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Identifying Source Soils in Contemporary Estuarine Sediments: A New Compound-Specific Isotope Method

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Abstract A new method is proposed for the identification and apportionment of contemporary source soils contributing to estuarine sediments. The method uses compound-specific isotopic analysis of naturally occurring biomarkers (fatty acids) derived from plants to link source soils to land use within a single catchment. For identification and apportionment of source soils in the estuarine samples, the method uses the isotopic mixing model, IsoSource. The feasible proportions obtained from IsoSource are then scaled to allow for the percent organic carbon in the source soils. With this approach, the estimation of each source soil contribution to a location in the estuary is independent of any degradation of the biomarkers through microbial or biogeochemical processes. Identification relies on the evaluation of the sediment sample relative to a "library" of reference source soils from different land use within the catchment. Selection of potential sources is geographically constrained by the requirement for a natural linkage between each source soil and the sediment site sampled. A case study, using this method, mapped the distribution of three main land use source soils (pasture, native forest, and pine forest) across the river delta in a small estuary fringed with mangroves. Rather than being uniformly distributed, the results indicated that the source soil contributions varied markedly across the delta, raising concerns about the validity of taking single cores to characterize the sediments of an estuary. Coupling the source apportionment results with land use data indicated that the mean percent contribution of pine forest soil in the river delta sediments was almost three times greater than the percent land use area of pine forest in the catchment. Furthermore, isotopic signatures indicated that most of the pine forest soil came from the much smaller areas exposed to erosion by clear cut harvesting and that the soil contribution from recently harvested areas of pine forest could be as much as 20 times greater than that land use area in this catchment. This is the first method that can identify and apportion, by land use on a catchment scale, the sources of soil contributing to the sediment at a location of an estuary. The results are given as a "best estimate", within definable limits, of the proportional contribution of each potential source soil. Information obtained using this method will allow development of management strategies to alter land use practices to reduce the sediment load to rivers, and thus, the impact on the aquatic ecosystem downstream in estuaries.

Keywords Compound-specific isotope analysis · FAME · Estuarine sediment · Land use soil sources · Identification and apportionment method · IsoSource · Management tool

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Introduction

Sediment and suspended solids can have major impacts on the macrobenthic community of an estuary (Ellis et al. 2002; Norkko et al. 2002; Thrush et al. 2003a; Lohrer et al. 2004, 2006). While wind waves enhance turbidity by resuspending sediments from intertidal zones, the origin of contemporary sediment source material is mostly from land use practices that left terrigenous soils vulnerable to erosion (Thrush et al. 2004). As suspended sediment is a major "contaminant" of surface water worldwide, there is a need to develop alternative land use practices that reduce soil transport. This requires the identification of the sources of soil that give rise to suspended sediments, and thus, the

land use practices which contribute excessive amounts of soil to surface waters.

As most catchments have multiple land uses and the soil may come from diffuse sources, apportioning the contribution of soil to each land use practice is difficult. Conventional methods of sediment source identification (e.g., Yeager et al. 2006) compare suspended sediments transported through stream systems with catchment and streambank soils using a range of physical, chemical, mineralogical, and isotopic (radio nuclide) analyses. In small catchments where geologic differences are small, those methods may be impractical.

An alternative approach has been to utilize suspended sediment properties for which equivalent values exit in the catchment soils and streambanks (i.e., fingerprinting). Several studies have linked lipid biomarkers, such as fatty acids, in sediments to terrigenous sources (Boon et al. 1975; Perry et al. 1979; van Vleet and Quinn 1979; Volkman 1986, 2006; Karlik and Szpakowska 2001; Shi et al. 2001; Mead et al. 2005; Ratnayake et al. 2005, 2006; Banowetz et al. 2006). Soil fatty acid methyl ester (FAME) analysis has provided fingerprints characteristic of soil organic components. Using the FAME profile of a soil compared with a library of similar profiles of soils from known geographical locations, it was possible to identify the soil's source (Kennedy 1998; Ibekwe and Kennedy 1999). However, whereas FAME profiles have been used to identify sources of soil in surface waters (Banowetz et al. 2006), the utility of this classification was limited to 1–2 weeks after test soils were submerged because the FAME profile degraded, i.e., the fatty acid concentrations changed during diagenesis.

Recent studies using ^{13}C and ^{15}N stable isotope analyses of organic matter (e.g., Cloern et al. 2002; Cook et al. 2004) were able to discriminate between terrigenous and estuarine sources, although the reliability of the results were confounded by seasonal changes in isotopic composition and microbial processes in the estuarine sediments. Other studies have found that the molecular isotopic composition of the organic biomarkers, i.e., compound-specific isotope analysis (CSIA), in sediment can resolve terrigenous from marine origin (Shi et al. 2001; Glaser and Zech 2005; Mead et al. 2005; Boyd et al. 2006; Hu et al. 2006; Sachse et al. 2006). The CSIA technique evaluates the $\delta^{13}C$ isotopic signature of each organic compound in the biomarker mixture (Boschker and Middelburg 2002) rather than the relative proportions of these compounds, as in FAME profiles.

Conceptually, the soil or sediment sample contains a "pool" of each organic compound. Each organic compound has a $\delta^{13}C$ isotopic signature that does not change once formed because non-degradative processes such as volatilization, dilution, dispersion, and equilibrium sorption do not cause significant isotope fractionation (Blessing et al. 2007 and references therein). If a portion of the pool of an organic compound is degraded by biological processes, the breakdown products have different chemical structures and are no longer part of that pool. Thus, while the size of the pool (i.e., concentration of the organic compound in the sample) decreases, the $\delta^{13}C$ isotopic signature of that compound does not change. This means that the CSIA technique does not rely on the absolute or relative concentrations of individual organic compounds, which may change considerably during weathering and decomposition processes (Boyd et al. 2006). Consequently, CSIA techniques may provide a more robust method for identifying the sources of soil in the estuarine sediment.

CSIA techniques have been used to apportion sources of polychlorinated biphenyls in food web studies (e.g., Yanik et al. 2003). In estuarine studies, the CSIA technique has mostly been used to examine the sources of organic matter in the estuarine sediments (e.g., Rieley et al. 1991; Collister et al. 1994; Canuel et al. 1997). Cifuentes and Salata (2001) compared bacterial fatty acid CSIAs and bulk carbon isotopic ratios in diverse terrestrial, estuarine, and marine environments. Goñi et al (1997) used CSIA of lignins to show that offshore lignins in the Gulf of Mexico were derived from erosion of grassland (C_4) soils, whereas inshore lignins mostly came from C_3 plant detritus from coastal forests. However, whereas these applications focused on the sources of organic matter, none attempt to determine and apportion the sources of soil contributing to estuarine sediment.

To achieve this, the source soils must have naturally occurring organic biomarker labels which can be used to link them to specific locations in the catchment. Likely biomarker labels are the organic compounds leached from plant leaves and roots. While some plants produce a range of organic compounds that are plant specific, they also produce a suite of fatty acids and other compounds that are common to most plants (Ibekwe and Kennedy 1999; Wiesenberg et al. 2004; Bi et al. 2005; Otto et al. 2005a, b). Leaf waxes and associated *n*-alkanes are not especially water-soluble, so these compounds may be trapped on the leaf litter or on the soil surface. Mid-chain length fatty acids (i.e., C12:0 to C24:0) are more readily soluble in water, and thus, can be carried deep into the soil by infiltrating rainwater. These fatty acids and other compounds become bound to mineral and clay particles in the upper soil (e.g., Thurman 1985; Williams et al. 2006), becoming labels for those soil particles. Different plants produce the same compounds (e.g., fatty acids) but with different compound-specific isotopic signatures (Chikaraishi and Naraoka 2003). This implies that those compounds are produced via different pathways in different plant groups or by different habitat conditions for similar plant groups (e.g., Collister et al. 1994). Once bound to the soil particles, the

isotopic values of the fatty acids (and other organic compounds) do not change (Blessing et al. 2007 and references therein). This fact has been used in geoarchaeological (e.g., Hayes et al. 1990; Simpson et al. 1999), palaeoclimate (e.g., Glaser 2005; Glaser and Zech 2005) and palaeodietary studies (e.g., Fogel and Tuross 2003; Tripp and Hedges 2004) where the isotopic values have remained unchanged for hundreds or thousands of years.

