



Evaluation of Terrestrial Sediment Spatial Patterns Throughout the Whitford Embayment and its Benthic Food Web Using Stable Isotope Techniques

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Evaluation of Terrestrial Sediment Spatial Patterns throughout the Whitford Embayment and its Benthic Food Web using Stable Isotope Techniques

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1 Executive Summary

This study uses stable isotope techniques to track the movement of terrestrial sediments through an estuary and to examine the impact of thin layers of terrigenous clay on the microscopic plant communities in the sediments. It is one of a series of studies commissioned by ARC to provide information on the threats to estuarine ecology posed by changes in land use (see also Berkenbusch et al. 2001).

Stable isotopic techniques were able to provide an estimate of the % clay distribution through the estuarine arms and across Whitford embayment. These measurements were closely correlated with the % clay distribution measured by particle size analysis. Although further work is required to refine the transformation algorithm, these results suggest that the use of stable isotopes may be a valid technique for estimating the % terrigenous clay in estuarine sediments.

While the stable isotope transformation data provided empirical evidence of terrigenous clay movement through the estuary, the natural abundance isotopic C and N data also provided information on a broader range of terrigenous inputs including possible waste-water contamination of beaches from urban storm-water drains and small stream inflows. There were also indications of correlations between benthic communities and their habitats.

Isotopic enrichment experiments provided information on the effect of thin layers (5 mm) of clay on sediment hydrology and the microscopic plant communities that live in the sediments. The results indicate that there is a very delicate balance between chemical fluxes across the sediment-water interface and primary production in the sediments for benthic communities. This balance can be affected by even small inputs of terrigenous clay. The degree of that effect is dependent upon the habitat impacted and the thickness of the clay layer. Significant ecological changes would depend on the frequency of clay deposition events.

The isotopic enrichment experiments demonstrated small scale (mm range) changes in hydrodynamics, and the natural abundance spatial patterns indicated large scale (km range) circulation and sedimentation patterns across the embayment.

This study has demonstrated that stable isotope techniques are valuable and highly versatile tools for assessment of coastal and estuarine environments, and evaluation of human impacts from catchment development.

2 Introduction

This study uses stable isotope techniques to track the movement of terrestrial sediments through an estuary and to examine the impact of thin layers of terrigenous clay on the microscopic plant communities in the sediments (microphytobenthos). It is one of a series of studies commissioned by ARC to provide information on the threats to estuarine ecology posed by changes in land use (see also Berkenbusch et al. 2001).

2.1 Rationale

Growing pressure on land use and urban development in the Auckland region poses a threat to marine ecosystems, due to increased sediment deposition associated with catchment development. Estuaries and tidal inlets are particularly vulnerable to increased levels of sedimentation, as they act as natural retention systems. Accelerated deposition of land-derived sediment leads to habitat modification, and impacts on estuarine ecology by directly and indirectly killing, displacing, or damaging components of the macro-invertebrate community, resulting in changes to the abundance and distribution of benthic organisms. The magnitude of impact depends on spatial scale and the frequency of depositional events, and ecological repercussions can be both short-term, catastrophic and long-term, chronic in nature.

A number of recent field and laboratory studies have examined the catastrophic effects of sudden sediment deposits on macrofauna communities in Okura Estuary (Norkko et al. 1999; Nicholls et al. 2000). From these studies it is evident that terrigenous sediment deposits deeper than 2-3 cm, and which cover the underlying sediment for 5-7 days, will smother natural sediments, turning them anaerobic and killing all resident macrofauna. With the exception of large highly mobile mud crabs and shrimps (Gibbs et al. 2001), common estuarine animals are unable to move through thick sediment deposits, and even if animals are not killed before the sediment is removed, individual animals are sufficiently stressed to be more susceptible to sub-lethal effects and predation.

