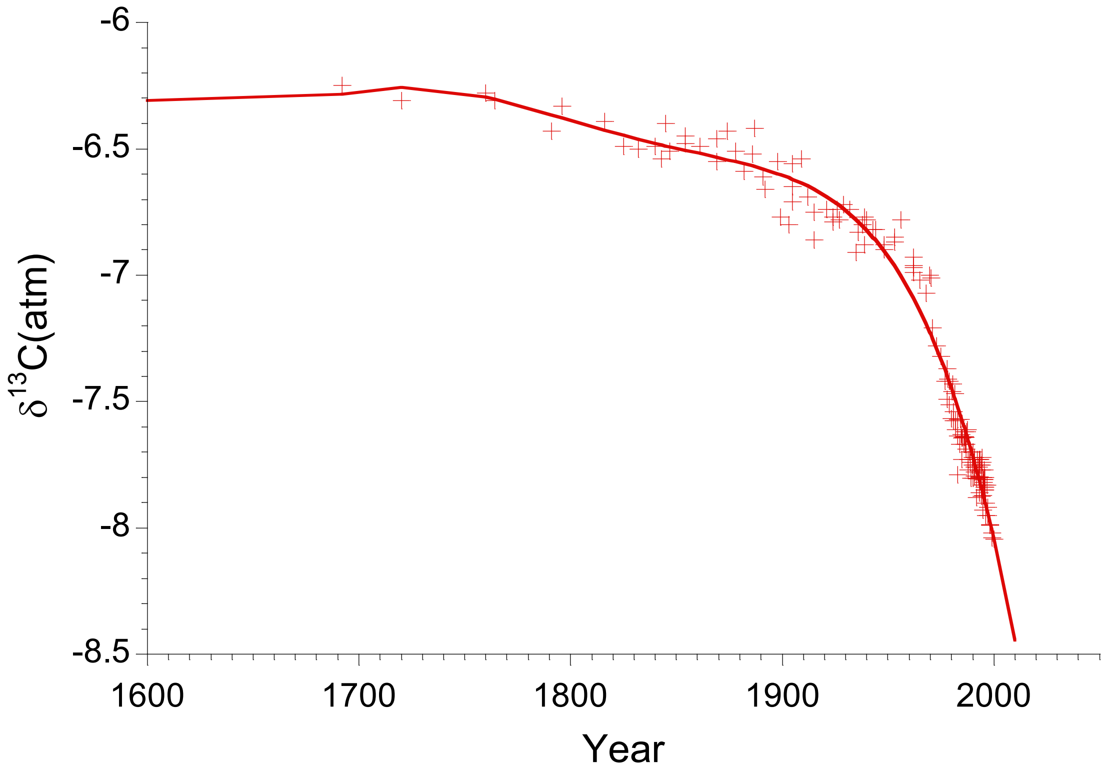

Figure B1: Historical change in atmospheric δ^{13}C (per mil) (1570–2010 AD) due to release of fossil carbon associated with anthropogenic activity (the so-called Suess effect), Source: Verburg (2007).

Table B2: Example of Suess correction applied to Palmitic Acid (C16:0) data from core RAN-5B.

Sample depth (cm)	**Age**	**Suess Correction (‰)**	**Raw δ^{13}C value**	**Corrected δ^{13}C value**
0–1	2010 AD	0.00	-28.44	-28.44
10–11	1977 AD	-1.08	-28.29	-29.37
70-71	633 AD	-2.15	-26.50	-28.65

IsoSources mixing model

The sources of terrigenous sediments deposited on the present-day seabed surface and at various times in the past, that are preserved in cores, were determined from analysis of the CSSI signatures of potential sources (i.e., soils) and mixtures (i.e., marine-sediment deposits). The library of isotopic signatures used included those derived from local (i.e., Bay of Islands) soils as well as other potential sources that were not sampled because (1) they could not be accessed or (2) no longer occur in the catchment (e.g., kumara gardens).

In the present study, the IsoSource mixing model (Phillips & Gregg, 2003) was used to evaluate the feasible sources of terrigenous sediments in the marine deposits. IsoSource requires a minimum of three sources and two isotopic tracers to run. In the present study, an iterative approach was taken to the selection of potential sediment sources, constrained by the recorded land-cover history. For example, citrus trees were not planted in large numbers in the Kerikeri catchment until the late 1920s (section 2.8.4) so that citrus is not a valid sediment source for sediments deposited before that time. The FA tracers Palmitic, Stearic and Arachidic Acids were most consistently present in the dated sediment cores and were most commonly used to evaluate historical sediment sources using IsoSource.

IsoSource is not a conventional mixing model in that it iteratively constructs a table of all possible combinations of isotopic source proportions that sum to 100% and compares these predicted isotopic values with the isotopic values in the sediment mixture (i.e., deposit). If the predicted and observed stable isotope values are equal or within some small tolerance (e.g., 0.1 ‰, referred to as the <u>mass-balance tolerance</u> by Phillips and Gregg, 2003) then that predicted stable-isotope signature represents a feasible solution. Within a given tolerance, there may be few or many feasible solutions.

The total number of feasible solutions (*n*) provides a measure of the confidence in the result. High values of *n* indicate many feasible solutions and hence there is low confidence in the result. As the value of *n* reduces towards 1 the level of confidence increases until *n* = 1, which represents a unique solution. It is rare to have an exact match or unique solution. In most cases there will be many feasible solutions and these can be statistically evaluated to assess the most likely combination of sources in the sediment sample. These feasible solutions are expressed as isotopic feasible proportions (%) with an uncertainty value equivalent to the standard deviation about the mean.