Because different land uses are often defined by the dominant plant species growing on the land, e.g., pasture, crops, forests etc., the CSIA of those compounds in sediment could be used to identify land use contributions to the estuary, i.e., the isotopic signatures of the fatty acids identifies that soil particle as coming from that land use.

The aim of this study was to develop a method that could identify and apportion the contribution of soils from different land uses to the sediments of an estuary. Preliminary investigations established that there were significant differences in abundance of naturally occurring fatty and resin acids as well as their compound-specific isotopic values in extracts from different land use soils and harbor sediments. This paper presents a technique using fatty acid CSIA of different land use soils coupled with an isotopic mixing model to identify and apportion their contribution to estuarine sediments. This was part of a case study of a New Zealand estuary where there have been changes in species diversity associated with a decline in sediment-sensitive macrobenthic species potentially caused by an increase in sediment flux and sedimentation (Ellis et al. 2002; Cummings et al. 2003).

Materials and Methods

Study Site

Mahurangi Harbour [36°26.1 S, 175°42.5 E] on the east coast of the North Island of New Zealand has a total catchment area of 117 km^2, about half of which is associated with the Mahurangi River system (Fig. 1). The

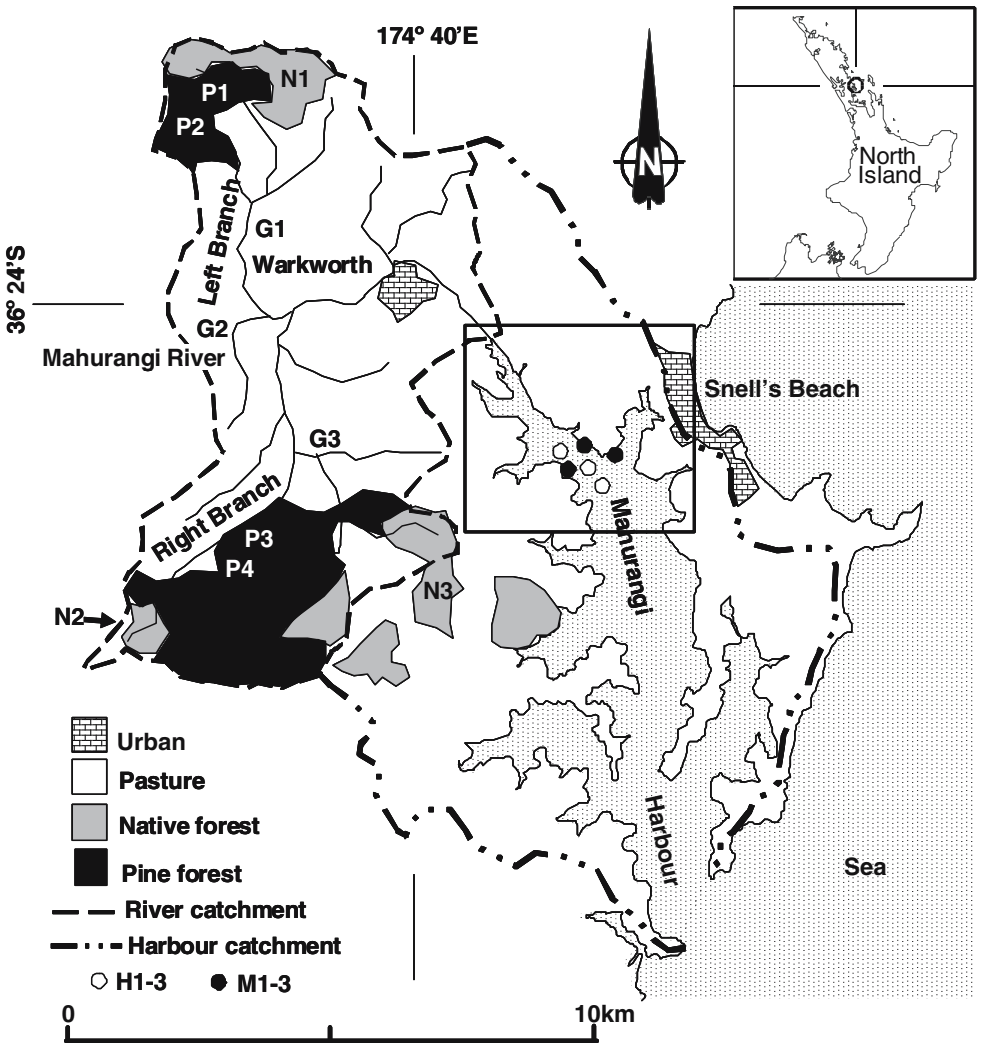

Fig. 1 Study site map with details of the Mahurangi catchment showing major areas of different land use around the Mahurangi River left and right branches (bounded by the *broken line*) and each side of the Mahurangi Harbour (bounded by the *broken* and *dotted line*) to the sea. Sampling points are described in Table 1. About 70% of the catchment is classified as agricultural, mainly in pasture. The *box* encloses the area examined in the case study (see text)

catchment has multiple land use estimated as about 70% agriculture—mainly pasture on the lower slopes and flatland; 20% native forest—in steep-sided gullies along the river and ephemeral stream channels and along the steep ridge tops around the catchment; 8% pine forest (*Pinus radiata*)—on the steep-lands around the headwaters of the left and right branches of the Mahurangi River; and about 4% urban—which includes roads and the settlements of Warkworth at the head of the harbor and Snell's Beach on the northern side of the harbor (Fig. 1).

The upper harbor is fringed with mangroves, *Avicennia marina*. The harbor is used for aquaculture and has extensive areas of rack-farmed Pacific oysters, *Crassostrea gigas*, on the intertidal sandflats. The harbor used to have large populations of the suspension-feeding pinnid bivalve, *Atrina zelandica*, which often formed large patches of up to 100 m^{-2} (Hewitt et al. 2002) on the seafloor. The recent decline in abundance of *A. zelandica* has been attributed to increased suspended solids in the harbor (Ellis et al. 2002), possibly associated with the harvesting of production pine forest in the catchment.

A series of geological and hydrological studies and models of the harbor and catchment for the Auckland Regional Council determined that there has been a change in the sediment accumulation rates (SAR) in the estuary since European settlement in the catchment in the 1850s (Swales et al. 1997, 2002). SARs were estimated to have increased tenfold in the last 150 years, with present day estimates in the upper estuary around the river delta at about 20 mm $year^{-1}$ (Swales et al. 2002). Catchment hydrological models indicated that about 30% of the annual sediment load to the harbor was delivered via the Mahurangi River, with the remaining 70% coming from small sub-catchments along both sides of the harbor from the river to the sea (Stroud and Cooper 1997). The predicted total annual sediment load (26 year average) was 45,852 t $year^{-1}$ (range 10,913 to 121,058 t $year^{-1}$) (Stroud and Cooper 1997), with an average of 330 day $year^{-1}$ producing sediment loads of about 1 t day^{-1} and four or five events per year producing sediment loads of 3,000 to 30,000 t day^{-1} (Stroud 2003). There was no indication from the modeling of the relative contributions of soil from the different land uses.

