

Historical changes in sources of catchment sediment accumulating in Whangarei Harbour

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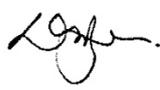
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Executive summary

Recent historical changes in the sources of sediment accumulating in Whangarei Harbour were determined using compound specific stable isotope (CSSI) analysis of dated cores, collected as part of the Whangarei Harbour Sedimentation Study (Swales et al., 2013). The results of the previous study indicate that sub soils derived from stream-bank erosion, gullyng and slips were major sources of contemporary sediments deposited in stream beds and at river deltas in the upper harbour. Native forest and pasture are the other primary sources of sediment. Sediments derived from the Hātea sub-catchment were the most widely dispersed and have accumulated in the upper and middle-reaches of Whangarei Harbour.

The potential adverse impacts of these various soil sources on aquatic receiving environments partly depends on the longevity or persistence of these sources over time. Sediments accumulating in receiving environments, such as Whangarei Harbour, can preserve long-term records to reconstruct environmental changes including sources of soil eroding from upstream land catchments.

The specific objectives of the present study are:

- Identify feasible sources of sediments in dated sediment cores using compound specific stable isotope tracers and an isotopic mixing model.
- Determine the persistence of the major soil sources over time.
- Relate changes in historical sediment sources to changes in sedimentation rates.
- Summarise the key results and their relevance to sediment management in the Whangarei Harbour system.

Accordingly, dated sediment cores previously collected from the Hātea arm of the upper harbour (WHG-11) and Parua Bay (WHG-14) by Swales et al. (2013) were selected for CSSI source analysis and modelling. These cores preserve records of sedimentation in the harbour over the last several decades, dating back to the mid-1970s (Hātea) and 1920s (Parua Bay) respectively.

CSSI data from the Swales et al. (2013) study were incorporated in the present work were possible to ensure continuity with the CSSI analysis of cores in the present study. Nine soil samples from the original study were re-analysed because of gaps in the CSSI data used for sediment tracing data. Sediment samples from replicate cores collected at sites WHG-11 and WHG-14 were also analysed for % carbon, bulk delta ¹³C stable isotope signatures as well as CSSI (fatty acids methyl ester, FAME). A FAME standard included with all three batches of samples analysed was used to correct data for inter-batch differences in delta ¹³C signatures for individual FAMEs. Close inspection of the corrected FA data for the potential soil sources determined that Myristic Acid (C14:0), Palmitic Acid (C16:0), Stearic Acid (C18:0) and Oleic Acid (C18:1) provided the most reliable tracers for modelling of historical changes in sediment sources. The bulk carbon stable isotope data were not incorporated in the analysis of soil sources due to the highly enriched isotopic signature of the Portland sediment source (core WHG-2, 0-1 cm, bulk delta ¹³C -10‰, per mil).

Isotope bi-plots of these tracers for potential sources and each sediment-core sample were used for selection of potential sources, which would be included in the IsoSource isotopic-mixing model. Outputs from the IsoSource model show the number of feasible solutions (*n*) and statistics (e.g., mean, median, min, max isotopic proportions). The isotopic tolerance, number and range of feasible

solutions provide measures of the reliability of the model estimates of the isotopic source proportions.

The Hātea core WHG-14 includes sediments dated back to the mid-1970s. At that time sediment accumulating at the core site were derived in approximately equal quantities from production (pine) forestry and native forest. Since the mid-1980s, the stable isotope data indicate that sediments derived from sub-soils (source: RBET, road cuttings) and reworked Portland sediments have dominated deposition (80–100%) at WHG-14. Abrupt changes in the relative proportions of the subsoil and Portland sources between dated core samples is likely to be partly due to the limited number of samples analysed so that transitions in sources over time are not well resolved. Regardless, these results suggests that subsoil erosion in the Hātea catchment (i.e., Raumanga type sediments) as well as Portland sediments, most likely reworked from the Mangapai Arm of the harbour, dominate sedimentation at site WHG-14. These results are consistent with the findings of Swales et al. (2013).

Parua Bay core WHG-11 includes sediments dating back to the mid-1920s and therefore provides a relatively long-term and detailed record of changes in the sources of eroded soil accumulating in the bay, associated with human activities in the catchment. The ^{210}Pb profile preserved in this core shows that SAR averaged $\sim 12 \text{ mm yr}^{-1}$ until the early-1950s and subsequently reduced to 2.9 mm yr^{-1} , most likely due to reduced sediment delivery as the intertidal flat has vertically accreted. Parua Bay is also remote from the areas of major land-use intensification and urbanisation in the upper-harbour catchments and rural land-use activities predominate to the present-day.

Analysis and modelling of the CSSI data indicates that soils derived from production (pine) forestry were the main sources of eroded soils accumulating in Parua Bay (at WHG-11) until at least the mid-1970s, accounting for 40–100% of the sediment deposited. Portland sediments are detected from the mid-1940s and until relatively recently (i.e., ~ 2003). The proportion of Portland sediments is highest in sediments deposited during the period ~ 1993 – 2003 , accounting for more than 90% of the intertidal sediments at this core site. Although dairy farming was practiced in the area since at least the early 1900s (appendix), soils associated with this land use were only detected in sediments deposited within the last decade (i.e., PASTURE-1, ~ 2007 onwards). Sediments derived from other eroded pasture (Ha-2b) and native forest are the other main contributors to recent sedimentation (Figure 13).

In summary, the CSSI data highlight the persistence and major contribution of the Portland sediment source over the last ~ 70 years, despite the fact that discharge of washings from the cement plant to the harbour ceased in the early 1980s. The long-term dispersal of these isotopically-distinctive sediments from the Mangapai arm, confirms that remobilisation and export of sediments by waves and tidal currents from the upper to the lower harbours is a key process controlling harbour sedimentation. In Parua Bay (WHG-11), pine and pasture are the major sources of eroded catchment soils, although the relative contribution of soil eroded from the Parua catchment in comparison to other sub-catchments (i.e., non-local sources) cannot be determined from these data. At Hātea (WHG-14) the dominance of the Portland sediment is consistent with its relatively close proximity to this source. These data also show that eroded sub-soils are the major source of catchment-derived sediments since the mid-1980s. These findings are consistent with those of previous studies using complimentary measurements and modelling (Millar, 1980; Swales et al. 2013).

1. Introduction

Recent historical changes in the sources of sediment accumulating in Whangarei Harbour were determined using compound specific stable isotope (CSSI) analysis of dated cores. These cores were collected as part of the 2012 NRC Whangarei Harbour Sedimentation Study (Swales et al. 2013). Cores from Parua Bay (WHG-11) and the Hatea Arm (WHG-14) of the upper harbour were analysed in the present study to reconstruct, in detail, the changes in the major sources of sediment accumulating at these sites over the last several decades (Figure 1).

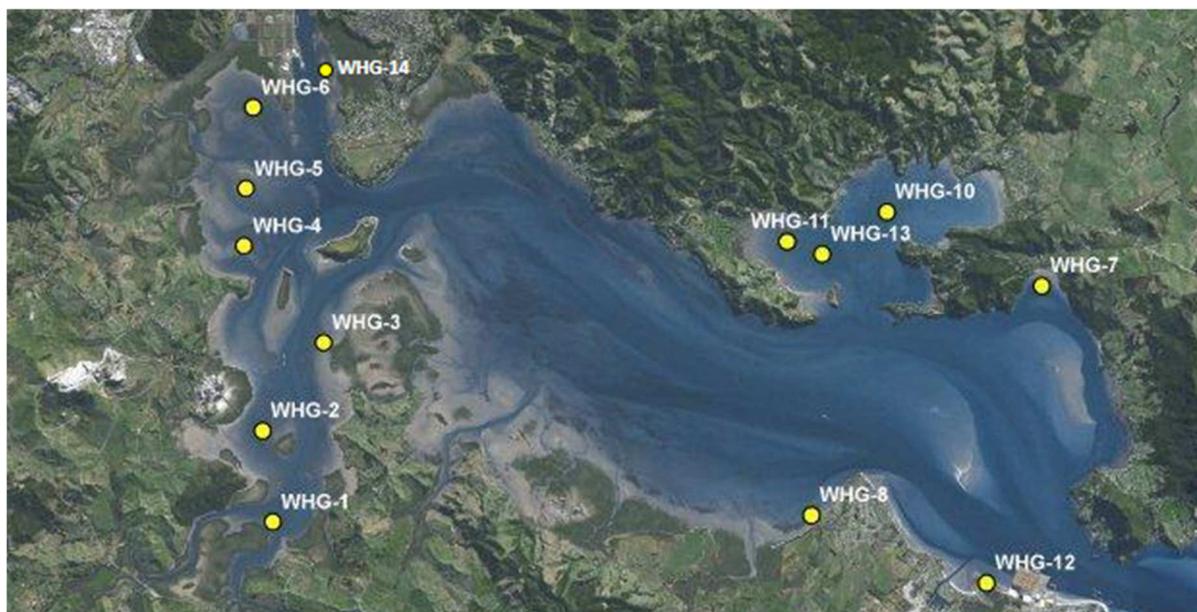


Figure 1: Location of sediment cores collected from Whangarei Harbour as part of the 2012 study. Catchment landcover has been substantially modified as a result of deforestation since the mid-1800s. Prior to arrival of people, the indigenous forest was composed of broadleaf community dominated by tararire, puriri, kohekohe and kahikatea close to the harbour and river flats, with kauri and podocarps on steep lands (New Zealand Soil Bureau 1968). Catchment deforestation and conversion for pastoral agriculture was largely completed prior to the 1920s, with most native forest remnants being in State Forest reserves. Saw mills did continue to operate at that time and logs were exported to Auckland from Parua Bay (Ferrar 1925). Today, indigenous forest accounts for ~20% of the total catchment area and is limited to isolated forest remnants in small sub-catchments north of the harbour and the Pukenui forest, which borders the western boundary of Whangarei City (Figure. 2). High producing exotic grassland, for cattle and dairy farming accounts for 50% of the total catchment area, with plantation forestry (10%) and urban areas (10%) being significant secondary land uses. Additional information on the land-use history of the Whangarei Harbour catchment since the mid-1800s was provided by Mr Bob Cathcart (Appendix).