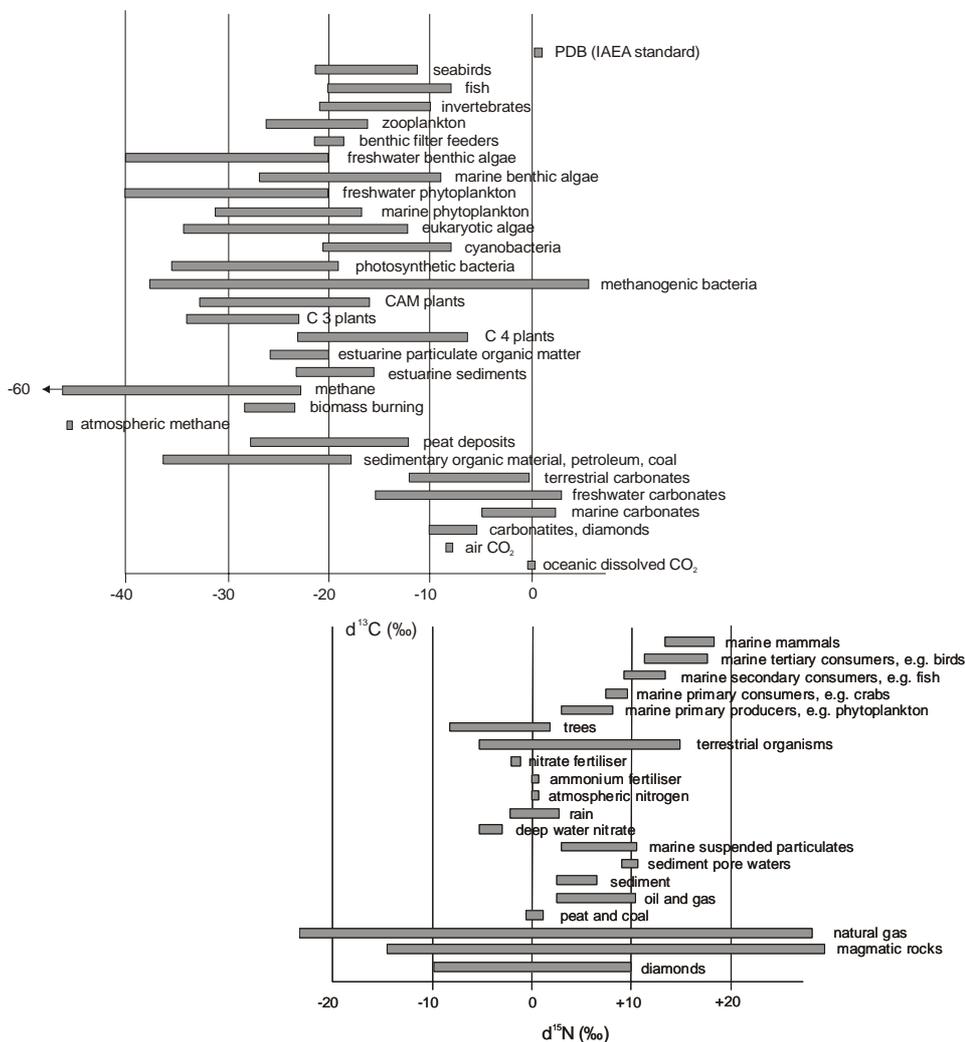
In contrast to sudden catastrophic events which are highly visible, more chronic inputs of terrigenous material may not be distinguishable from ambient sediments although they may cause long-term pervasive, sub-lethal effects on the benthic community. Consequently the distribution and abundance of benthic organisms across the estuary may change without obvious cause as catchment development alters the quantity and timing of terrigenous inputs to the estuary.

Terrigenous inputs are not the only source of sediments in an estuary and it is generally recognised that the sediments in estuarine areas originate from multiple external and internal sources. External inputs include terrigenous clay as well as organic matter delivered from riverine inflow and adjacent coastal waters, atmospheric fallout, and industrial and municipal discharges. Internal sources include organic matter produced within the estuary itself from primary and secondary production. These

diverse inputs produce different sediment characteristics across the estuary. Consequently discriminating between sediment inputs and determining the source of particulate material in the estuary by conventional means is difficult.

Recent research using the non-radioactive stable isotopes of carbon (^{12}C , ^{13}C) and nitrogen (^{14}N , ^{15}N) has shown that different types of particulate matter can be characterised by their nitrogen and carbon natural abundance signatures (Fig. 1).

Fig. 1 Typical isotopic carbon and nitrogen signatures for environmental and ecological matter (redrawn from Bury 1999). (Units are explained in methods).



The natural abundance signatures of each organisms are generally determined by their food source (e.g. Kaehler et al. 2000). The natural abundance signature of the non-refractive component of the terrigenous inputs, however, remains essentially unchanged in the sediments. As the non-refractive component of sediment is generally several orders of magnitude larger than the biological component, the source of that sediment may be determined from the bulk natural isotopic abundance signature relative to known sources.