Sampling

Soils Soil samples (about 2 kg) were collected from the three main land use types (i.e., pasture, native forest, pine forest) at selected locations in the catchment (Table 1; Fig. 1). The sampling procedure involved removing the leaf litter layer before taking a scrape of the top 20 mm of exposed soil using a stainless steel spade. At each location, multiple subsamples from an area of about 10–20 m^2 were combined in a clean dry 5-l sealable plastic bucket as a bulk sample to ensure the sample was representative of that land use. For pasture samples, shallow sods were turned over and the soil shaken from the grass roots.

Table 1 Initial method development source soil and sediment sample locations and land use descriptions

Soil/sediment CODE	Land use description
Pasture	
G1	Grass—flat flood-plain near river (left branch)
G2	Grass—flat flood-plain near ephemeral channel (left branch)
G3	Grass—rolling hillside near river (right branch)
Native forest	
N1	Native forest—steep (Nikau, Rimu, Titoke, tree ferns; left branch)
N2	Native forest—steep (Nikau, Rimu, Titoke, Taraire; right branch)
N3	Native forest—steep (Kauri, Rimu, Tanekaha, Titoke, Kanuka; right branch)
Pine forest	
P1	Undisturbed mature pine—steep (left branch)
P2	Soil/subsoil in recent clear cut pine—steep (left branch)
P3	Undisturbed mature pine—steep (right branch)
P4	Soil/subsoil in recent clear cut pine—steep (right branch)
Harbor mangrove	
M1	Edge of mangroves in side arm (left bank)
M2	Under large mangroves along main channel (left bank)
M3	Under large mangroves along main channel (right bank)
Harbor intertidal	
H1	Upstream end of mud bank on river delta (right bank)
H2	Outside edge of mud bank in middle of river delta (right bank)
H3	Downstream end of mud bank on river delta (right bank)

Locations are marked on the site map (Fig. 1)

Sediments Sediment samples (Table 1) for the initial method development were collected in autumn (March 2005) from the surface sediments (top 20 mm) at six locations spaced across the river delta zone at the head of the Mahurangi Harbour, including three from open mudflats and three from beneath fringing mangroves. At each location, multiple subsamples were collected from an area of several square meters using either a core tube (100-mm diameter), which was sectioned to recover the surface 20-mm layer, or a scoop between the mangrove roots. The subsamples were combined in a single 5-l plastic bucket to produce a bulk sample which was representative of the estuarine location.

During a survey of Mahurangi Harbour in spring (November–December 2005), 77 sediment samples were collected at irregular spatial intervals across the whole estuary. Thirty of those intertidal and sub-tidal sediment samples, collected across the Mahurangi River delta and upper harbor sidearms, have been used as a case study to evaluate the spatial distribution of source soils entering the upper harbor via the Mahurangi River. An additional sample from the entrance to the Mahurangi Harbour was used as the coastal endmember in the modeling phase.

Analytical Methods

Processing Each bulk soil or sediment sample was mixed and sieved through a stainless steel 1-mm mesh to remove stones, shells, plant material, invertebrates, and benthic macrofauna. The buckets were sealed for transport to the laboratory where they were stored in the dark at 4°C pending processing within 7 days. An aliquot of each sample was taken for gravimetric determination of moisture content, after drying at 105°C, and organic content, by loss on ignition at 550°C. The remainder of each sample was dried at 60°C in a large flat aluminum tray in an air-fan oven. There have been differing opinions about the use of air drying versus freeze drying of samples. Dannheim et al. (2007) raised the possibility that freeze drying could affect the organic carbon stable isotope ratios, whereas McClymont et al. (2007) recommends freeze drying of marine sediment for certain analyses. The dry sample was ground to a fine powder using a heavy duty stainless steel coffee grinder. Coarse materials were removed by sieving (100-μm mesh, stainless steel) and reground. The ground sample was stored in a screw-cap wide-mouth polyethylene terephthalate (PET) plastic jar at room temperature in the dark. All processing equipment was cleaned between samples using warm water to remove solid particles and solvents (acetone and ethanol) to remove any residual organic material. The size of each bulk sample being processed was considered to effectively reduce the consequence of any cross contamination by dilution. While the PET storage jars could potentially contaminate the sample with phthalates, these would be excluded from the FAME analyses by the gas chromatography (GC) column separation. No phthalates were detected in any sample.

Soil Mixtures Four soil mixtures were prepared to test the recovery of the extraction procedures and the accuracy of the apportioning method. Artificial mixtures of three or four of the ground source soils were combined by weight to provide artificial "sediments" of known source soil proportions. The measured quantities of dried ground soil were shaken together in an inflated and sealed plastic bag with sufficient volume to allow free mixing of the soil particles when shaken but without loss of dust. These test mixtures were extracted and analyzed with the source soils and sediments.

C and N stable Isotope Analyses A small aliquot (2–5 g) of each sample was acidified to remove inorganic carbonates by shaking the sample with 2 ml of 1 N hydrochloric acid (HCl) and allowing the suspension to stand overnight. Further HCl was added as required until no further effervescence occurred. The use of weak (1–2 N) HCl solution has been shown to be the most appropriate acid for the removal of inorganic carbon from natural materials requiring elemental and isotopic analysis (Kennedy et al. 2005). The acid was removed by decanting after centrifuging at 3,000 rpm. The acidified sample was rinsed twice with deionized water (Milli-RQ) by shaking and then centrifuging. It has been a suggested that rinsing might cause a small loss of organic carbon (Jacob et al. 2005, Carabel et al. 2006). This potential error was considered to be minor compared with the errors associated with not removing the inorganic carbonate. The sample was dried at 60°C and then hand-ground to a fine powder in a mortar and pestle.

The C and N stable isotope composition of each acidified sample was determined by isotope ratio mass spectrometry (IRMS) as follows: About 20 mg of sample was weighed into a pure tin (Sn) capsule which was combusted at 1,020°C in a NR1500 elemental analyzer (Fisons Instruments, Radano, Italy) with a pulse of oxygen in a helium carrier gas. The carbon combustion products were converted to CO_2 in a copper reduction furnace at 600°C before the gas stream was coupled via a Finnigan Con-flo II gas injection interface to a DeltaPlus (Thermo Finnigan, Bremen, Germany) continuous flow, IRMS. Pulses of working standard CO_2 gas were injected at the beginning and end of each sample run to correct for intra-sample drift. Stable isotope ratios are reported in standard delta (δ) notation per mil (‰) as: $\delta X = \left[\left(R_{\text{sample}}/R_{\text{standard}}\right) - 1\right] \times 10^3$ where

X is ^{13}C or ^{15}N and $R=^{13}C/^{12}C$ or $^{15}N/^{14}N$, respectively. Standard reference materials were PDB limestone for carbon (a calibrated working standard of CO_2 gas was used), and air was the standard for nitrogen (a calibrated working standard of N_2 gas was used). Analytical precision for $\delta^{13}C$ and $\delta^{15}N$ were 0.1 and 0.2 ‰, respectively.

The percent carbon (%C) data produced by the IRMS are percent organic carbon because inorganic carbonates had been removed from the samples by acidification prior to analysis.

Organic Compounds Because the fatty acid biomarkers were likely to be at low concentrations in the soil and sediment samples and acidification may reduce the organic carbon concentration in sediments (Kennedy et al. 2005), soil samples for FAME analyses were not acidified.

Initial FAME analyses relied on the commercial analytical laboratories for the soil extraction, methylation, and compound analysis. Subsequently, the soil extraction procedures were done in-house and standardized as follows: An aliquot (20 g) of each sample was extracted in a Dionex ASE 200 accelerated solvent extractor. It has been found that the ASE gives more consistent and reproducible stable carbon isotopic data than Soxhlet or sonication extraction methods (Graham et al. 2006). To ensure low blanks, the ASE extraction pressure vessels, glass vials, and septa were rigorously cleaned before use as follows: The pressure vessels were completely disassembled and ultrasonically cleaned in distilled solvent, i.e., one cycle in acetone followed by two cycles in dichloromethane (DCM). Vial septa were ultrasonically cleaned in distilled acetone. The glass ASE vials were soaked for 24 h in a solution of laboratory glassware cleaner (we use Pyroneg; Intermed Scientific NZ Ltd) and rinsed with deionized distilled water before baking at 400°C for 12 h.