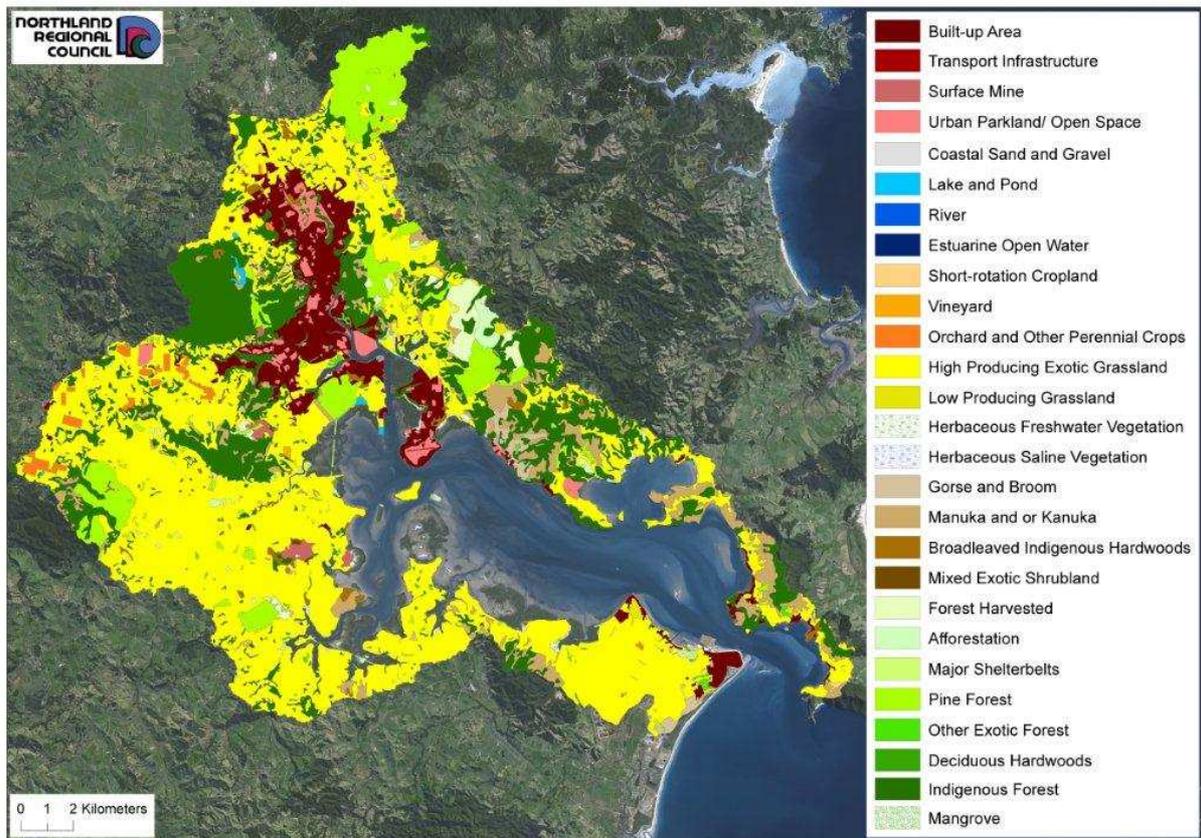


Figure 2: Present-day land use in the Whangarei Harbour catchment. Source: New Zealand Land Cover Database (LCDB2, 2001) and Northland Regional Council.

The specific objectives of the present study are:

- Identify feasible sources of sediments in dated sediment cores using compound specific stable isotope tracers and an isotopic mixing model.
- Determine the persistence of the major soil sources over time.
- Relate changes in historical sediment sources to changes in sedimentation rates.
- Summarise the key results and their relevance to sediment management in the Whangarei Harbour system.

2. Previous work

The Whangarei Harbour Sedimentation Study 2012 included an assessment of contemporary terrigenous sediment sources and their dispersal in the harbour. The results of that study indicate that:

- Sediments derived from the Hātea sub-catchment were the most widely dispersed and had accumulated in the upper and middle-reaches of Whangarei Harbour (Figure 3). The spatial distribution pattern indicated that sediment from the Hātea River system had also dispersed east along the northern shores beyond the Onerahi Peninsula.

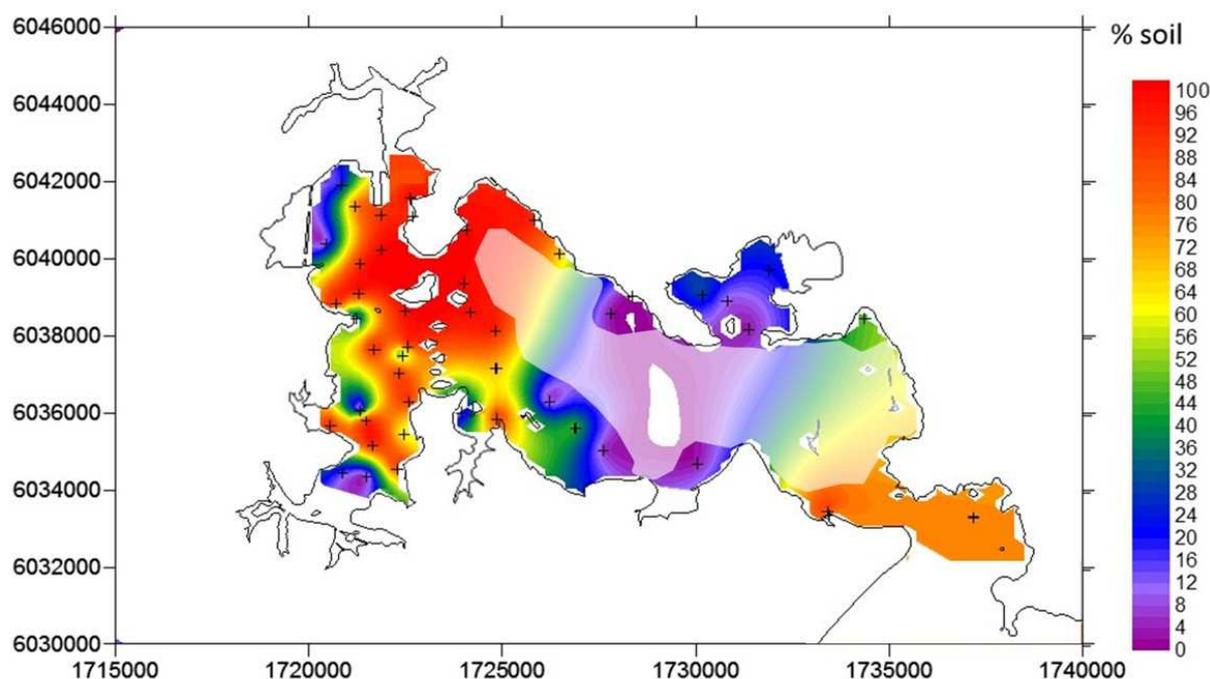


Figure 3: Proportion of Hātea sub-catchment soils in harbour sediments. The fogged area covers indicative extrapolated areas with no data support. Map co-ordinate system: NZTM2000. Source: Swales et al. (2013).

- Sediments derived from Otaika and the Mangapai sub-catchments and Portland cement works have accumulated near these sources (Figures 4 and 5). Portland sediments were also present in the surficial sediments of Parua Bay and elsewhere in the middle reaches of the harbour in the late 1970s (Millar 1980). This indicates that these montmorillonite-clay rich sediments were more widely dispersed during the 74 years (1918–1982) that the cement plant discharged reject washings to the upper harbour. The present-day distribution of the Portland sediments reflects the large quantities of this material deposited in the Mangapai arm close to the source.

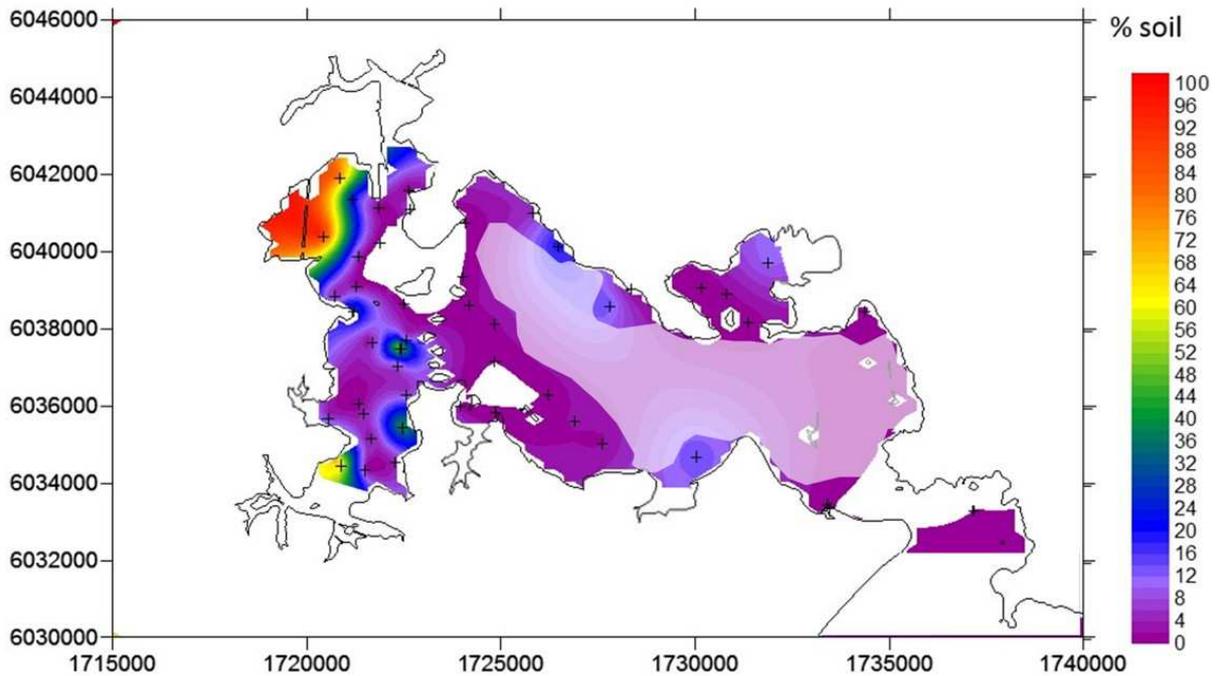


Figure 4: Proportion of Otaika sub-catchment soils in harbour sediments . The fogged area covers indicative extrapolated areas with no data support. Map co-ordinate system: NZTM2000. Source: Swales et al. (2013).

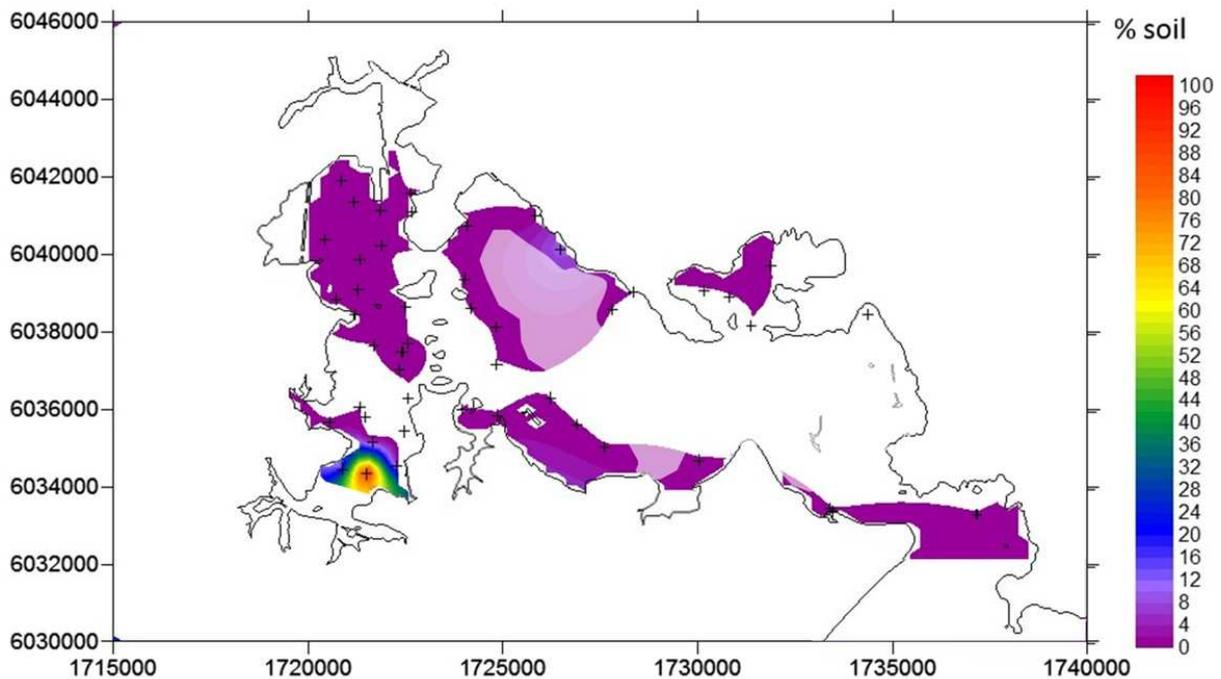


Figure 5: Proportion of Mangapai sub-catchment soils in harbour sediments. The fogged area covers indicative extrapolated areas with no data support. Map co-ordinate system: NZTM2000. Source: Swales et al. (2013).