In practice, the tolerance is reduced by iteration within the IsoSource model to obtain the lowest *n* and therefore the highest confidence in the result. The tolerance required to obtain any feasible solutions will be greater than 0.1 ‰ if the isotopic values of the source tracers differ markedly from those of the sediment mixture in the receiving environment. Together, the tolerance and number of feasible solutions (*n*) for each sediment mixture provide measures of uncertainty in the results in addition to the standard deviation and the range of the isotopic proportions for each soil source. An example result from this analysis is shown in Table B1 below.

Table B1: Example of IsoSource model result, Core RAN-5B (Waikare Inlet), 30–31 cm depth (1914 AD). The mean, median and standard deviation (SD) values are shown.

Tolerance	n	Nikau			Kauri			Bracken		
		mean	median	SD	mean	median	SD	mean	median	SD
0.9	3	0.317	0.32	0.006	0.55	0.55	0.01	0.133	0.13	0.006

This sample comes from core RAN-5B, which was collected in the Waikare Inlet. The catchment even today remains largely under native forest and scrub land cover, so that sediments deposited in the inlet should reflect these land cover signatures. The sample was taken from 30–31-cm depth in the core, with radioisotope dating indicating that it was deposited in the early 1900s. The feasible isotopic proportions of the three major sediment sources are shown in the table (range = 0–1, where 1 = 100%). Although mean, median and standard deviation values are shown, minimum and maximum values of the feasible isotopic proportions for each source are also calculated. **The reporting solely of mean values is not adequate** and a measure of uncertainty, such as the minimum, maximum and/or standard deviation should be included in the results (Phillips & Greg, 2003).

The results indicate that the soils that make up the sediment-core sample are largely derived from native forest (kauri and nikau associations), with a small contribution from bracken. The presence of bracken is a key indicator of catchment disturbance/forest clearing. The presence of bracken pollen in sediment deposits has long been used in historical reconstructions of the New Zealand environment (e.g., McGlone 1983). However, bracken pollen reflects the presence of these plants growing in the general area and may or may not be indicative of bracken soils being eroded. By comparison, the presence of a CSSI bracken signature in a deposit positively indicates that some proportion of the sediment sample is composed of eroded bracken soil. The tolerance at 0.9 ‰ is a mid-range value, with values as low as 0.01 ‰ possible in some of the samples that were analysed. The number of feasible solutions (*n* = 3) is low, which also provides high confidence in these results.

Typically less than 5% of most sediment samples is composed of carbon, and the isotopic balance evaluated by IsoSource is only applicable to the carbon content of each source. These isotopically feasible proportions must therefore be converted to soil proportions using a linear scaling factor to estimate the percent contribution of each feasible soil source. This conversion of feasible isotopic source proportions to soil source proportions is described in a following section.

Conversion of isotopic proportions to soil proportions

The IsoSource model provides estimates of the isotopic-proportional contributions of each land-cover (i.e., soil) type in each marine sample. Thus, these results are in terms of carbon isotopic proportions and not source soil proportions. Furthermore, the stable isotope tracers account for a small fraction, typically less than 2%, of total organic carbon (OC) in the soil and OC accounts for typically <10% of the soil by weight. These factors mean that the contribution of each source soil to a sediment mixture will scale with the soil carbon content. Consequently, a linear correction based on the soil OC is required to estimate the proportion of each soil source in a sediment sample from a receiving environment (Gibbs 2008).

To convert the isotopic proportions to soil proportions ($S_n\%$) the simple linear correction equation below was used:

$$S_n\% = \frac{{}^{I_n}\!/_{C_n\%}}{\sum_n^1 \left({}^{I_n}\!/_{C_n\%}\right)} * 100$$

Where I_n is the mean feasible isotopic proportion of source soil *n* in the mixture estimated using an isotopic mixing model and $C_n\%$ is the percentage organic carbon in the source soil.

Because this calculation only uses the OC% in the source soils for linear scaling, the proportional contribution of each source soil is not influenced by any loss of carbon (e.g., total carbon, Fatty Acids etc.) in the sediment mixture due to biodegradation. The level of uncertainty in the mean soil proportion is the same as that defined by the standard deviation about the mean isotopic proportion.

A simple example of this linear correction is illustrated here by considering a solution composed of an equal mixture of three different sodium (Na) salts (3 x 1/3 each): sodium chloride (NaCl, molecular weight 58.45); sodium nitrate ($NaNO_3$, mw 85.0); and sodium sulphate (Na_2SO_4, mw 142.0). Consider each of these salts to represent a different source soil, each of which are present in a sediment mixture. The %Na represents the % carbon in each source soil. The %Na in each salt is calculated by dividing the atomic weight of sodium (23) by the molecular weight of each salt compound.

Table B3 below presents the calculations required to apply the linear correction equation using the sodium salts example. The ratio M%/S% for each salt and sum of this ratio (4.14) represent the numerator and denominator respectively in the conversion equation. Thus, for example the proportion of NaCl salt in the mixture is given by (0.85/4.14)*100 = 20.5%.

In the present study this linear conversion of isotopic proportions to soil source proportions was applied to the present-day surficial sediments. This correction process was not applied to the historical soil-source data from cores because %C data was not available for all soil sources. For example, although kumara and potato cultivation were important landcover types in some sub-catchments in the past this is no longer the case. In this situation the isotopic signatures of the plants themselves and not the labelled soils were used in the isotope modelling.

Table B3: **Example of the linear correction method to convert the isotopic proportions to soil proportions using sodium (Na) salt compounds as analogies to various soil sources present in a mixture.**

Salt type	%Na in salt (S%)	%Na in mixture (M%)	M%/S%	% salt in mixture
$NaCl$	39.4	33.3	0.85	20.5
$NaNO_3$	27.1	33.3	1.23	29.8
Na_2SO_4	16.2	33.3	2.06	49.7
SUM			4.14	