The soil extraction method used double distilled DCM as the solvent, heated to 100°C and raised to a pressure of 2,000 psi for 10 min. The extraction solvent was drained and flushed with clean solvent into a collection vial, and the extraction cycle was then repeated. A rinse cycle was used between each sample to prevent cross-contamination. The DCM extract from each sample was reduced to near-dryness by rotary evaporation at 30°C and then transferred to a 2-ml vial (Argilent wide-mouth screw-cap). The sample was allowed to evaporate to dryness at room temperature in a gentle nitrogen gas flow before the vial was sealed. All sample vials were sent to Iso-trace New Zealand Ltd (Dunedin) for CSIA.

The free fatty acids were methylated with 5% concentrated HCl in methanol or 5% BF_3 in methanol to form FAMEs which were extracted into hexane (after Medina et al. 1992). While strong acid methylation gives consistent and reproducible results, the use of BF_3 has been shown to give low recoveries of unsaturated and cyclic fatty acids due to variable trans-esterification of the double bonds (Klopfenstein 1971; Moss et al. 1974 and references therein). The effect was most noticeable when high levels (50%) of BF_3 were used or the methylation time was extended. GC traces showed that the artifacts produced did not interfere with the source FAME, but the concentration, and thus recovery, was reduced.

Stable isotope ratios of FAMEs were analyzed using a Trace GC (Thermo Finnigan, Milan, Italy) coupled to a DeltaplusXP IRMS (Thermo Finnigan, Bremen, Germany). Samples were injected into a split/splitless injector at 300°C and separated using a BP225 GC column (25 m, 0.25 mm i.d., 0.25-μm film; SGE, Melbourne, Australia). The GC oven was held at 50°C for 5 min before being ramped to 230°C at 7°C/min where it was held for 10 min. The carrier gas was helium at a flow rate of 1.8 ml/min).

Pulses of working standard CO_2 gas were injected at the beginning and end of each sample to correct for intra-sample drift. A mixture of standardized FAMEs were analyzed every six samples and used to correct for instrumental drift during batch analysis and to standardize FAMEs to the PDB scale. The CSIA values of FAMEs were corrected for the methylation carbon added during derivatization by co-methylating three standard fatty acids (C16:0, C19:0, and C22:0) and using a mass balance equation:

$$\delta^{13}C_{FA} = \frac{\delta^{13}C_{FAME} - (1-X)\delta^{13}C_{Methanol}}{X}$$

where X is the fractional contribution of the free fatty acid to the methyl ester. Analytical precision for standard fatty acids was below 0.5‰.

Another aliquot (5 g) was similarly extracted, methylated, and analyzed for fatty and resin acid concentrations by GC mass spectrometry at RJ Hill Laboratories Ltd (Hamilton).

Data Interpretation

Mixing Models The method development strategy was to construct a library of CSIAs of fatty acids in potential source soils from different land uses from the estuary catchment. Identification and apportionment of these source soils in the harbor sediment samples would be determined by modeling using either multivariate statistics (e.g., Boyd et al. 2006) or a source partitioning mixing model, e.g., IsoSource, (Phillips and Gregg 2001, 2003). IsoSource was used in the method development because it was simple to use and is readily and freely available from the USEPA website: www.epa.gov/wed/pages/models/stableIsotopes/isosource/isosource.htm.

IsoSource was designed for food web studies where there were too many sources for linear models and has been successfully tested in several studies (e.g., Newsome et al. 2004; Benstead et al. 2006). As IsoSource requires two or more stable isotopes to evaluate the composition of a mixture relative to potential sources, the $\delta^{13}C$ isotopic values of the bulk soil and each individual fatty acids in that soil were treated as different "isotopes". This gave a choice of up to 13 isotopes for use in IsoSource. The limitation is that the selected isotopes must be present in all sources and samples.

IsoSource Operation Whereas linear isotope mixing models using n isotopes will allow the unique determination of, at the most, $n+1$ sources in a mixture, IsoSource statistically constrains the relative proportions of the various sources in the mixture by evaluating all possible combinations of each source (from 0–100%) in user-defined increments to identify source combinations that sum to the known isotopic signature of the mixture to within a prescribed small tolerance in per mill. These source combinations are collated into a distribution of the frequency and range of feasible source contributions. Consequently, IsoSource does not offer a unique solution when there are too many sources, but allows evaluation of the statistical constraints on the relative contributions of each source (Phillips and Gregg 2001, 2003; Newsome et al. 2004).

For IsoSource to work, the isotopic value of the mixture being evaluated must be within the isotopic values of the source endmembers. In food web studies, the isotopic values used in the "consumer" must be corrected for the isotopic fractionation that occurs during assimilation of the food endmembers. This correction is not necessary for sediment mixtures, as there should be no fractionation during transport from the soil sources to the estuary. For the feasible solutions to be valid, it must be geographically possible for the source endmembers to reach the location of the sediment mixture being evaluated. This "reality check" constraint was applied to the model during selection of potential sources as endmembers.

While each feasible solution may be the correct solution, the number of times any given proportion of each source occurs is summed to produce a frequency distribution which can be evaluated statistically to give the mean percent contribution. The range of feasible solutions rather than the statistical mean should be reported wherever possible. When interpreting the model output, the total number of feasible solutions found by the model is an indication of the reliability of the result, with reliability increasing as the number of feasible solutions decreases towards 1, which is a unique solution.

Results

Organic Matter, C, and N Content

The average organic content of the native forest soils was generally higher than in pasture and pine forest soils. There was a significant reduction in average organic content in the harbor and mangrove sediments (Table 2). Also, whereas the average carbon content in the terrigenous soils were comparable at 5.3–7.8%, the carbon contents of estuarine sediments were substantially lower at 1.5–2.5%. The carbon to organic ratio was also significantly lower in the estuarine samples (Table 2), indicating that carbon had been lost from the estuarine sediments.

Fatty Acids and Resin Acids

Concentration The amount of each fatty acid from C10:0 to C24:0 varied between the different land use soils, with concentrations ranging from <0.5 mg kg^{-1} (dry weight) to 130 mg kg^{-1} (Table 3). A similar degree of concentration variability was found in the estuarine sediment samples, although the fatty acid concentrations were lower than in the land use source samples (Table 3). A complete suite of fatty acids was not always present in each sample. Myristic (C14:0), palmitic (C16:0), stearic (C18:0), oleic (C18:1), arachidic (C20:0), behenic (C22:0), and lignoceric (C24:0) acids were most consistently present in all source soils and the estuarine sediments.