In this aspect of the Whitford study we use stable isotope techniques to provide empirical evidence of the movement of terrestrial sediment and in particular, clay, through Whitford estuary and embayment. *In situ* experiments at a number of locations were also used to indicate the impact of thin layers of clay on sediment nutrient dynamics and microphytobenthos (i.e., the microscopic plant community) production.

3 Methods

3.1 Spatial survey

Short cores (2 cm deep, 2.5 cm diameter) were collected from about 200 locations across the intertidal flats and subtidally within the confines of Whitford Estuary (Fig. 2). These samples were collected and processed for habitat evaluation, measurement of clay and silt fractions, and chlorophyll *a* content. Residual freeze dried sediment from each core was sieved (300 μm mesh) to remove shell fragments, then finely ground with a pestle and mortar before weighing small quantities (< 50 mg) into pure tin (Sn) capsules for carbon and nitrogen stable isotope analysis. The samples were combusted at 1020°C in a Fisons NA1500 CHN elemental analyser with oxygen in a flow of helium carrier gas. Following separation of N_2 from CO_2 in the gases produced, on a Poropak Q column at 40°C, the nitrogen and carbon isotopic ratios were determined on a DeltaPlus continuous flow, isotope ratio mass spectrometer (Finnigan MAT). The data were converted to contour plots using Surfer32[®] using Krigging¹. Krigging is the best interpolation method for data that are not sampled on a regular grid (Legendre & Legendre 1998).

Stable isotope results are expressed in delta (δ) notation as the isotopic ratio of heavy to light isotope:

$$\delta R = [(X_{\text{sample}} - X_{\text{standard}})/X_{\text{standard}}] \times 1000 \quad (\text{‰})$$

where $R = {}^{13}\text{C}$ or ${}^{15}\text{N}$, and $X = {}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{15}\text{N}/{}^{14}\text{N}$. The normal working standard for carbon was CO_2 gas calibrated relative to NBS19, a secondary standard which was originally calibrated against the primary PDB limestone (now exhausted). Atmospheric N_2 was used as the working standard for nitrogen.

¹ Note: Because of the paucity of spatial data, contour plots provide an indication only of likely spatial distribution patterns and not absolute values.

Photo 1 Mosaic of aerial photos taken in March 2001 at about low tide. This mosaic gives an overall view of the catchment development around the Whitford embayment and shows the main inflow channels through the intertidal sand flats to the open water. It also allows an assessment of the coverage obtained with the spatial sediment sampling programme (Fig. 2).