The major sources of sediment by land use and sub-catchment were also evaluated for the Hātea, Otaika and Mangapai catchments. The results of that work relevant to the present study indicate that:

- Sub soils derived from stream-bank erosion, gullyng and slips are major sources of sediments deposited in stream beds and at river deltas in the upper harbour. Native forest and pasture are the other primary sources of sediment. The contributions from pasture and subsoil are likely to reflect bank erosion by stock direct access to streams rather than erosion from flat paddocks.
- **Hātea:** almost all (>90%) of the recent sediment in the Hātea River at Mair Park came from the catchment upstream of Tikipunga with <10% coming from the Otangarei Stream system and the steep forest land on the eastern side of the river. That sediment is composed of soils from pine forest (24%), pasture of all types (11%), pasture sub-soil (7%) and native forest including totara (59%). It should be noted that the soils under pasture that have recently been established following deforestation will retain the stable-isotope signature of the original forest for several years or more.
- The disproportionately low proportion of upper Hātea River sediment in the river delta sample is most likely due to the blending of stable-isotope signatures associated with the disturbance of delta sediment deposits resulting from the extensive dredging and reclamation works at the Port of Whangarei since the 1950s. The few mm of recent Hātea sediment would be diluted by this blended sediment in the 20-mm thick surficial sediment samples that were analysed.
- In the Raumanga Stream, most (90%) of the stream sediment were composed of sub-soils most likely derived from bank erosion and slips in the Maunu Road tributary. This source potentially includes the Waiarohia Stream although the latter was not sampled. The main Raumanga Stream contributed up to 5% as subsoil with up to 4% native forest including totara. Pasture signature was present but at <1 %.
- **Otaika:** 65% of the sediment comes from the upper catchment (above the Puwera Stream confluence), including the Otakaranga Stream catchment and the Otaika Valley streams. The remaining sediment is contributed from pasture (25%) and native forest (8%) from the steeper northern hills.
- **Mangapai:** Sediment in the Mangapai River delta was collected at core site WHG-1. The catchment sediment source contributions were evaluated using the land-use soil (stable-isotope) signatures. The results indicate that around 75% of the sediment was derived from bank erosion, which includes dirt roads and road cuttings. The rest of the sediment came from pine forestry (10%), pasture (7%) and native forest (8%).

On a *pro rata* basis the best estimate of the four main soil source land-use types discharged into the upper harbour from the three river inflows is summarised in Figure 6. The subsoil component includes bank erosion and native forest component includes totara. There is high uncertainty on the proportions of soil from the Hātea River because of the isotopic disconnect in the lower Hātea River (Swales et al. (2013).

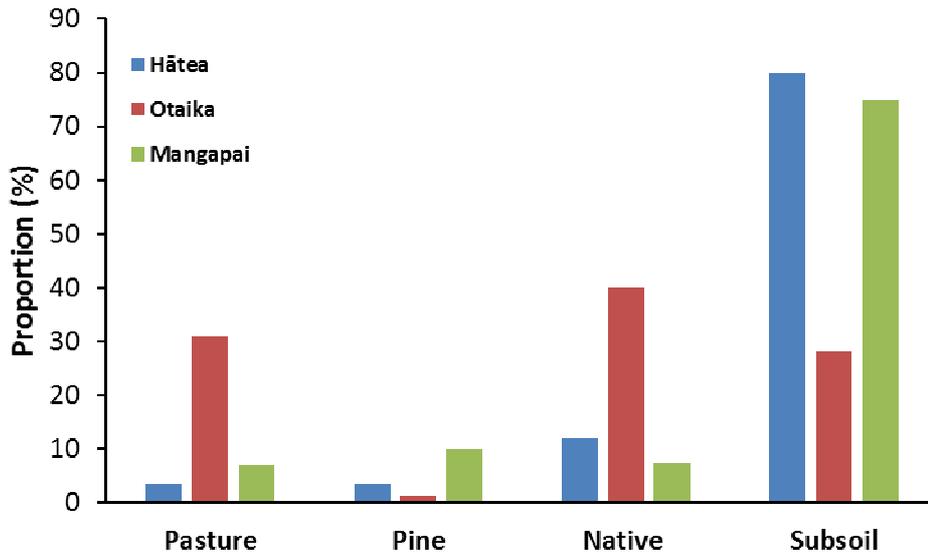


Figure 6: Summary of the proportions of land use soils discharged from the three main inflows. Source: Swales et al. (2013).

Sediment accumulation rates (SAR) were determined from lead-210 (^{210}Pb) and caesium-137 (^{137}Cs) dating of the sediment cores. This analysis showed that:

- The upper harbour has substantially infilled with eroded catchment soils. Mud is exported from the upper to the lower harbour where it has been accumulating in the bays and inlets that indent the northern shoreline.
- In the Mangapai arm, ^{210}Pb SAR have averaged 3–4.9 mm/yr over the last 40–100 years. Apparent declines in SAR during the early–mid 20th century are most likely due to reduced sediment delivery associated with a reduction in tidal inundation as the intertidal flats have accreted over time.
- In the Hātea arm, muds are accumulating on intertidal flats in the lee of the Onerahi Peninsula. ^{210}Pb SAR at core sites WHG-6 and WHG-14 were 2.8 and 6.5 mm/yr respectively (Figure 6). By contrast, long-term mud accumulation is not occurring on the intertidal flats west of Limestone Island most likely due to their exposure to 5 km+ east–west wave fetch.
- In Parua Bay, rapid vertical accretion of the intertidal flats occurred until the early 1950s when reduced tidal inundation sediment delivery (Figure 7). Today, the intertidal flat is accumulating sediment (2.9 mm/yr) at a similar rate to the central sub-tidal basin (2.2 mm/yr).

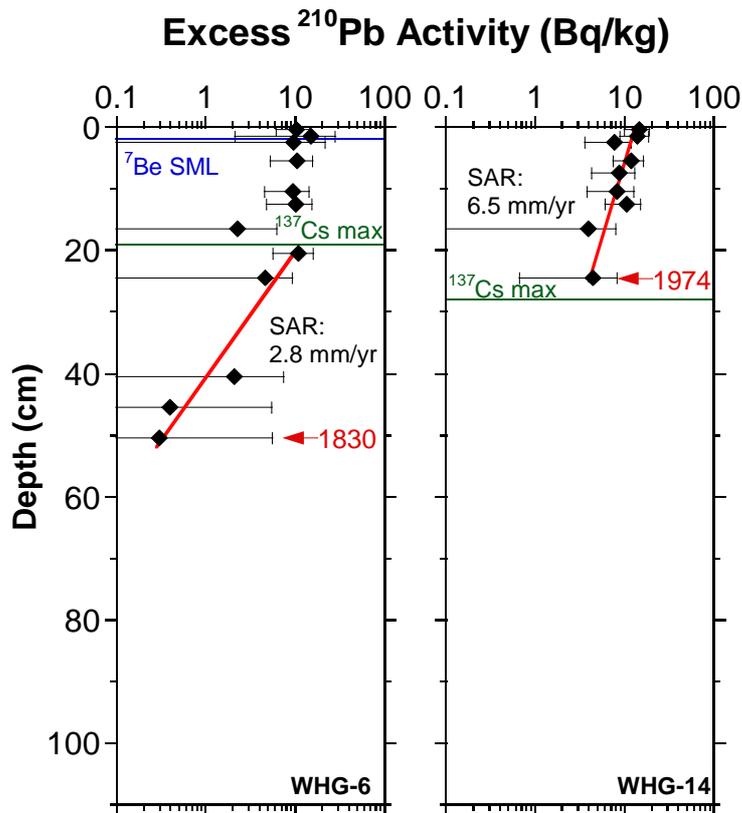


Figure 7: Hātea Arm: sediment accumulation rates (SAR) at core sites WHG-6 and WHG-14. Excess ^{210}Pb activity profiles with 95% confidence intervals show. Time-averaged SAR derived from regression fit to natural-log transformed data, with estimated ages of key depth horizons (red text). The beryllium-7 (^7Be) surface mixed layer (SML) and maximum depth of caesium-137 (^{137}Cs max) in each sediment core is also shown. Sediments below the ^{137}Cs max depth were deposited before the 1950s. Radioisotope activities are expressed in S.I. units of Becquerel's (Bq), which is equivalent to one radioactive disintegration per second. Source: Swales et al. (2013).

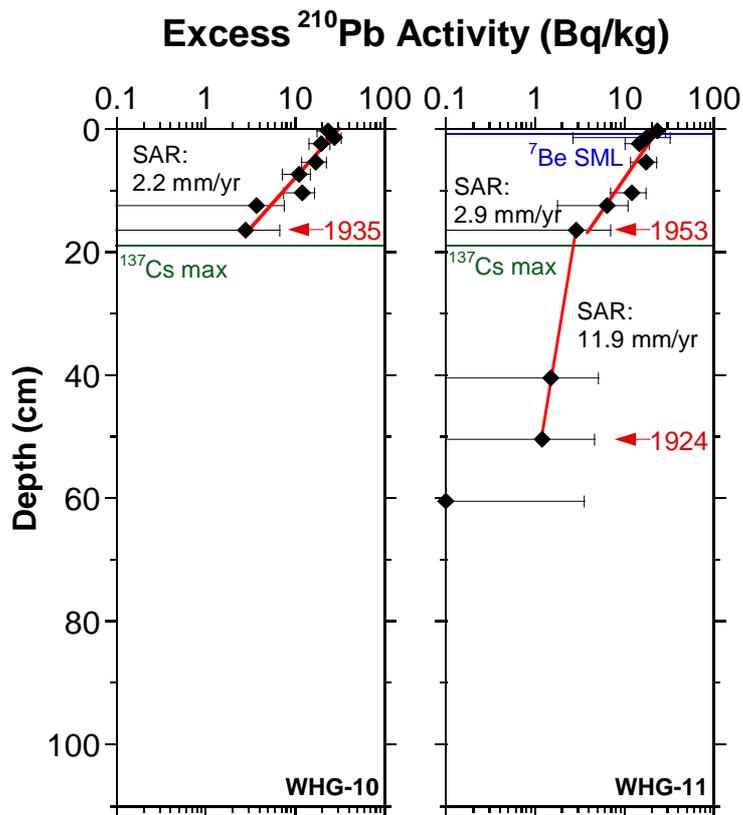


Figure 8: Parua Bay: sediment accumulation rates (SAR) at core sites WHG-10 and WHG-11. Excess ^{210}Pb activity profiles with 95% confidence intervals show. Time-averaged SAR derived from regression fit to natural-log transformed data, with estimated ages of key depth horizons (red text). The beryllium-7 (^{7}Be) surface mixed layer (SML) and maximum depth of caesium-137 (^{137}Cs max) in each sediment core is also shown. Sediments below the ^{137}Cs max depth were deposited before the 1950s. Radioisotope activities are expressed in S.I. units of Becquerel's (Bq), which is equivalent to one radioactive disintegration per second. Source: Swales et al. (2013).