Abietic acid, a resin acid derived from pine trees, was also found at different concentrations in most soils (Table 3). It was found at highest concentrations in the upper pine forest soils and in the native forest soil beneath the New Zealand conifer, the Kauri (*Agathis Australis*), but was only present at low concentrations in the pine forest subsoil. Traces of abietic acid were also found in some pasture soils and in all estuarine sediment samples (Table 3). Breakdown products of abietic acid, i.e., dehydroabietic acid (DHAA), pimaric acid, isopimaric acid, and sandaracopimaric acid, were also

Table 2 Averaged parameters from samples collected in autumn (March) 2005

Land use	Pasture	Native	Pine	Harbor	Mangrove
% moisture	28.40	38.80	21.30	51.90	58.20
% organic	13.20	18.30	14.10	8.60	11.50
% carbon	5.73	7.76	5.33	1.54	2.51
% nitrogen	0.46	0.38	0.34	0.13	0.23
%C/%organic ratio	0.43	0.42	0.38	0.18	0.22

Table 3 Fatty acid and resin acid composition matrix of land use soil samples and estuarine sediments

	Land use soil sources										Estuarine sediments					
	Pasture			Native			Pine				Mangrove			Harbor		
Samples	G1	G2	G3	N1	N2	N3	P1	P2	P3	P4	M1	M2	M3	H1	H2	H3
Fatty acid (mg kg^{-1})																
Decanoic (C10:0)			1.31	0.44		2.71	0.74		4.04		1.33	0.85	0.98	1.89		1.44
Lauric (C12:0)	2.64	0.52	2.42	1.71		1.10	4.20		21.3		0.65	0.33				
Myristic (C14:0)	1.20	0.50	1.20	1.30	4.50	1.80	4.30	0.80	23.0		5.20	1.90	2.30	0.50		0.50
Pentadecanoic (C15:0)	1.05	1.95	3.62	1.20		2.42	2.48		12.1		9.84	1.28	1.40	1.16	0.90	1.10
Palmitic (C16:0)	15.0	4.00	22.0	15.0	33.0	34.0	32.0	7.00	76.0	1.20	15.8	10.0	10.0	2.70	1.00	3.10
Stearic (C18:0)	6.00	1.50	5.40	3.70	9.00	7.00	14.0	2.60	20.0	0.60	3.50	2.20	2.50			0.80
Oleic (C18:1)	2.20	0.50	4.80	3.10	7.00	9.00	15.0	2.50	23.0		1.90	1.40	1.70			0.70
Linolenic (C18:2)	0.60		1.20	0.90	1.70	2.60	1.60	0.60	6.50				0.50			
Arachidic (C20:0)	7.00	1.20	7.60	2.70	3.60	15.0	16.0	4.00	22.0	0.70	1.10	0.90	1.20	0.30	0.30	0.50
Behenic (C22:0)	28.0	4.90	17.0	13.0	12.0	48.0	57.0	15.0	46.0	3.70	3.60	2.40	3.30	1.70	1.40	2.20
Lignoceric (C24:0)	110	12.0	40.0	20.0	30.0	60.0	130	40.0	50.0	11.0	12.0	8.00	9.00	7.00	5.00	6.00
Resin acid (mg kg^{-1})																
Abietic	0.12		0.01			7.87	8.88	3.14	6.50	0.07	0.05	0.08	0.06	0.22	0.04	0.12
Dehydroabietic	0.40	0.08	0.04	0.02	0.20	0.40	11.7	6.01	17.0	0.17	0.08	0.05	0.05	0.06	0.03	0.11
Isopimaric	0.78	0.03		0.69	0.60	0.12	1.74	1.18	4.30		0.02	0.06	0.03	0.05	0.02	0.03
Pimaric						2.05	10.0	3.40	2.30	0.04	0.07	0.13				1.35
Sandaracopimaric	0.24	0.03	0.10	0.29	0.80	5.08	1.20	0.50	0.90		0.11	0.13	0.12	0.16	0.08	0.14

Values given in mg kg^{-1} dry weight rounded to three significant numbers or two decimal places; missing values were less than detection limit. Sample codes are as per Table 1.

found in the pine forest soils and at trace levels in the estuarine sediments (Table 3). The importance of abietic acid and DHAA will be discussed later.

Stable Isotopes The $\delta^{13}C$ isotopic values of the bulk soil and sediment samples (Table 4) showed relatively large differences between different land use soils as well as similar land use soils at widely different locations within the catchment. There were also differences between the $\delta^{13}C$ isotopic values of the terrigenous soils and the estuarine sediments, although the isotopic values of the estuarine sediments were all within the range of the isotopic values of the terrestrial soils.

The variability in the fatty acid concentrations (Table 3) was also observed in the CSIA results (Table 4), with some fatty acids not being found in some samples or being present below confidence levels. Resin acid methyl esters were mostly below confidence levels, and only abietic acid was consistently reported (Table 4).

The $\delta^{13}C$ isotopic values of the fatty and resin acids were generally more depleted than the $\delta^{13}C$ isotopic values of the whole sample with the exception of oleic and linolenic acids, which were often slightly more enriched.

Test Soil Mixtures The analytical results of the test soil mixtures were evaluated in terms of concentrations and stable isotopic ratios of each compound (fatty or resin acid) in the mixture. Concentrations and isotopic ratios were calculated for each compound using the measured values in each source soil and the known proportion of that source soil in the mixture. The measured values for each compound in each mixture were expressed as a percent recovery by using the calculated values for each compound in each mixture (Table 5).

Based on concentrations, the mean recovery of the bulk carbon from the four mixtures was 103.9% (range 86–111%). Recoveries of individual fatty and resin acids were more variable than the bulk carbon for each compound within and between soil mixtures. The most consistent fatty acid recoveries were of palmitic, stearic, and oleic acids, with mean recoveries of about 112% from the four soil mixtures, but individual recovery analyses ranged from 75–178%, 101–123%, and 93–154%, respectively, from each mixture (Table 5).

In contrast, most of the isotopic recovery ranges were within 10% of the mean as well as the theoretical 100% recovery (Table 5). Because the pattern of isotopic recoveries for each suite of compounds was different from the pattern of recoveries based on concentration, this was interpreted to indicate that the isotopic values of the bulk carbon and fatty acids were not influenced by the variability in their concentrations in the soil mixtures. Apart from the

Table 4 $\delta^{13}C$ isotopic signatures (‰) of bulk sample and CSIA of the methyl esters of fatty and resin acids extracted from land use soil and estuarine sediment samples

	Land use soil sources										Estuarine sediments					
	Pasture			Native			Pine				Mangrove			Harbor		
Samples	G1	G2	G3	N1	N2	N3	P1	P2	P3	P4	M1	M2	M3	H1	H2	H3
Bulk sample																
$\delta^{13}C$ (‰)	−25.5	−26.9	−22.2	−28.0	−28.2	−25.1	−27.7	−24.1	−28.7	−26.2	−23.1	−24.1	−24.4	−25.0	−25.1	−25.0
%C	7.4	4.2	5.6	8.3	8.6	6.3	10.7	4.4	12.0	0.9	2.3	2.2	3.0	1.4	1.5	1.8
Fatty acid ($\delta^{13}C$ ‰)																
Decanoic (C10:0)			−29.3	−34.3		−30.3	−32.5		−32.9		−31.1	−31.5	−31.6	−30.5		−31.5
Lauric (C12:0)	−32.6	−29.6	−27.1	−34.1		−28.9	−34.0		−36.1		−24.6	−30.0				
Myristic (C14:0)	−28.9	−29.3	−27.0	−32.6	−33.1	−28.9	−37.0	−33.7	−40.7		−26.0	−27.3	−30.2	−28.2	−28.9	−30.2
Pentadecanoic (C15:0)	−28.7	−36.0	−21.3	−30.3	−27.7	−26.9	−32.3	−31.2	−30.0		−19.2	−26.1	−22.4	−21.5	−22.6	−27.4
Palmitic (C16:0)	−26.0	−28.0	−24.0	−30.6	−30.6	−25.6	−31.7	−27.6	−32.4	−29.2	−24.3	−28.4	−28.6	−28.5	−28.4	−30.0
Stearic (C18:0)	−31.5	−28.8	−26.7	−30.0	−29.5	−25.4	−31.1	−26.0	−32.1	−28.8	−26.8	−30.7	−29.8	−30.1	−30.1	−31.8
Oleic (C18:1)	−23.4	−24.9	−21.6	−28.7	−28.3	−27.8	−28.3	−25.4	−29.5	−25.0	−21.5	−26.5	−27.3	−22.6	−23.2	−22.4
Linolenic (C18:2)	−28.5	−25.5	−24.1	−28.3	−29.0	−25.6	−35.0	−26.5	−30.8	−30.8	−34.3	−29.5				
Arachidic (C20:0)	−30.2	−27.5	−24.5	−32.6	−34.8	−29.8	−32.0	−25.4	−33.1	−27.4	−27.6	−29.2	−30.5	−28.2	−28.1	−30.6
Behenic (C22:0)	−34.3	−27.6	−30.1	−33.1	−34.0	−31.8	−30.6	−30.5	−33.2	−29.3	−27.2	−27.1	−30.0	−19.4	−24.4	−29.5
Lignoceric (C24:0)	−31.4	−30.3	−29.2	−31.4	−34.4	−29.1	−30.6	−31.3	−33.2		−25.9	−30.6	−27.5	−26.0	−28.8	−29.7
Resin acid ($\delta^{13}C$ ‰)																
Abietic acid*	−31.7	−30.8	−27.1	−32.1		−31.7	−32.3		−34.5	−37.7	−28.7	−30.0	−30.7			−29.5