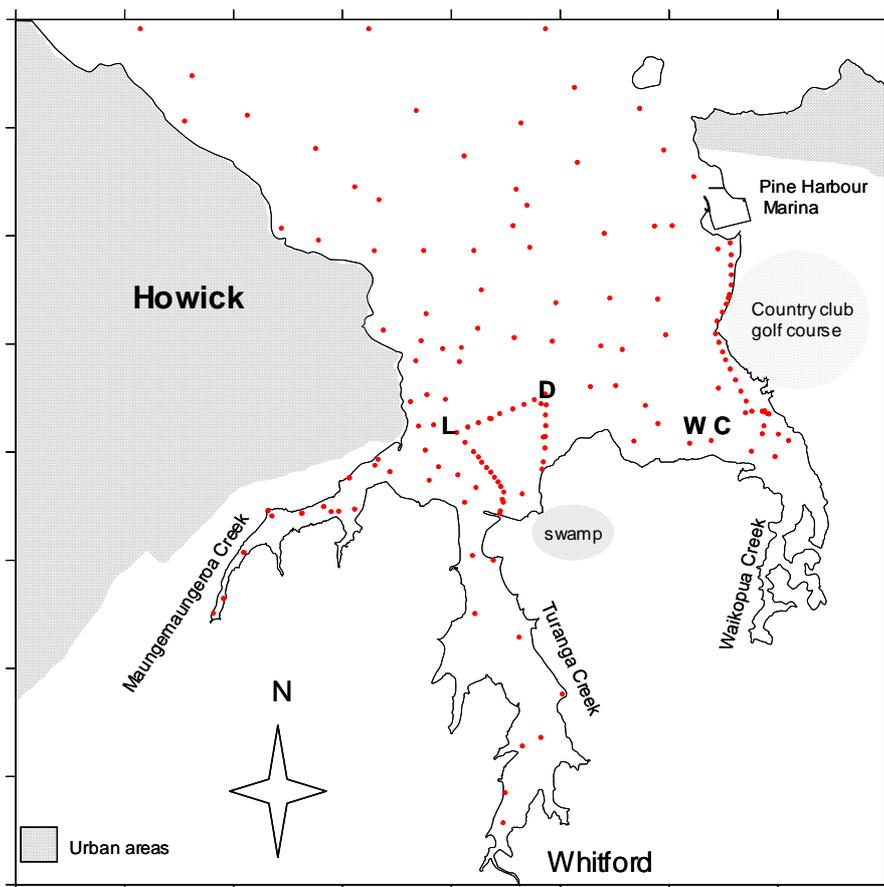
3.2 *In situ* experiments

At 4 sites across the estuary, "Cockle" (Fig. 2, **C**), "Worm" (Fig. 2, **W**), "Diatom" (Fig. 2, **D**), and "Low" (Fig. 2, **L**), stable isotope enrichment experiments were conducted concurrently with other experiments using the application of thin clay smears. Sites C and W were examined in November 2000, sites D and L were examined in January 2001. These experiments were designed to evaluate the depth distribution of the benthic microphyte community in the intertidal sediments and the potential for their removal by tidal flushing, by following an isotopic label incorporated into their cell structure.

At 3 of these sites, C, W, and L, potassium bromide solution was used as a conservative tracer for solute diffusion, and to determine the depth of hydraulic flushing, with and without the clay smear.

Sediment nutrient flux estimates were made at sites D and L and those experiments are described in a separate report (Berkenbusch et al. 2001).

Fig. 2 Spatial distribution of sampling positions (red dots) across Whitford embayment. Letters indicate positions of in situ experiments as used in the text. L= Low, D = Diatom, W = Worm, C = Cockle. Map scale on 1 km grid. See Photo 1 for details of inflow channels and land development.



3.2.1 Stable isotope enrichment experiment

After the method of Middleburg et al. (2000), soon after the sediment was exposed on the receding tide at each site, a dilute solution of ^{13}C enriched sodium bicarbonate in ambient seawater was sprayed evenly within two plots ($\approx 2\text{-}3\text{ m}^2$ each) defined by 20 cm wide metal bund rings. One plot was designated to be the clay treatment plot (**T**) while the other was to remain untreated as a control (**Ctrl**) for the effect of the clay smear. Short (5 mm deep) plugs of the surface sediments were collected from the control plot at timed intervals over the next 3 hours to examine the uptake rate of the ^{13}C by the microphytobenthos. Each plug of sediment was immediately placed in a 10 ml plastic vial with a drop of concentrated hydrochloric acid to stop further tracer uptake by removing any free sodium ^{13}C -bicarbonate as $^{13}\text{CO}_2$. The vials were left open for 1 hour after applying the acid to allow the $^{13}\text{CO}_2$ to escape to the atmosphere.

After the 3 hours, a slurry of about 50% clay in ambient seawater was evenly applied by watering-can to the "treated" plot to give a final clay layer thickness of 5 mm and left to settle for about 1 hour. Just before tidal inundation of the site, pairs of 10 cm deep 2.5 cm diameter cores were taken from each plot and the adjacent untreated sediments were sampled as background (**BG**) for isotopic analysis. Further cores were taken from each plot after one tidal cycle and then daily over the next few days.

Each core was sectioned at 0-2, 2-4, 4-6, 6-8, 8-10, 10-15, 15-20, 20-25, 25-30, 30-40, 40-50, 50-70, 70-100 mm slices. Each slice was oven dried at 60 °C for 24 hours, sieved to remove any shell fragments before grinding and analysing for stable isotopes as for the spatial survey.

3.2.2 Bromide tracer experiment²

At sites C and W, a solution containing 0.7 g of potassium bromide was applied inside a 0.5 x 0.5 m square aluminium frame pressed c. 3 cm into the surface of each plot after the clay smear had been applied. The solution was poured onto a plastic sheet to prevent disturbance of the sediment surface or the clay layer. The plastic was removed and the bromide solution was allowed to infiltrate the sediments. Immediately before tidal inundation of the plots, pairs of 10 cm deep by 2.5 cm diameter cores were taken from inside each frame and sectioned as for the isotope cores. The frames were then removed but their locations were marked with wire pegs. Further pairs of cores were collected from the bromide zones after 1 tidal cycle. This experiment was intended to evaluate the infiltration of the bromide through the clay and any subsequent tidal flushing of the bromide from the sediments.