3. Methods

The present study incorporates CSSI soil source data from the earlier Swales et al (2013) study. Nine soil samples from the original study were reanalysed (November 2014) because of gaps in the Fatty Acid Methyl Ester (FAME) data, most likely due to low concentrations of these compounds in those soil samples. Larger sub-samples were therefore extracted to provide reliable stable isotope signatures for the FAME tracers. This included the Portland sediment from core site WHG-2 (0-1cm sample) used in the Swales et al. (2013) study. Results from seven of the nine reanalysed soil samples were adopted in the present study, although not the Portland WHG-2 data, as the suite of FAME tracers adopted were included in the 2012 data (Table 1).

Sediment samples from replicate cores collected at sites WHG-11 and WHG-14 were also analysed for % carbon, bulk delta ^{13}C stable isotope signatures as well as CSSI (fatty acids).

A NIWA FAME standard included with all three batches of samples were used to correct raw data for inter-batch differences in FAME values. The data were also subsequently corrected for the methyl-group (MeOH) delta ^{13}C signature of each batch. Corrected CSSI sediment-core data were also adjusted for the Suess Effect, which is the progressive depletion of the atmospheric CO_2 signature largely due to the combustion of fossil fuels. This process also results in a depletion of soil delta ^{13}C signatures as plants utilise CO_2 in photosynthesis and subsequently label potential soil sources. The annual rate of delta $^{13}\text{CO}_2$ depletion in New Zealand is 0.025‰ per year (source: NIWA). In the present study the sediment core data were corrected to the year 2010. This correction of sediment-core data (i.e., mixtures) for the Suess Effect enables direct comparison of the historical sediment signatures with those for the contemporary soil and river-sediment signatures (i.e., potential sources). Full details of the CSSI method are included in the appendices.

Close inspection of the final $\delta^{13}\text{C}$ FA data bi-plots for potential soil sources indicated that Myristic Acid (C14:0), Palmitic Acid (C16:0), Stearic Acid (C18:0) and Oleic Acid (C18:1) provided the most reliable tracers for modelling of historical changes in sediment sources (Table 1). The latter three FA tracers were used to model sources in core WHG-11 whereas C14:0, C16:0 and C18:0 were used in core WHG-14, as informed by the isotopic bi-plots (Figures 9–11).

The bulk carbon stable isotope data were not incorporated in the analysis of soil sources due to the highly enriched isotopic signature of the Portland sediment source (core WHG-2, 0-1 cm, bulk delta ^{13}C -10‰, per mil).

Table 1: Compound-specific stable isotope signatures of the Whangarei soil and sediment used to model historical changes in sediment sources. Note: C12:0 and FAME-specific corrections were applied to original 2012 sample data so that data was consistent with December 2014 soil re-analysis data.

Sources_ Site ID	Land use	Sample ID	Batch (year)	C14:0	C16:0	C18:0	C18:1
Otaika-2	Old totara with understory	OA157/51	2014	-33.37	-31.92	-30.77	-33.07
Ha-2a	Pasture (steep, horses)	OA157/59	2014	-30.57	-28.38	-28.67	-28.81
Ha-2b	Kiripaki loam – flat eroded pasture	OA157/60	2014	-30.29	-26.91	-27.77	-24.12
RAU-B1	Raumanga bank erosion	OA157/64	2014	-27.97	-29.47	-29.00	-27.86
RBET	Road cutting	OA157/70	2014	-27.93	-28.29	-27.94	-28.12
Pine-385	Forest recent fell	OA157/86	2014	-29.42	-28.26	-27.83	-27.65
Pine-386	Forest Mature	OA157/87	2014	-31.58	-25.25	-26.19	-23.41
PASTURE-1	Dairy pasture	OA157-81	2012	No data	-22.59	-29.06	-22.12
TOTARA	Totara (generic)	OA157-82	2012	No data	-29.96	-30.35	-29.60
OTAIKA-2 NF	Flood-plain native forest, NE of Otaika	OA157-83	2012	-35.97	-31.34	-34.44	-31.97
NATIVE	Native (generic)	OA157-84	2012	-32.48	-29.44	-25.44	-23.11
Portland cement	Core WHG-2 (0-1 cm), Mangapai Arm	OA157/37	2012	-26.50	-21.83	-20.39	-22.85
Portland cement	Core WHG-2 (0-1 cm), Re-analysis December 2014	OA157/37	2014	-24.66	-22.90	-23.57	-22.45

The isotopic bi-plots of the C14:0, C16:0, C18:0 and c18:1 tracers for potential sources and sediment-core samples were used for initial selection of potential sources (Figures 9 to 11). The plots show the relative isotopic distance of potential catchment soils from each sediment-core sample (i.e., mixture). Generally, potential sources within ~3 per mil of a given sediment-core sample were initially included in the model run to estimate source contributions (i.e., isotopic proportion) to each dated sediment-core sample. The sources included in the final model run for each mixture were refined by iteration of the IsoSource model. This was achieved by progressive reduction of the isotopic tolerance (minimum 0.05), with isotopic proportions calculated at 1% increments. Outputs from the IsoSource model also include the number of feasible solutions (n) and statistics (e.g., mean, median, min, max isotopic proportions).

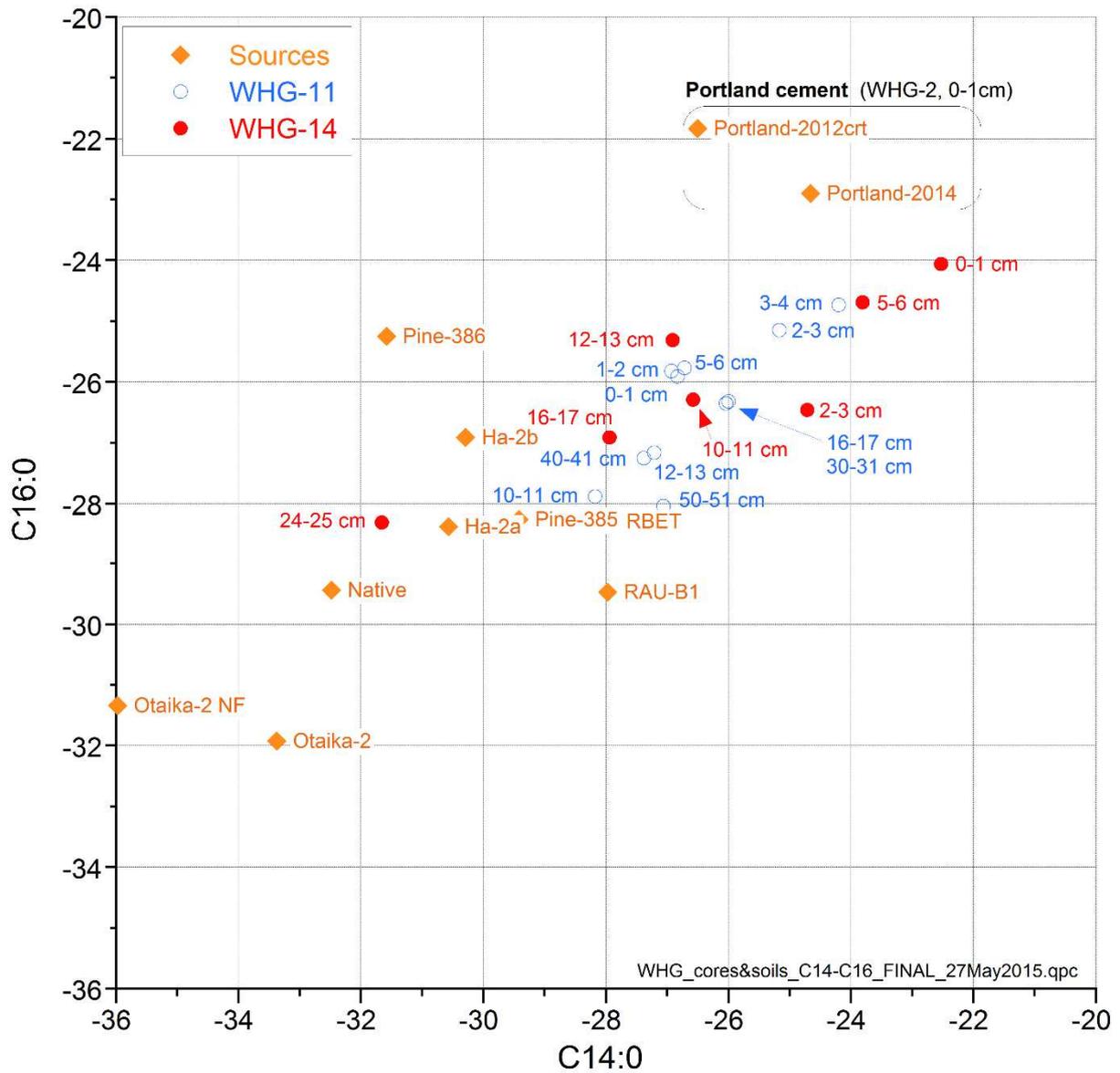


Figure 9: Isotope bi-plot of Myristic Acid (C14:0) and Palmitic Acid (C16:0) for Whangarei catchment soils (potential sources) and dated sediment-core samples (mixtures). The multiple symbols for cores WHG-11 and WHG-14 represent the isotopic signatures from each dated sediment layer, with depth range shown. The isotopic differences indicate differences in the mix of sediment sources for that dated layer.