Missing values less than detection limit. Sample codes are as per Table 1.

Table 5 Mean bulk carbon, fatty acid, and resin acid recoveries (%) as determined by concentration and $\delta^{13}C$ isotopic values from the four artificial soil mixtures

	Concentration		$\delta^{13}C$ isotopes	
	Mean (%)	Range (%)	Mean (%)	Range (%)
Bulk soil C	103.9	86–111	98.8	96–106
Fatty acid				
Myristic	114.0	78–151	164.0	110–290
Pentadecanoic	124.5	95–182	187.0	106–343
Palmitic	112.9	75–178	94.7	85–105
Stearic	112.0	101–123	99.1	93–106
Oleic	112.3	94–154	103.6	99–103
Linolenic	84.0	76–93	102.3	80–147
Arachidic	131.3	100–187	95.0	92–102
Behenic	125.4	74–167	91.5	81–97
Lignoceric	114.7	72–138	171.0	102–278
Resin acid				
Abietic	117.8	83–134	100.2	96–104

Recoveries were estimated from the difference between the result of the analysis of the mixture and the expected result calculated from the measured values of the source soils used and the proportions of each soil in the mixture, assuming a homogeneous mix.

bulk carbon with a percent recovery of 98.8% (range 96–106%), there were four fatty acids (palmitic, stearic, oleic, arachidic) and one resin acid (abietic) which had mean recoveries close to 100% with ranges of <10% of the mean (Table 5). Linolenic acid (C18:2) and behenic acid also had mean percent recoveries near 100%, although the ranges between soil mixtures were larger.

Discussion

The analytical results confirmed that there are measurable differences in the $\delta^{13}C$ isotopic values for individual organic compounds extracted from the soils from different land uses. The test soil mixture analytical results and percent recovery estimates (Table 5) validate the concept that physical mixing does not induce isotopic fractionation in the individual organic compounds. Thus, the mass and the $\delta^{13}C$ isotopic value of an organic compound in the mixture is a function of the proportional contribution of the mass and the $\delta^{13}C$ isotopic values of that organic compound in each source endmember. Consequently, it should be possible to back-calculate the proportional contribution of each endmember in a mixture from the analytical data for each endmember and the mixture using the IsoSource mixing model.

The mean IsoSource results for each test soil mixture (Table 6) showed that there was a general pattern of agreement with the actual proportion of each source soil in the test soil mixture. These results were from 15 model runs using the mass and $\delta^{13}C$ isotopic values of one or more organic compounds. While the overall mean results show

Table 6 Summary of source proportions in four soil mixtures

Soil mixture	Actual proportion (%)	Mean feasible proportions			
		Best (%)	Worst (%)	Mean (SD) (n=15)	Range (n=15)
Soil mixture 1		(A)	(C)		
Pasture	80	82.0	94.0	79.5 (7.1)	71.0–94.0
Native	10	11.5	2.0	9.5 (5.3)	1.9–18.3
Pine	10	6.5	<0.1	10.7 (5.8)	<0.1–20.6
Soil mixture 2		(Ab)	(O)		
Pasture	50	54.7	24.0	51.4 (11.9)	24.0–71.7
Native	25	17.0	32.5	15.3 (9.7)	4.5–32.5
Pine	25	28.7	43.5	33.3 (11.1)	6.5–45.8
Soil mixture 3		(O+C)	(O)		
Pasture	10	10.9	18.4	16.5 (7.9)	0.8–26.2
Native	25	24.3	22.3	15.8 (7.8)	6.4–29.2
Pine	65	64.8	59.2	67.7 (4.8)	55.1–78.7
Soil mixture 4		(O+C)	(P)		
Pasture	9.7	8.8	1.0	4.8 (3.1)	1.0–13.5
Native	9.7	10.1	0.6	6.3 (5.8)	0.6–19.1
Pine	48.5	48.6	67.1	54.8 (11.1)	32.0–70.5
Estuarine	32.1	32.5	31.3	34.0 (10.2)	17.5–55.1

IsoSource proportions based on isotopic values of one or more fatty acids and the fatty acid concentration. Mean and range results are for 15 different combinations of fatty acids. "Best" and "Worst" are the results closest to or farthest from the actual proportions in the soil mixtures and were obtained using the specified compounds.
A Arachidic acid, *Ab* abietic acid, *C* bulk $\delta^{13}C$, *O* oleic acid, *P* palmitic acid

promise, there was considerable variability in the results from each run for each mixture. This is seen in the range of results (Table 6), which also shows the organic compound (s) that gave the closest (best) and the farthest away (worst) mean feasible proportions compared with the actual proportions in the test soil mixtures.

The degree of variability in the IsoSource results for the known mixture proportions was traced to the analytical variability in the concentration of the organic compounds in the source soils and mixtures and the inclusion of concentrations in the IsoSource mixing model. The organic carbon content of the source soils and sediment mixtures ranged from 7.8% down to 1.5% (rounded), which were measured to 0.01% accuracy. While the bulk organic carbon concentrations were at the milligram per gram level, the fatty acid concentrations were at the milligram per kilogram level, and thus, any losses during analysis would cause increased variability in the IsoSource model output.

A fundamental and often unstated assumption of most isotopic mixing models is that the proportional contribution of a source to the mixture is similar for each element (C, N, O, H, and S) in the source (Phillips and Koch 2002). In food web studies, this assumption is reasonable if the elemental concentrations of each source are similar and of equal digestibility (e.g., for animals on all meat or all plant diets). Under these circumstances, there is no need to consider concentration when evaluating the mixture relative to sources, and the isotopic balance in IsoSource will provide a range of valid feasible solutions. If this assumption is not valid, a concentration-dependent mixing model might be needed (Phillips and Koch 2002; Newsome et al. 2004).

The logic of constraining the IsoSource model feasible solution output by a concentration term in the model was realistic for the test soil mixtures and any other natural sediment where there has been no degradation process that might reduce the concentration of the source compound(s) being used as biomarkers. However, apart from losses during analysis, the literature presents many examples which demonstrate biodegradation of fatty acids in marine sediments (e.g., Banowetz et al. 2006). The concentrations of fatty acids in the sediment samples collected in this study (Table 3) were lower than in the potential source soils, indicating some degree of degradation in the sediments. To overcome this problem, the source identification and apportioning model needs to be independent of the concentration of each biomarker in the mixture.