In January 2001, only site L was treated with bromide solution. At this site a small volume of higher concentration potassium bromide solution was sprayed onto the surface of each plot inside a 0.5 x 0.5 m square aluminium frame resting on the surface, before the clay was applied. The plots were sampled as above immediately before tidal inundation and after 1 tidal cycle. This experiment was intended to

² These experiments were conducted with Dr. Peter Herman, Netherlands Institute of Ecology (NIOO-CEMO) while on a NIWA visiting scientist fellowship to collaborate in our FRST research programme: Effects of Sediments on Estuarine and Coastal Ecosystems. (

evaluate the efficiency of the clay layer as a barrier to tidal flushing, rather than the infiltration of the bromide through the clay.

Each slice of sediment was suspended in 5 ml of distilled water by vigorously shaking for 30 seconds in a 10 ml centrifuge tube several times over a period of about 1 hour to allow the bromide and seawater chloride to equilibrate from the sediment pore water. The sediment was then centrifuged at 3000 rpm for 10 minutes and the supernatant liquid transferred to clean vials for analysis of bromide and chloride (R.J. Hill Laboratories, Hamilton). Bromide concentrations in each core slice were normalised for comparison using the seawater chloride data to correct for differences in pore water volume and the amount of sediment in each slice.

4 Results and Discussion

4.1 Spatial distribution

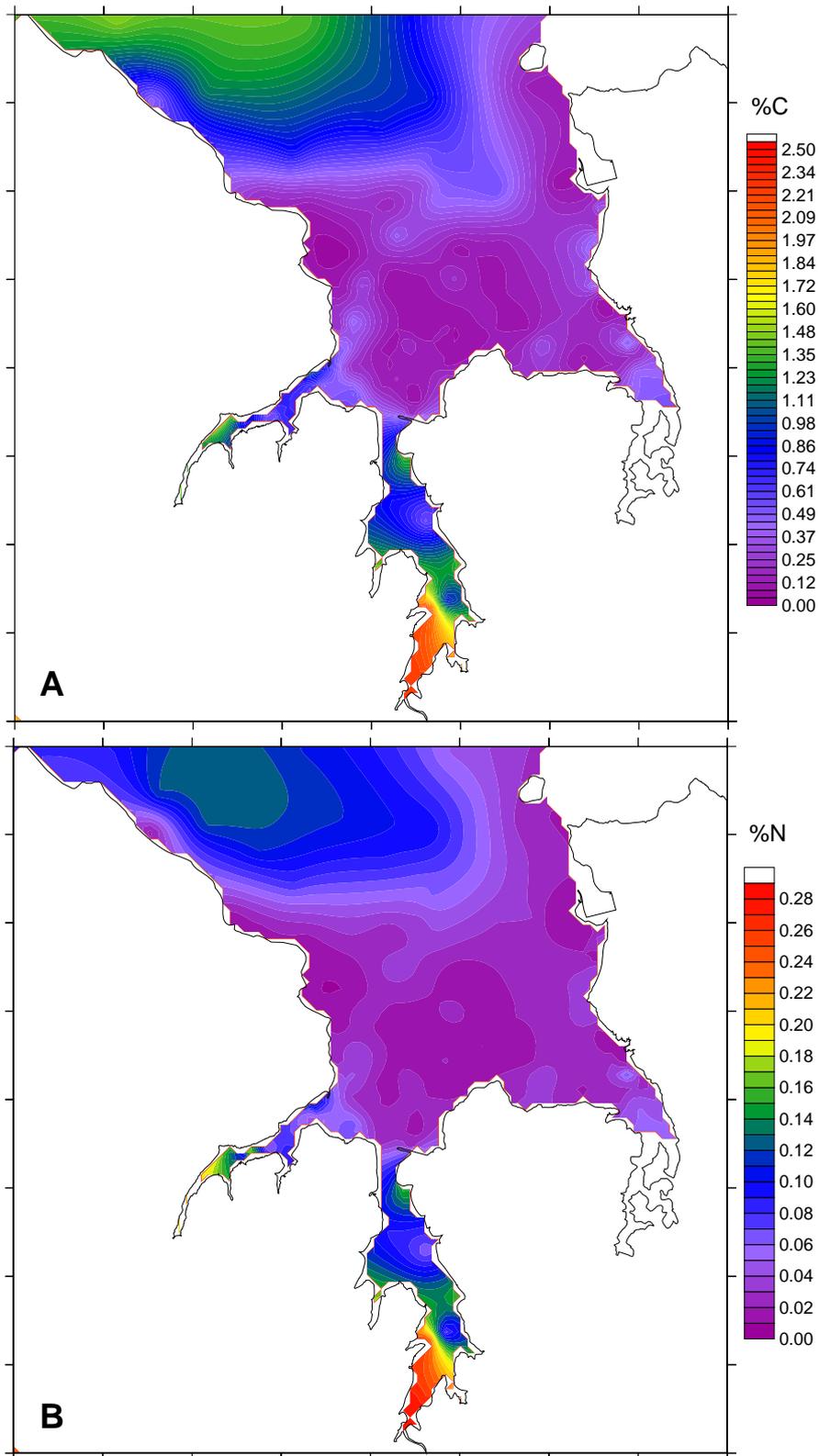
The percentage carbon and nitrogen, and their associated stable isotopic distribution patterns, are presented as individual contour plots within the confines of the estuary arms and Whitford embayment. The patterns produced are indications of likely distribution and are not absolute values.