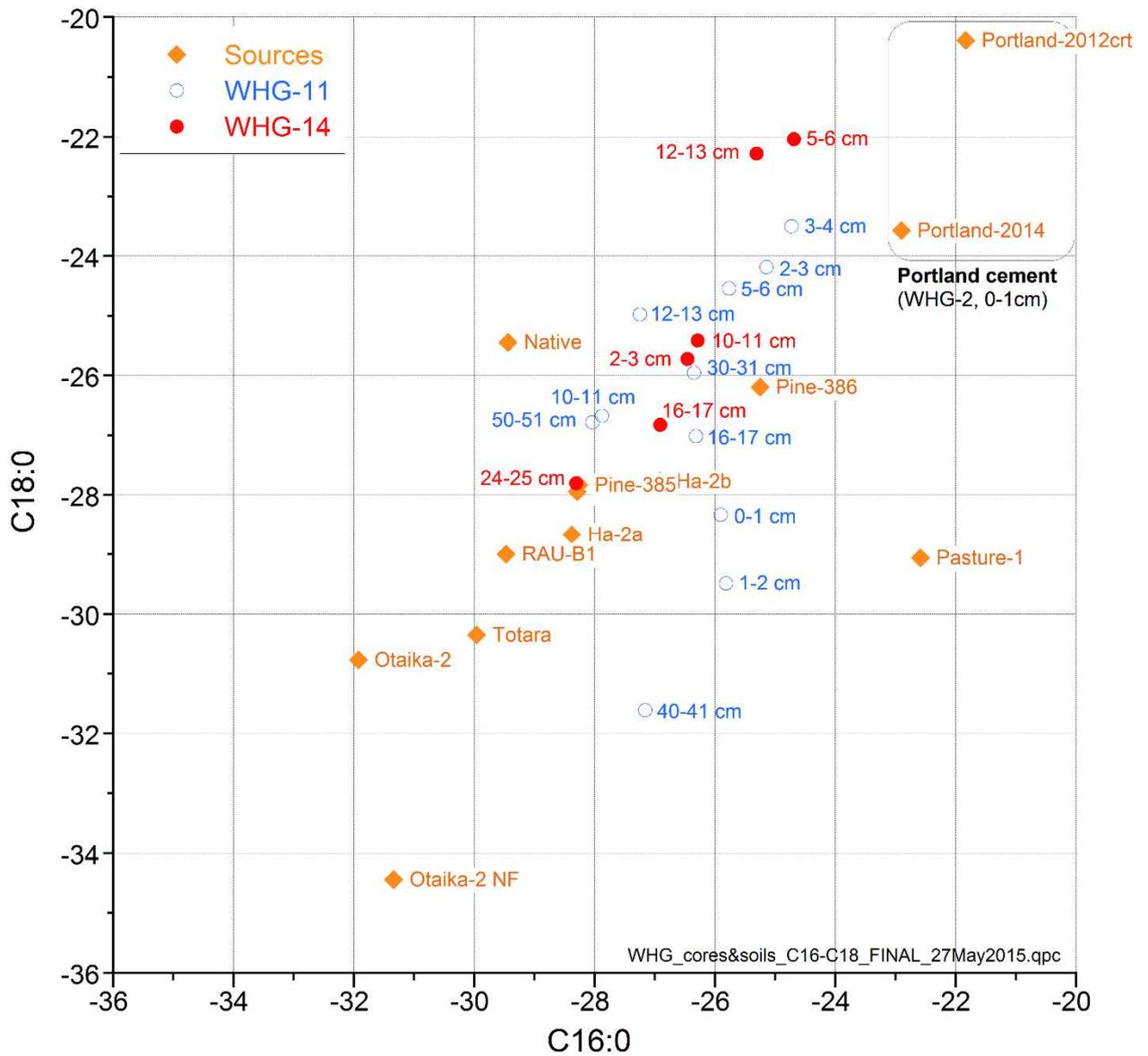


Figure 10: Isotope bi-plot of Palmitic Acid (C16:0) and Stearic Acid (C18:0) for Whangarei catchment soils (potential sources) and dated sediment-core samples (mixtures). The multiple symbols for cores WHG-11 and WHG-14 represent the isotopic signatures from each dated sediment layer, with depth range shown. The isotopic differences indicate differences in the mix of sediment sources for that dated layer.

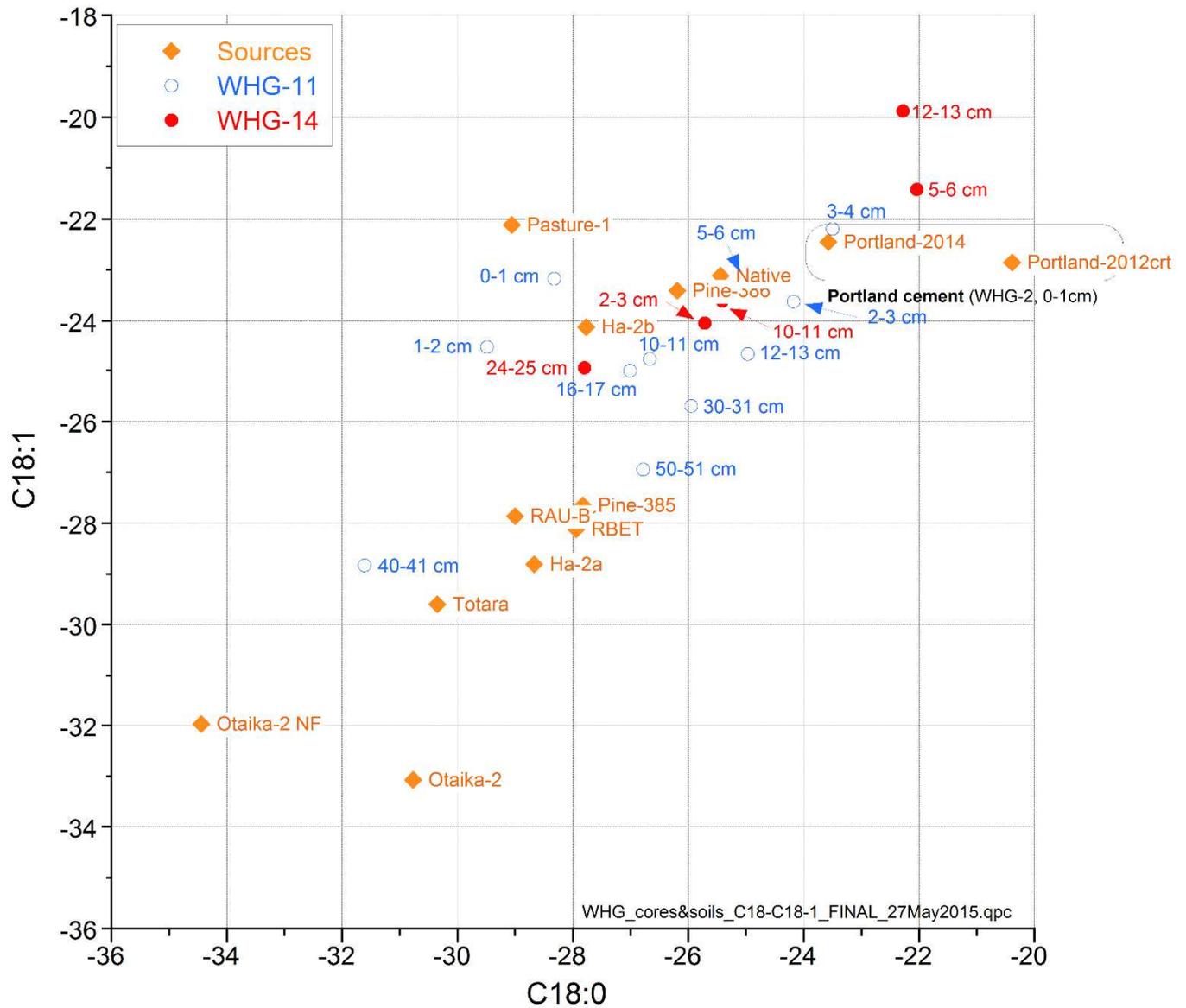


Figure 11: Isotope bi-plot of Stearic Acid (C18:0) and Oleic Acid (C18:1) for Whangarei catchment soils (potential sources) and dated sediment-core samples (mixtures). The multiple symbols for cores WHG-11 and WHG-14 represent the isotopic signatures from each dated sediment layer, with depth range shown. The isotopic differences indicate differences in the mix of sediment sources for that dated layer.

Tables two and three summarise the performance of the IsoSource mixing model for each dated sediment-core sample. A small isotopic tolerance, small number and range of feasible solutions provide measures of the reliability of the model estimates of the isotopic proportions.

Table 2: Core WHG-11 (Parua Bay). Summary of IsoSource model performance for each sediment-core sample, where the tolerance (per mil) is the minimum tolerance for which a solution can be obtained. The number of feasible solutions (*n*) provides a measure of the uncertainty of the calculation. A value of unity indicates only one possible solution. Note that a minimum of 3 sources are required for modelling, although in some cases only two sources may contribute to the sediment mixture.

Sample depth (cm)	Tolerance	<i>n</i>	No. of sources
0–1	0.27	1	4
1–2	0.63	3	3
2–3	0.67	1	3
3–4	0.47	1	2
5–6	0.19	34	4
10–11	0.05	35	4
12–13	0.51	2	3
16–17	0.12	11	4
30–31	0.18	1	3
40–41	1.5	1	2
50–51	0.61	2	3

Table 3: Core WHG-14 (Hātea). Summary of IsoSource model performance for each sediment-core sample, where the tolerance (per mil) is the minimum tolerance for which a solution can be obtained. The number of feasible solutions (*n*) provides a measure of the uncertainty of the calculation. A value of unity indicates only one possible solution. Note that a minimum of 3 sources are required for modelling, although in some cases only two sources may contribute to the sediment mixture.

Sample depth (cm)	Tolerance	<i>n</i>	No. of sources
0–1	data	not	reliable
2–3	1.33	1	2
5–6	1.6	1	2
10–11	0.34	2	3
12–13	0.59	19	3
16–17	0.05	112	4
24–25	0.38	11	4

The mean isotopic proportions calculated by the IsoSource model were converted to soil proportions using the % carbon content. The stable isotope tracers account for a small fraction, typically less than 2%, of total organic carbon (OC) in the soil samples 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 mean isotopic proportions to soil proportions ($S_n\%$), the simple linear correction equation below was used:

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

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 organic carbon content (C %) 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.

4. Results

The Swales et al. (2013) found that the major sources of contemporary catchment-derived sediments delivered to Whangarei Harbour, in order of contribution, are: subsoils, soils from native forest, production (pine) forestry and pasture (Figure 5). The subsoil source also includes bank erosion.

Historically, the Portland cement works was a major source of fine sediments discharged to the harbour (1918–1982). In fact, discharge records for the cement works also indicate that sediment inputs to the harbour from the plant during the 1960s and 1970s exceeded sediment delivery to the harbour from rivers. Evidence presented by Swales et al (2013) as well as the previous work of Millar (1980) suggests that a large fraction of the Portland clay washing were exported from the upper to the lower harbour and preferentially deposited in Parua Bay. Stable-isotope data show that the present-day distribution of Portland sediments is limited to the intertidal surficial sediments in the immediate vicinity of the Portland wharf in the Mangapai arm of the harbour.

Reconstruction of historical changes in sources of eroded soils accumulating in the Hātea Arm of the upper harbour and Parua Bay determined from CSSI analysis and modelling of samples from the dated sediment cores reveals the major sources of soils and their persistence over time. Mean soil proportions (%) determined for sediment cores WHG-11 (Parua Bay) and WHG-14 (Hātea Arm) are presented in figures twelve and thirteen. Tables four and five present data for mean isotopic proportions (%) and range (i.e., minimum and maximum values). These tabulated data show that the absolute range of feasible isotopic proportions in most cases are relatively narrow (i.e., within $\pm 5\%$ of the mean) or have unique solutions so that we can have confidence in the estimated mean soil proportions.

Note that in interpreting figures twelve and thirteen, the years plotted on the y axis represent the lead-210 (^{210}Pb) age for the mid-depth of each slice. For example, the core sediments were sampled as 1-cm slices so that the lead-210 year is the mid-range age for that slice. In core WHG-14, ^{210}Pb SAR has averaged 6.5 mm yr^{-1} since the mid-1970s so that each 1-cm slice represents a relatively short (~ 1.5 years) time period. By comparison, ^{210}Pb SAR in core WHG-14 has averaged 2.9 mm yr^{-1} since the early-1950s, so that each 1-cm slice represents a longer (~ 3.5 year) time period (Figures 7 and 8).

4.1 Hātea (core WHG-14)

The Hātea core WHG-14 includes sediments dated back to the mid-1970s. At that time sediment accumulating at the core site were derived in approximately equal quantities from production (pine) forestry and native forest (Figure 12). Since the mid-1980s, the stable isotope data indicate that sediments derived from subsoils (source: RBET, road cuttings) and reworked Portland sediments have dominated deposition (80–100%) at the WHG-14 core site. Figure 12 shows abrupt changes in the relative proportions of the subsoil and Portland sources between dated core samples. This is likely to be at least partly due to the discrete sampling of the core and limited number of samples analysed so that transitions in sources over time are not well resolve. Regardless, these results suggests that subsoil erosion in the Hātea catchment (i.e., Raumanga type sediments) as well as Portland sediments, most likely reworked from the Mangapai Arm of the harbour, dominate sedimentation at site WHG-14. These results are consistent with the findings of Swales et al. (2013).