This means that the IsoSource model should be run using only isotopic values. Consequently, as the isotopic values are all related to the carbon content of the source soils and the percentage carbon could be different in each source soil, the IsoSource model feasible proportion data need to be scaled by the percentage carbon in each source soil. This conversion from isotopic proportion to proportion of source soil uses the formula:

$$\%\text{source}_n = \frac{\left(I_n/\%C_n\right)}{\sum_{n}^{1}\left(I_n/\%C_n\right)} \times 100$$

where I_n is the mean feasible proportion of source n in the mixture as estimated from isotopic value by IsoSource, and $\%C_n$ is the % carbon in the source n soil. Because this calculation only uses the %C of the source soils for scaling, the proportional contribution of each source soil is independent of any loss of total carbon or fatty acids in the mixture through biodegradation.

This approach was tested using the four test soil mixtures (Table 7). For each test soil mixture, the bulk $\delta^{13}C$ value of each source soil and mixture was used as the first element in the IsoSource mixing model. As one objective of this study was to develop a simple method for identification and apportionment, testing was limited to the use of $\delta^{13}C$ values of two or three FAMEs as the other elements in IsoSource. The results of all tests were then assessed relative to the actual source proportions in the test soil mixture. The mean of all modeled proportions (Table 7) showed that there was a reasonable correspondence with the actual proportions, but the standard deviations show that variability was high.

Table 7 Summary of source proportions in four soil mixtures

Mixture	Actual proportion (%)	Mean (SD)		
		All (%, n=7)	No Ab (%, n=5)	C,O,P (%, n=3)
Soil mixture 1				
Pasture	80	70.9 (9.3)	75.3 (5.7)	79.5 (0.6)
Native	10	7.9 (5.1)	8.5 (5.8)	11.6 (5.4)
Pine	10	21.2 (12.4)	16.2 (10.9)	8.9 (6.0)
Soil mixture 2				
Pasture	50	41.6 (10.0)	46.1 (7.8)	50.3 (4.4)
Native	25	24.0 (13.3)	27.1 (14.9)	34.9 (14.8)
Pine	25	34.4 (19.8)	26.8 (18.3)	14.9 (10.5)
Soil mixture 3				
Pasture	10	10.8 (4.8)	13.1 (3.4)	11.9 (2.2)
Native	25	18.9 (13.4)	24.6 (11.1)	31.8 (6.6)
Pine	65	70.1 (16.3)	62.1 (11.3)	56.0 (7.7)
Soil mixture 4				
Pasture	9.7	8.0 (5.6)	9.6 (5.9)	12.6 (5.9)
Native	9.7	8.3 (2.3)	7.5 (1.8)	6.5 (1.7)
Pine	48.5	47.7 (6.3)	47.2 (4.3)	49.2 (4.7)
Estuarine	32.1	36.1 (7.7)	35.8 (8.4)	31.7 (8.9)

Mean percent IsoSource proportions (±SD) based on the isotopic values bulk $\delta^{13}C$ plus three or more different fatty acid combinations, scaled to %C.
Ab Abietic acid, *C* bulk $\delta^{13}C$, *O* oleic acid, *P* palmitic acid

Because abietic acid rapidly decomposes in sunlight (McMartin 2003), and thus may not always be present in the estuarine samples, the results of tests using abietic acid were eliminated to produce a new mean "Mean (No Ab)" (Table 7). The result of this simplification improved the modeled proportions correspondence with the actual proportions in the mixtures.

The simplification process was repeated by selecting the results of tests which included palmitic acid and oleic acid, as these were the fatty acids present in the highest concentrations in all soils analyzed. The new mean modeled proportions "Mean (C,O,P)" obtained using combinations of bulk carbon, oleic acid, and palmitic acid (Table 7) had similar or better correspondence with the actual proportions in the test soil mixtures. These results show that the "COP" results produced patterns of results which were consistent with the source soil proportions in the mixtures for a broad range of source soil proportions.

Exact matches were not obtained. This is consistent with the output from IsoSource which only provides a range of feasible proportions including the absolute solution. Using the statistical mean of the feasible proportions to simplify the mathematics does not alter that range of feasible proportions. Interpreted in this way, it can be seen that an exact match lies within the range of the mean±the standard deviation (Table 7). This means that the proposed method gives a "best estimate" within definable limits of the proportional contribution of each potential source soil to the sediment mixture.

While the bulk carbon, oleic acid, and palmitic acid isotopic values were found to be the optimum elements for source soil identification and apportionment, the inclusion of abietic acid in the suite of organic compounds analyzed from the source soils offers a positive link and a timeline where pine forest soils are potentially contributing to estuarine sediments. Because of its rapid breakdown in sunlight, if abietic acid is present, the sediment contains a soil endmember from pine forestry, and that soil was deposited in the estuary within about the last 30 days. This time can vary depending on local environmental conditions (McMartin 2003). The absence of abietic acid does not preclude an endmember from pine forestry that was deposited earlier.

Natural Sediments

Harbor Sediments The "COP" approach was applied to the harbor sediments. Trial IsoSource runs using eight sources with three isotopes were very slow (hours) to run but demonstrated that several of the sources were likely to be present in relatively small proportions (<1%). Although these low proportions were informative about where soil may not be coming from, the study objective was to identify major contributing sources. Consequently, sources which contributed only very small proportions (e.g., mature undisturbed pine forest, native forest with Kauri, and flat farmland) were omitted from subsequent IsoSource runs, which then focused on the major sources. The omission of potential sources was justified by the same logic that allows the lumping together of similar sources in food web studies using IsoSource (Phillips and Gregg 2003). These "truncated" results (Table 8) showed that at the time of sampling, the major sources of soil to the harbor sediments came from clear cut pine forest and rolling pasture with a much smaller contribution from broadleaf native forest. While the total contribution from pine forest was around 80%, the "COP" method results indicated that the pine forest soil came from two widely separated areas of recently harvested forest around the left branch and right branch of the Mahurangi River (Fig. 1). The higher proportion of pine forest soil from the right branch area was consistent with active logging activity in that area.

The results also indicated that there were proportional contribution differences between the open harbor and mangrove sites which implied spatial differences in sedimentation across the Mahurangi River delta and in the sidearms. This is comparable with the differences in organic content between the harbor and mangrove sites (Table 2). The proportions of soil from the two areas of pine forest were markedly different beneath the mangroves compared to the open intertidal sandflats, and there were higher proportions of rolling pasture source soil in the sediment from a sidearm dominated by this type of pasture (Table 8).

Case Study The "COP" approach was applied to an additional 30 sediment samples collected in November and December 2005 from an irregular spatial grid across the Mahurangi River delta and upper harbor. These samples were part of a larger, full harbor sediment survey, which will be reported elsewhere. The soil source identification

Table 8 Relative proportions of major source soils in harbor sediment samples in March 2005 as determined using the "COP" approach, corrected for %C in the source soils

Sediment	Source soil			
	G3 (%)	N1 (%)	P4 (%)	P2 (%)
H1	11.3	3.6	78.0	7.3
H2	10.1	2.3	74.5	13.1
H3	16.6	4.5	59.0	20.0
M1	73.0	1.0	23.5	2.3
M2	3.5	7.2	24.0	65.3
M3	3.3	12.7	29.9	55.4

The values are the means of three IsoSource runs using C+O, C+P, and C+O+P where C=bulk δ^{13}C, O=oleic acid, and P=palmitic acid. Sample codes are as per Table 1.

and apportionment results from these additional samples confirmed the initial results (Table 8), which showed high proportions of source soils from pine forest land use. However, they also showed relatively large spatial differences in total source soil contributions from the three main land use types at different locations across the Mahurangi River delta and the presence of an "estuarine" sediment component (Fig. 2).