Distribution data of sediment types based on particle size analysis is being prepared but is not presently available (NIWA report for Manukau City Council due for completion in 2002). Data on the % clay in the spatial sediment samples were made available for this report. Intertidal sediments are typically sandy with habitat changes from worm and diatom dominated areas to more silty substrates associated with several large beds of the cockle, *Austrovenus stutchburyi*. These latter areas, including sites L and C, typically have an anaerobic layer 30-40 mm below the surface. In the sandy areas, however, free water and hence oxygen movement is indicated by the lack of anaerobic conditions in the upper 100 mm of sediments. Subtidal sediments were generally more silty across the embayment and further off-shore. There are areas which have courser sands and gravel close to shore near Howick and near the Pine Haven Marina.

Water circulation within the Whitford embayment is dominated by the tide and the inflows from the estuarine arms of the embayment on the outgoing tide.

4.1.1 Percent carbon and nitrogen

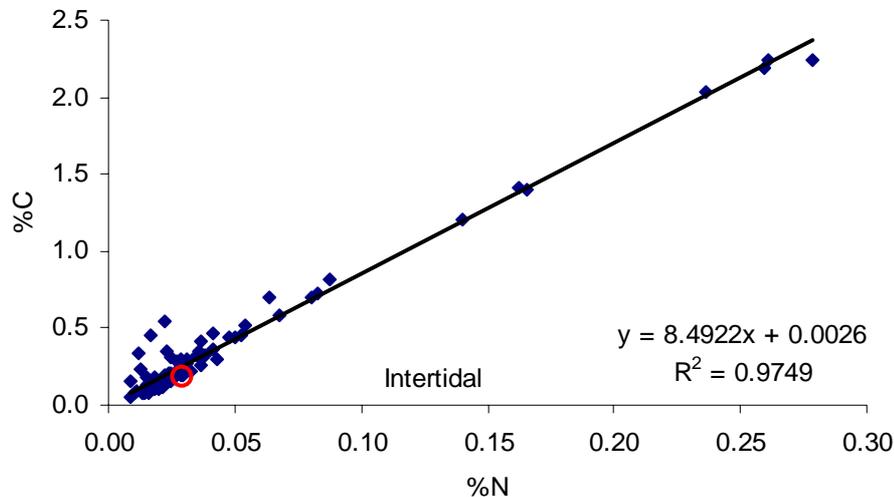
Fig. 3 Contour plots of spatial distribution of % carbon (A) and % nitrogen (B) in the estuary arms and across Whitford embayment. (Patterns are indications of likely distribution and not absolute values.)



There is close correlation between the %C and %N data (Fig. 3A,B) with higher percentages of C and N in the upper reaches of the inflow arms than in the open embayment. This distribution pattern is consistent with organically enriched terrigenous inputs entering the estuary arms and flocculating out of the water column as the freshwater mixes with the seawater. The three input arms of the Whitford embayment are fringed with mangroves which tend to trap suspended matter allowing the terrigenous inputs to settle within these arms during the incoming and high phase of the tide. When the tide recedes or is low, the current flow from the input streams would carry the terrigenous material along the low water flow channels to subsequently settle in the open embayment or disperse into the adjacent coastal waters.