Core WHG-14: Hatea

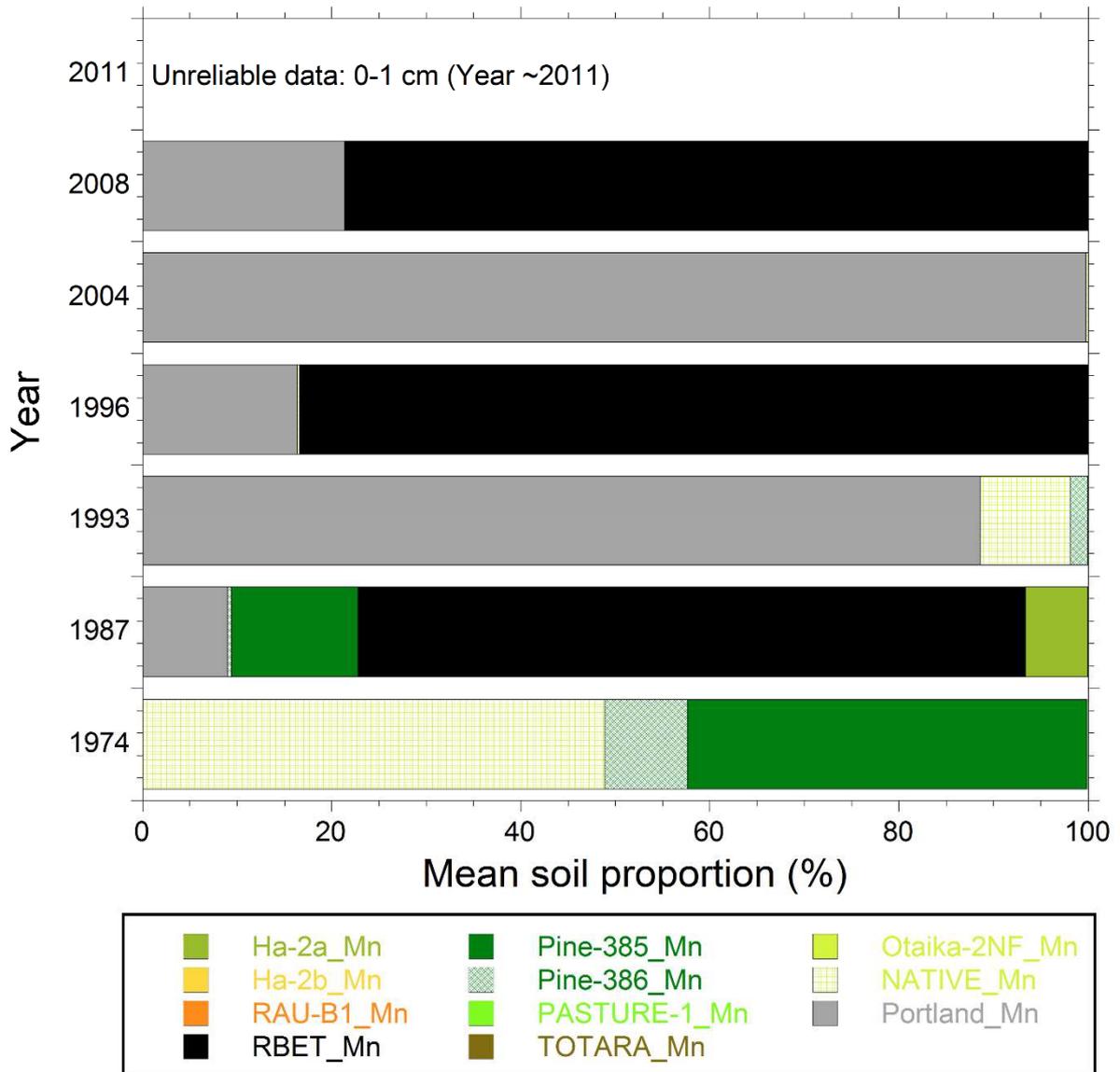


Figure 12: Core WHG-14 (Hatea). Mean soil proportions (%) for each dated sediment-core sample estimated from: (a) IsoSource modelling of isotopic proportions; and (b) linear scaling to soil % based on source-soil carbon content. Land uses are of the type indicated in the key: Pasture steep (Ha-2a); Kiripaki loam –flat eroded pasture (Ha-2b); Raumanga Bank erosion (RAU-B1); Road cutting (RBET); Pine-recent fell (Pine-385); Pine-mature fell (Pine-386); Dairy pasture (PASTURE-1); Flood plain native forest NE of Otaika (Otaika-2NF); Portland sediment at WHG-2, Mangapai Arm (Portland). Results from 2011 are considered unreliable and have not been plotted.

4.2 Parua Bay (core WHG-11)

Parua Bay core WHG-11 includes sediments dating back to the mid-1920s and therefore provides a relatively long-term and detailed record of changes in the sources of eroded soil accumulating in the bay, associated with human activities in the catchment. The ^{210}Pb profile preserved in this core shows that SAR averaged $\sim 12 \text{ mm yr}^{-1}$ until the early-1950s and subsequently reduced to 2.9 mm yr^{-1} , most likely due to reduced sediment delivery as the intertidal flat has vertically accreted (Figure 7).

Parua Bay is remote from the areas of major land-use intensification and urbanisation in the upper-harbour catchments and rural land-use activities predominate to the present-day (Figure 2).

The reconstruction indicates that soils derived from production (pine) forestry were the main sources of eroded soils accumulating in Parua Bay (at WHG-11) until at least the mid-1970s, accounting for 40–100% of the sediment deposited. Portland sediments are detected from the mid-1940s and until relatively recently (i.e., ~ 2003). The proportion of Portland sediments is highest in sediments deposited during the period ~ 1993 – 2003 , accounting for more than 90% of the intertidal sediments at this core site. Although dairy farming was practiced in the area since at least the early 1900s (appendix), soils associated with this land use were only detected in sediments deposited within the last decade (i.e., PASTURE-1, ~ 2007 onwards). Sediments derived from other eroded pasture (Ha-2b) and native forest are the other main contributors to recent sedimentation (Figure 13).

Sediment-transport modelling undertaken by Swales et al. (2013) and mapping of surficial sediment (clay) mineralogy by Millar (1980) indicates that a substantial fraction of the sediment accumulating in this basin is likely to have been derived from sources other than Parua Bay catchment. In particular, sediment has been exported from the Hātea and Otaika rivers due to infilling of the upper harbour at least since the 1970s. Millar's (1980) study indicated the presence of Portland clays in Parua Bay surficial sediments in the late 1970s. The presence of Portland sediments in core WHG-11 over several decades (1940s –early-2000s) and long after discharge of Portland washings to the harbour ended (1982) indicates that Portland sediments reworked from the upper harbour have been a persistent and large source of fine sediment accumulating in Parua Bay.

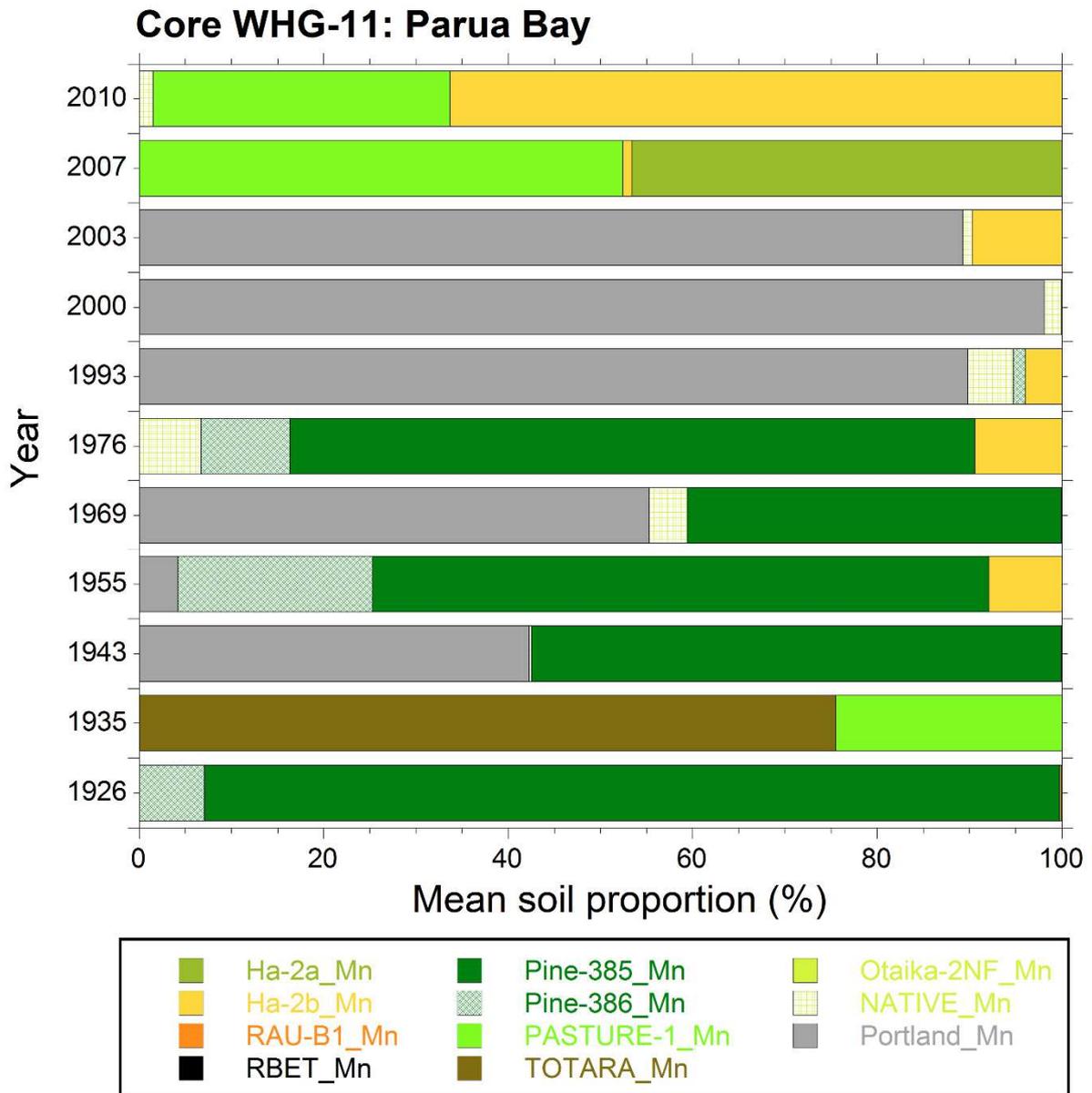


Figure 13: Core WHG-11 (Parua Bay). Mean soil proportions (%) for each dated sediment-core sample estimated from: (a) IsoSource modelling of isotopic proportions; and (b) linear scaling to soil % based on source-soil carbon content. Land uses are of the type indicated in the key: Pasture steep (Ha-2a); Kiripaki loam-flat eroded pasture (Ha-2b); Raumanga Bank erosion (RAU-B1); Road cutting (RBET); Pine-recent fell (Pine-385); Pine-mature fell (Pine-386); Dairy pasture (PASTURE-1); Flood plain native forest NE of Otaika (Otaika-2NF); Portland sediment at WHG-2, Mangapai Arm (Portland).