While the hydrological modeling (Swales et al. 2002) indicates that these "estuarine"-influenced sediments are most likely of terrigenous origin, the enrichment of the bulk carbon and CSIA $\delta^{13}C$ isotopic signatures suggest a source closer to the coastal endmember than the terrigenous endmembers. Early diagenesis of the terrestrial soils that have been in the estuary for an extended period may contribute to this enrichment (e.g., van Vleet and Quinn 1979). However, deposition of pelagic marine algae or resuspended benthic microphytes and sediment from other areas of the downstream estuary are a more likely source (e.g., Canuel et al. 1997). Because C17 and C19 fatty acids were not detected in the case study samples, bacterial sources were likely to be a minimal. The most likely source for the estuarine influenced sediment was a large intertidal area, about 500 m downstream from the river delta area, where benthic primary production was high and there was extensive rack-culture of Pacific oysters. A sediment sample from that area was used as the "estuarine" endmember to identify and apportion source soils across the Mahurangi River delta (Fig. 2).

The case study results showed that while the contemporary surface sediments of the river delta contained, on average, about 20% of the "estuarine" component, the river delta sediment also contained about 46% pine forest, 19% pasture, 14% native forest soil. As these three main land use types occupy 16, 64, and 18%, respectively, of the catchment, assuming a uniform baseline with percent soil contribution proportional to the land use area, it can be seen that pine forest was contributing almost three times the expected sediment load to the river delta at the time of sampling.

A closer examination of the IsoSource modeling results indicates that there was almost no sediment contribution from mature, undisturbed pine forest and that the pine forest soils mostly came from clear cut areas of recently harvested pine forest. Using a pine forest harvest rotation of 25 years and a vegetation recovery of 6–8 years to return to the sediment yield of undisturbed pine forest (Phillips et al. 2005; Marden et al. 2006), the pine forest soil in the river delta sediments may have been coming from <15% of the

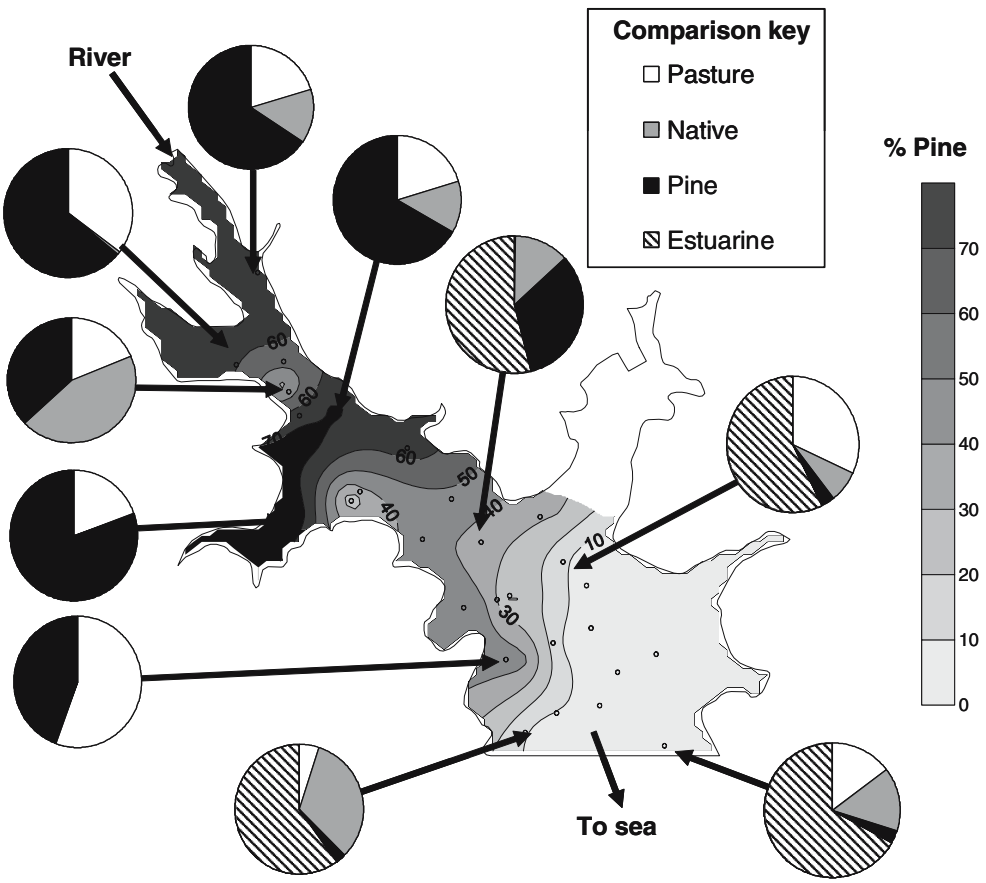

Fig. 2 Comparative distribution (pie charts) of pine forest, pasture, and native forest soils in the recent sediments of the upper Mahurangi Harbour at selected locations across the river delta. The exact nature of the component labeled as "estuarine" has yet to be determined (see text). The base map is a contour plot of the % pine soil (*right-hand scale*) in the upper harbor, drawn from 29 sampling points (*dots*). The outer edge of the river delta corresponds approximately with the 40% pine soil contour line

land use under pine forest. This suggests that the clear cut areas of harvested pine may have been producing as much as 20 times the expected sediment load per unit area of land use at the time of sampling.

This finding is consistent with results from the Pakuratahi Land Use Study (Eyles and Fahey 2006) which included a comparison of sediment yield from paired forestry and pasture catchments. That study determined that over a 12-year period, "the farmed catchment produced almost four times more suspended sediment than the catchment in mature forest", which is consistent with the minimal sediment from undisturbed mature pine forest found in this study. However, the Pakuratahi Land Use Study also found that "during harvesting, sediment yields from the forested catchment were two and a half times more than the farmed catchment, and six times higher than before harvesting."

In the context of an estuary, the macrobenthic community is likely to adapt to the chronic exposure to low levels of suspended sediment from farmed land. However, when the forests are harvested, the sixfold or greater average increase in suspended sediment from forestry land may occur in several short duration acute events and have a catastrophic impact on those communities. If benthic communities remain smothered with a 2-cm layer of mud for more than 7 days, they are unlikely to survive (Norrko et al. 2002; Thrush et al. 2003b), and recovery of the macrobenthic community in the estuary will be driven by recolonization by species more tolerant of fine sediments and mud.

The Pakuratahi Study suggests that "within two to three years the sediment produced from the forest catchment had fallen to pre-harvest levels." This is a faster time frame than the 6–8 years suggested by Phillips et al. (2005), but serves to highlight the prolonged period of high acute suspended sediment yield that could occur after forest harvesting, unless sediment yield is managed.

Conclusion

The method developed in this study gives a "best estimate" within definable limits of the proportional contribution of each potential source soil to the sediment mixture based on land use and on a catchment scale. This forensic use of stable isotopes provides a powerful tool which can be used by managers to modify land use practices and develop strategies that will reduce sediment transport loads to rivers, and thus, estuaries.

The case study demonstrated the use of the new method to determine the distribution pattern of pine forest soil proportions in the sediments across the Mahurangi River delta (Fig. 2, base map) and the disproportionate contribution of pine forest soil to the estuary relative to the catchment area occupied by that land use (Fig. 2, pie charts). This enhanced soil contribution appeared to be related to the removal of vegetation cover during clear cut forest harvest, leaving the bare soil vulnerable to erosion during heavy rain. This result is consistent with the findings of other studies. Other land use practices which produce large areas of bare soil for extended periods (e.g., tillage for crops), as well as road cuttings, site excavations, and land slippage, are also likely to produce enhanced sediment loads during periods of intense rainfall.

The patterns of source soil distribution across the upper estuary show that catchment sediment loads are not deposited uniformly across the river delta. This indicates that water sorting and estuarine hydrodynamics may be important factors to consider when sampling estuarine sediments for river-borne soils and other contaminants. These factors should also be considered when designing monitoring programs and studies of estuarine environments.

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