There are apparent distributions pattern across the embayment which indicate subtidal sedimentation along the flow channels to the open water beyond the intertidal zone. There is also a zone of apparently higher %C and %N towards the outer edge of the embayment off-shore from Howick, which may be associated with a deposition zone for sediment from the Whitford inflows or adjacent coastal inputs. Carbon and nitrogen content were generally low across the intertidal zone of the embayment.

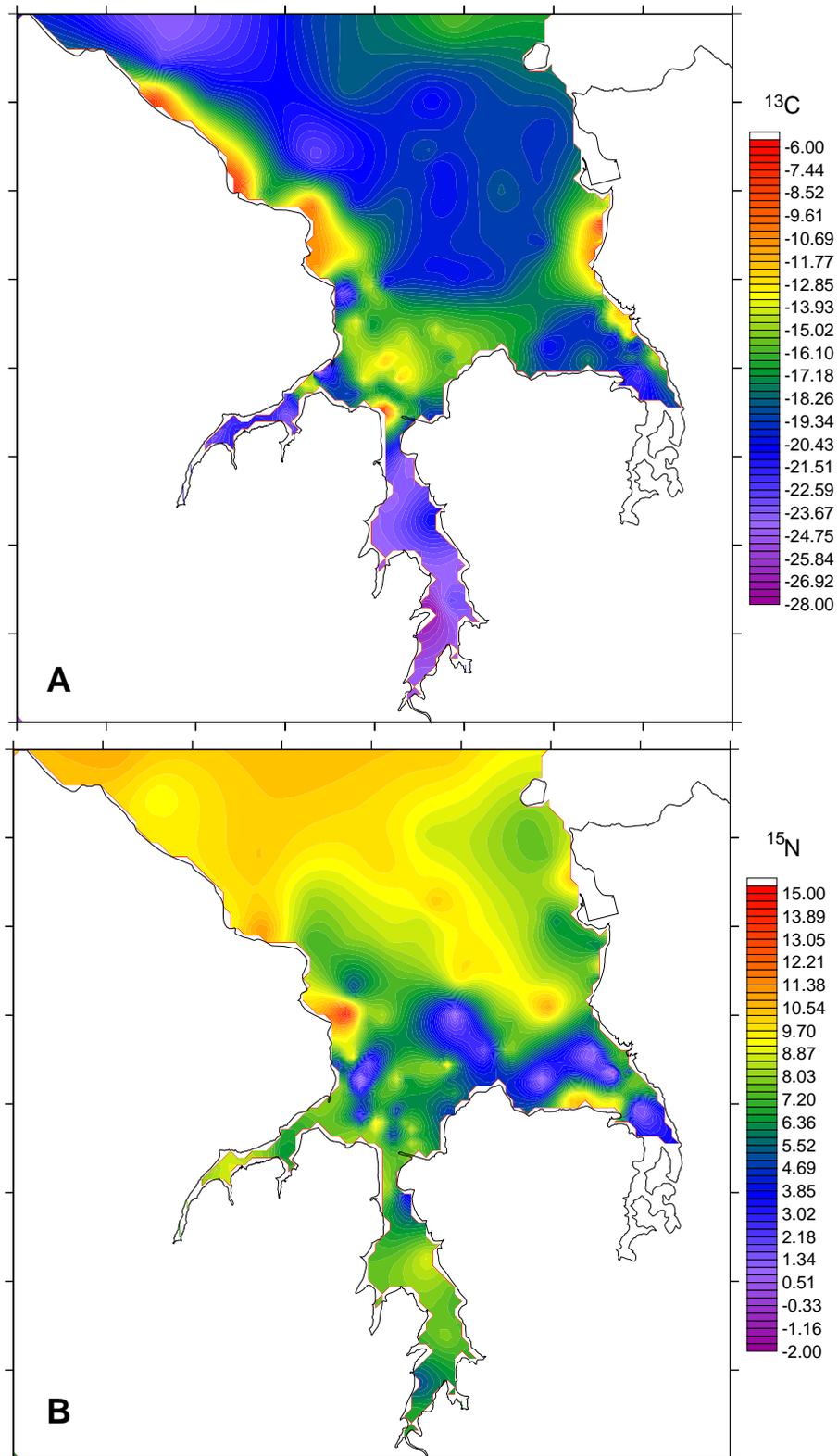
Fig. 4 Relationship between %C and %N across the intertidal zone of Whitford embayment. Data from mangrove areas have been excluded (see text). The C:N ratio of terrigenous clay is indicated by the red circle.