The relative contribution of catchment sources (soils by major land-use types) and Portland sediments to sedimentation at Hatea (WHG-14) and in Parua Bay (WHG-11) are summarised in Figure 14. These data highlight the persistence and major contribution of the Portland sediment source over the last ~70 years, although discharge of washings from the cement plant to the harbour ceased in the early 1980s. The long-term dispersal of these isotopically-distinctive sediments from the Mangapai arm, confirms that remobilisation and export of sediments by waves and tidal currents from the upper to the lower harbours is a key process controlling harbour sedimentation.

In Parua Bay (WHG-11), pine and pasture are the major sources of eroded catchment soils, although the relative contribution of soil eroded from the Parua catchment in comparison to other sub-catchments (i.e., non-local sources) cannot be determined from these data. At Hātea (WHG-14) the dominance of the Portland sediment is consistent with its relatively close proximity to this source. These data also show that eroded sub-soils are the major source of catchment-derived sediments since the mid-1980s.

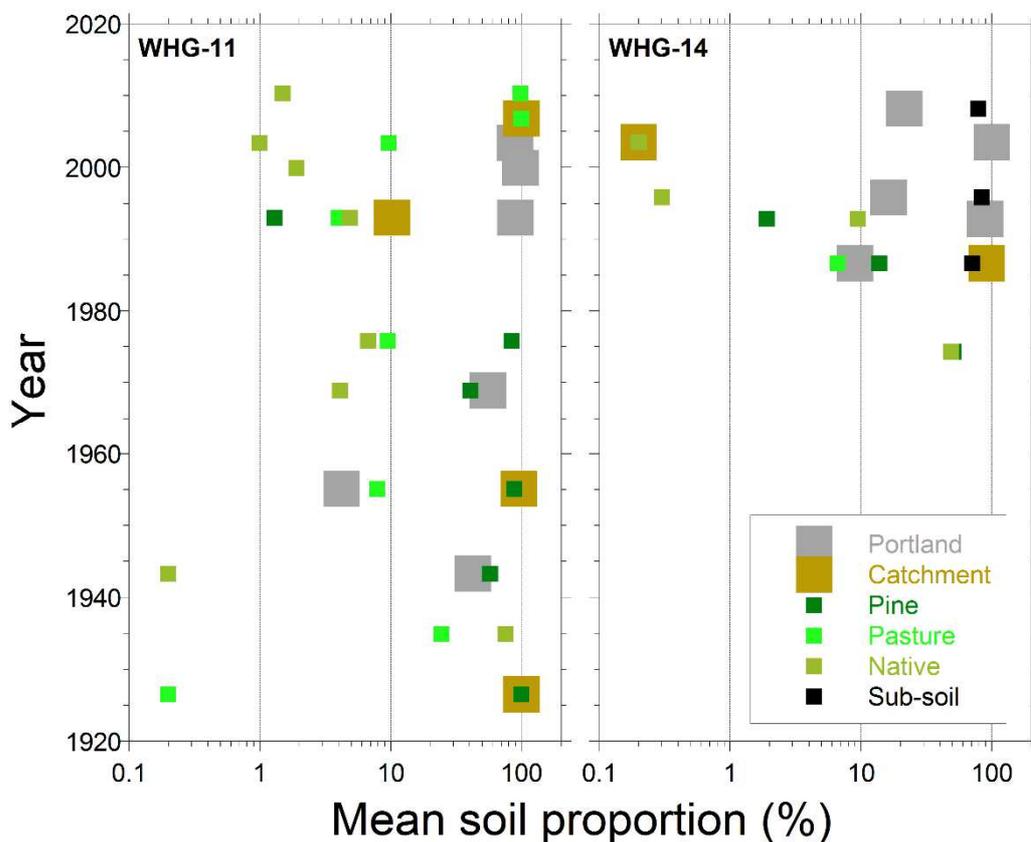


Figure 14: Changes in major sediment sources over time, cores WHG-11 (Parua Bay) and WHG-14 (Hātea).

Mean soil proportions (%) estimated from: (a) IsoSource modelling of isotopic proportions; and (b) linear scaling to soil proportion (%) based on source-soil carbon content (%). Sources are aggregated by major types: Portland; Catchment (all sources); Pine [Pine-385 (recent fell) and 386 mature]; Pasture [Ha-2a (steep), Ha-2b (flat-eroded), PASTURE-1 (Dairy)]; Native (Totara, Otaika-2NF, NATIVE) and sub-soil (RBET). Refer to Figure 13 caption for additional source description. **Note:** mean soil proportion (%) is plotted on a log-scale.

Table 4: Core WHG-11 (Parua Bay, Whangarei Harbour). Mean isotopic proportions by source (%), with min–max ranges shown in brackets. (* indicates a unique solution).

Year	Depth (cm)	Ha-2a	Ha-2b	RAU-B1	RBET	Pine-385	Pine-386	Pasture-1	Totara	Otaika-2NF	Native	Portland
2010.3	0.5		0.63 (*)								0.05 (*)	
2006.8	1.5	0.447 (0.44–0.45)	0.01 (0–0.02)					0.32 (*)				
2003.4	2.5		0.26 (*)					0.543 (0.54–0.55)			0.1 (*)	0.64 (*)
1999.9	3.5										0.21 (*)	0.8 (0.79–0.8)
1993.0	5.5		0.085 (0.04–0.12)				0.04 (0–0.11)				0.37 (0.34–0.41)	0.51 (0.47–0.54)
1975.8	10.5		0.137 (0.1–0.18)			0.32 (0.3–0.33)	0.2 (0.18–0.23)				0.34 (0.33–0.36)	
1968.9	12.5					0.29 (*)					0.355 (0.35–0.36)	0.355 (0.355–0.36)
1955.1	16.5		0.133 (0.08–0.2)			0.335 (0.33–0.35)	0.514 (0.41–0.57)					0.02 (0–0.06)
1943.3	30.5					0.59 (*)					0.02 (*)	0.39 (*)
1934.9	40.5							0.18 (*)	0.82 (*)			
1926.5	50.5		0.005 (0–0.01)			0.725 (0.72–0.73)	0.27 (*)					

Table 5: Core WHG-14 (Hatea Arm, Whangarei Harbour). Mean isotopic proportions by source (%), with min–max ranges shown in brackets. (* indicates a unique solution).

Year	Depth (cm)	Ha-2a	Ha-2b	RAU-B1	RBET	Pine-385	Pine-386	Pasture-1	Totara	Otaika-2NF	Native	Portland
2011.2	0.5	No reliable	data									
2008.2	2.5											0.58(*)
2003.5	5.5				0.42 (*)						0.03 (*)	0.97 (*)
1995.8	10.5										0.095 (0.09–0.1)	0.45 (*)
1992.8	12.5				0.455 (0.45–0.46)		0.045 (0–0.1)				0.56 (0.49–0.63)	0.39 (.37–0.41)
1986.6	16.5					0.37 (0.12–0.58)	0.052 (0–0.13)					0.23 (0.19–0.25)
1974.3	24.5	0.60 (0.6–0.61)			0.35 (0.17–0.56)	0.025 (0–0.06)	0.025 (0–0.06)				0.347 (0.34–0.36)	

5. References

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6. Appendices

Appendix A1: catchment history

Source: Bob Cathcart, email: 3 October 2014

Search of old soil bureau papers and excerpts from newspapers from about 1880 onwards. Other sources: David Reyburn ph.438 2769 (direct descendent of the original settlers), re general history or where to find it, and John Rawson, ph. 438 9265) a professional forester who managed the pine forests on Parahaki/Parihaka for the Whangarei City Council.

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Colenso believed there were only 273 Maori in the Whangarei/Whangarei Harbour area in 1839, the rest being dispersed by wars, particularly Ngapuhi pushing southwards. Pohe Island stop-banked in 1925.

Topdressing started about 1905 but not generally applied until 1919. One of the common fertilisers used back then was basic slag, ground up slag from iron smelting which contained phosphate as well as other elements. Basic slag is a by-product of steelmaking using the basic version of the Bessemer process or the Linz-Donawitz process. It is largely limestone or dolomite, which has absorbed phosphate from the iron ore being smelted. Because of the slowly released phosphate content, and because of its liming effect, it is valued as fertiliser.

Pine

I have found some old photos from 1946 showing very poor quality *P. radiata* on Parihaka and Memorial Drive only recently constructed. The pines could be 20 years old, even older, but are very spindly showing extreme phosphate deficiency. John Rawson later topdressed these trees and cut 'biscuits', cross-sections of logs to show the effect of topdressing. Those same biscuits should tell when the trees were planted.

Dairy

Dairy factories draining into Whangarei harbour - their waste disposal was simply a drain out the back and into the stream. They were sited on riverbanks for that very purpose. You may identify milk waste products in the sediments. There were also two meat works in Limeburners Creek catchment, both now closed and for some time, they and the City sewage discharged almost untreated waste directly to Limeburners within its tidal reaches. A meat works at Reotahi discharged directly to the harbour making the Marsden Point area a great shark fishery.

Gas works

The other industry which may have left markers in the sediments was a gas works in Water Street, about 80 metres from the NRC office which would have discharged to the Waiarohia Stream, possibly near the confluence of the Waiarohia, Kirikiri and Raumanga.

Gum digging

Gum digging era, 1900 to 1925. The Puwera and Otaika catchments both had extensive Gumfields. Max mentioned a spike siliceous sediments in the Waitangi which coincided with the Polynesian/Maori burning of gumland scrub (to encourage moa?) and then the even more destructive gum digging times. The burning of the gumland scrub, which remained a sport until afforestation of large areas in the Kawakawa River and Waitangi catchments, encouraged the large amphitheatre-shaped gullies in the Ngatuturi shales, which would have added to the silica levels.

The first European settler, William Carruth, arrived in Whangarei in 1839 and so you can expect exotic pollen from about that date. Someone, Carruth or Reyburn, planted a Norfolk pine beside the Town Basin (see the old photographs of this area).

Chronology

1882: first four acres of Dobbie's orchard planted.

1885: enough dairy cows to establish a cheese factory at Maungakaramea. [Hikurangi dairy factory 1901-2, Whangarei dairy factory 1908, Maungatapere dairy factory (in Otaika Stream catchment) 1907].

1888: first 'vinery', vineyard established "1/2 mile above the wharf on the other side of the river below Parahaki", that puts it the end of Vale Road, May 1888.

- *April 1888* – Driest season in living memory – 9,000 acres of 48,000 acre kauri forest on Puhipuhi burns.
- *June 1888* – Orchard Act to deal with Codlin moth – "with the quantity of acacia hedges and furze growing about the district it will find a congenial home" – so gorse was well distributed then. Already a flour mill and jam factories milling local produce – apples, pears, plums, quince, peach, citrus, and blackberry. Enough apples to attempt export to UK. Whangarei was supplying most of Auckland's fruit and veg at this time. Also –trial plantings of **tea**, **tobacco** and **broom corn** (12 feet high!)
- *December 1888* – meeting at Kamo with a proposal to establish a **dairy factory** in the Whangarei area – there were 500 cows in the immediate area.

1889: May 1889, record crops of wheat and oats.

1890: March 1890 – Phylloxera found in two vineyards, had been found in Auckland a couple of years before. April 1890 - Exceptional floods due to 11 days of NE – 20,000 acres flooded in Hikurangi Swamp (but this should show up in WHG Harbour as well.)

1896: February 1896 Very dry and **many bush fires**.

1897: drought continues into 1897, more firs on Puhipuhi.

1898: Drought broke 14/1/1898. November 1898 Murray Bros start a dairy factory on the banks of the Waiarohia Stream (Caltex Service Station through to Spotlight).

1902: February 1902 NZ Portland Cement factory on Limestone Island gutted by fire.

March 1903 – Sand dunes advance inland between Marsden Point and Waipu (Probably at Uretiti).

1903: September 1903 – Ragwort plants from roadside on show in shop window to raise awareness of this pest plant.

1904: August 1904 – **Parua Bay dairy factory built** (now the Parua Bay Pub). October 1904 – Tree planting operations in progress at Puhipuhi and over 100 acres planted. [This was in response to the almost complete loss of the 48,000 acres on Puhipuhi mentioned above – pines, eucalypts, cypresses, etc., to find what to grow. Trials also in what is now Glenbervie Forest.

1905: January 1905 – Forestry Department last year winter/spring 1904, planted a total of 200 acres at Puhipuhi with 90,000 totara and **40,000 gums**.

- *June 1905* – Mananui Butter Factory in Upper Banks Street built (more recently a well-known ‘watering hole’) – this drained to a tidal stream that flowed northwards through Laurie Hall Park and into the Hatea River upstream of the upper bridge (opposite the swimming pool).
- Further 30,000 totara and 120,000 eucalypts planted at Puhipuhi. While the forestry Department concentrated its efforts on Puhipuhi, its Depot and nursery was on Springs Flat, Kamo, (where the Virgin Concrete and Kamo Scrap Metal are sited. Specimen trees of various conifers were planted at their depot, some still there, and in the Otaika Cemetery, next to Harvey Norman. The Department also planted blocks of *Acacia mearnsii* and *A. delbata* and *A. decurrens* to provide sap for tanning leather. I understand those blocks, all in the Limeburners Creek catchment, were all planted sometime between 1905 to 1908. They all produce copious quantities of pollen so should have provided a marker.

1908: March 1908 – Practically no rain for 8 weeks. Bush fires been burning for last 2 months (mainly burning cut bush.)

- August 1908 – Kangaroo acacia, original planted as a hedge, becoming a pest plant.
- December 1908 – Peach trees have and a bad attack of curly leaf despite being sprayed with Bordeaux Mix (copper sulphate and slaked lime) – Most of these orchards were within the current Whangarei city urban area – the Avenues, Mill Road and Otaika-Raumanga so any downstream effects should appear in the Hatea River, Waiarohia, Kirikiri and Raumanga Streams and Limeburners Creek.

1909: February 1909 – ‘Swift’s Arsenate’ being used to control Codlin moth in apple orchards (same areas as for peach orchards above.

- *May 1909* – 17 foot coal seam discovered at Kamo – source of any coal found in the Hatea River upstream of Hatea Basin. Older mines (from 1880s) in the Waiarohia may have contributed coal to that stream. Kamo later worked from between McMillan Ave and Whau Valley Road, the outflow from which is under the Whau Valley shops and into the Waiarohia near Bedlington Street.

Appendix A2: Summary of CSSI method

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 (¹⁴C). 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 (¹²C) and heavy (¹³C) isotopes. Both of these stable isotopes of carbon have the same chemical properties and react in the same way. However, because ¹³C has the extra neutron in its atom, it is slightly larger than the ¹²C atom. This causes molecules with the ¹³C atoms in their structure to react slightly slower than those with ¹²C atoms, and to pass through cell walls in plants or animals at a slower rate than molecules with ¹²C atoms. Consequently, more of the ¹²C isotope passes through the cell wall than the ¹³C isotope, which results in more ¹²C 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 ¹³C 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., δ¹³C. The units are expressed as “per mil” which uses the symbol “‰”. The delta value of a sample is calculated using the equation:

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

where *R* is the molar ratio of the heavy to light isotope ¹³C/¹²C. The international reference standard for carbon was a limestone, Pee Dee Belemnite (PDB), which has a ¹³C/¹²C ratio of 0.0112372 and a δ¹³C 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 δ¹³C value.

Atmospheric CO₂, which is taken up by plants in the process of photosynthesis, presently has a δ¹³C value of about -8.5. In turn, the δ¹³C signatures of organic compounds produced by plants partly depends on their photosynthetic pathway, primarily either C₃ or C₄. During photosynthesis, carbon passes through a series of reactions or trophic steps along the C₃ or C₄ pathways. At each trophic step, isotopic fractionation occurs and organic matter in the plant (i.e., the destination pool) is depleted by 1 ‰. The C₃ pathway is longer than the C₄ pathway so that organic compounds produced by C₃ plants have a more depleted δ¹³C 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value obtained is referred to as the bulk $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ value increases by $\sim 1\text{‰}$ for each step. Pasture land cover and marine sediments typically have bulk $\delta^{13}\text{C}$ values in the range -24‰ to -26‰ and -20‰ to -22‰ , respectively. Waste water and dairy farm effluent have bulk $\delta^{13}\text{C}$ values more enriched than -20‰ . Consequently, a dairy farm where animal waste has been spread on the ground as fertilizer, will have bulk $\delta^{13}\text{C}$ values higher (more enriched) than pasture used for sheep and beef grazing.

There are occasions when the inorganic component of the soil imparts a highly modified $\delta^{13}\text{C}$ isotopic signature to the soil such that the $\delta^{13}\text{C}$ value cannot be used for modelling of soil sources. This phenomenon occurs in Karst (limestone) soils and as occurs in the upper Whangarei Harbour associated with the Portland sediment.

In addition to the bulk $\delta^{13}\text{C}$ value, organic carbon compounds in the sediment can be extracted and the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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, $\delta^{15}\text{N}$, 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 $\delta^{15}\text{N}$ cannot be used to identify sediment sources. The fractionation step for N is around +3.5‰ with bulk $\delta^{15}\text{N}$ values for forest soils in the range +2‰ to +5‰. Microbial decomposition processes result in bulk $\delta^{15}\text{N}$ values in the range 6‰ to 12‰ while waste water and dairy effluent can produce bulk $\delta^{15}\text{N}$ values up to 20‰. However, the use of synthetic fertilizers such as urea, which has $\delta^{15}\text{N}$ values of -5‰, can result in bulk $\delta^{15}\text{N}$ 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 $\delta^{13}\text{C}$, 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 °C) 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 $\delta^{13}\text{C}$ values i.e., CSSI values. Method details and data interpretation protocols were described previously by Gibbs (2008).

Data processing and presentation

The %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 \pm SD.

CSSI Method

The CSSI method applies the concept of using the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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.

Correction of CSSI signatures 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 $\delta^{13}\text{C}$ signature has resulted in a decline in $\delta^{13}\text{C}$ in atmospheric CO_2 ($\delta^{13}\text{CO}_2$). 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 $\delta^{13}\text{CO}_2$ is of the order of 2 ‰ since 1700 and has accelerated substantially since the 1940s (Verburg 2007). Thus, the $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ signature was stable until 1700 AD, with subsequent depletion of $\delta^{13}\text{C}$ due to release of fossil carbon.

In the present study, we use this atmospheric $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values of the FA from the potential catchment sources are modern (i.e., 2010 AD), and are therefore depleted due to the Sues effect. For example, the $\delta^{13}\text{C}$ 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 on age. Examples of this correction process for isotopic data for sediments taken from core RAN-5B are presented in Table B2.

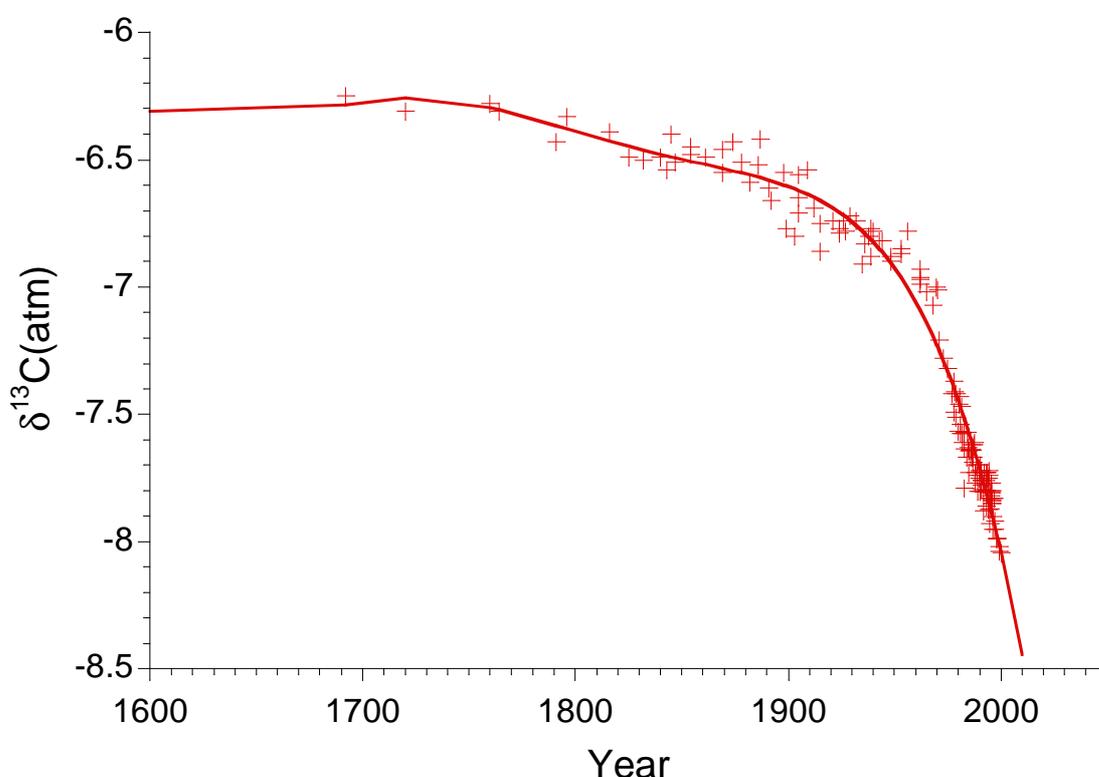


Figure A1: Historical change in atmospheric $\delta^{13}\text{C}$ (per mil) (1570–2010 AD) due to release of fossil carbon associated with anthropogenic activity (the so-called Sues effect), Source: Verburg (2007).

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 estuarine 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, in the Bay of Island's, citrus trees were not planted in large numbers in the Kerikeri catchment until the late 1920s so that citrus is not a valid sediment source for sediments deposited before that time.

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 mass-balance tolerance 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 for a Bay of Islands sediment sample is shown in Table D-1 below (Swales et al. 2012).

Table D-1: 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 & Gregg 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:

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

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 a mixture of three different sodium (Na) salts which provide equal proportions of Na to the mixture (3 x 1/3 each): sodium chloride (NaCl, molecular weight 58.45); sodium nitrate (NaNO₃, 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, but also recognising how many atoms of sodium are present in the molecule.

Table D-2 below presents the calculations required to apply the linear correction equation using the sodium salts example in order to determine how much of each salt is in the mixture. The ratio M%/S% for each salt and sum of this ratio (3.11) represent the numerator and denominator respectively in the conversion equation. Thus, for example the proportion of NaCl salt in the mixture is given by $(0.85/3.11)*100 = 27.3\%$.

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 land use 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 D-2: 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 ₂ SO ₄	32.4	33.3	1.03	33.1
SUM			3.11	