The ratio of %C:%N (Fig. 4) was essentially constant across the intertidal zone at 8.5 (r^2 0.975, $n = 107$) with a higher C:N ratio in the subtidal (10.1, r^2 0.859, $n = 35$) but lower C:N ratio in the areas dominated by mangroves (5.1, r^2 0.90, $n = 16$). C:N ratios of 8-10 are consistent with plant material including benthic microphytes whereas the value of 5 is more characteristic of detritus and animal waste. The C:N ratio of the local clay was 6-7.3.

4.1.2 Stable isotopes

Fig. 5 Contour plots of spatial distribution of $\delta^{13}\text{C}$ (A) and $\delta^{15}\text{N}$ (B) natural abundance signatures in the estuary arms and across Whitford embayment. (Patterns are indications of likely distribution and not absolute values.)



4.1.2.1 $\delta^{13}\text{C}$ data

The contour plot of $\delta^{13}\text{C}$ data (Fig. 5A) revealed a pattern of very negative values at -28 to -24 ‰ in the upper reaches of the inflow arms and values of -20 to -17 ‰ in the mid to outer reaches of the embayment (subtidal zone). Between these zones the $\delta^{13}\text{C}$ values are more positive at up to -12 ‰, and values of about -6 ‰ were found adjacent to inflows draining urban areas around Howick to the west and farmland to the south and east. There was no apparent correlation between $\delta^{13}\text{C}$ and %C or %N.

Interpretation of these $\delta^{13}\text{C}$ values is that the mid-range values of -20 to -17 ‰ are typical of estuarine sediments (Fig. 1), where values can range from -25 to -15 ‰, and can be considered to be the background $\delta^{13}\text{C}$ levels for sediment in Whitford embayment.

Sediment with more positive $\delta^{13}\text{C}$ values than this background are likely to be of organic origin and most likely of terrigenous origin. The more positive values of -9 to -6 ‰ adjacent to obvious inputs such as storm-water drains from Howick and small, farm run-off streams indicate that these inflows are likely to be contaminated with animal excrement and possibly domestic sewage. The values of -5.7 to -7 ‰ adjacent to a small stream from below the Formosa Auckland Country Club may indicate septic tank contamination of that inflow. The lack of increased %C associated with these $\delta^{13}\text{C}$ values indicates the inputs are likely to be in soluble form such as bicarbonate, whereas the more positive $\delta^{13}\text{C}$ values indicate multiple biological processing of organic matter (food) including C4 plants, such as corn.

The band of sediments with $\delta^{13}\text{C}$ values of -17 to -12 ‰ extending across the intertidal zone of the embayment appears to originate from the stream entering the estuary beside the Pine Harbour Marina. Other point sources, such as the inflow draining swamp land in the centre of the estuary, also contribute to this spatial pattern. The resultant $\delta^{13}\text{C}$ spatial distribution pattern (Fig. 5A) indicates a clockwise circulation flow pattern on the inflowing tide when sedimentation is most likely to occur, i.e. freshwater flocculating and sedimenting from slow moving water over the intertidal zone around high tide. The lack of $\delta^{13}\text{C}$ values of -17 to -12 ‰ extending northwards across the entrance to the Pine Harbour Marina indicates that either the water does not carry the carbon source in that direction or that carbon sedimentation does not occur in that region (Fig. 5A).

Sediment with $\delta^{13}\text{C}$ values more negative than background are likely to be related to non-refractive terrigenous material such as clay which has a $\delta^{13}\text{C}$ value of about -26 to -28 ‰. The occurrence of more negative $\delta^{13}\text{C}$ values in the upper reaches of the inflow arms is consistent with clay mineral sediment being trapped within these arms by the mangroves at high water, as described for the %C and %N data.

4.1.2.2 $\delta^{15}\text{N}$ data

The contour plot of the $\delta^{15}\text{N}$ data (Fig. 5B) shows a general similarity to the $\delta^{13}\text{C}$ distribution pattern (Fig. 5A) in that the $\delta^{15}\text{N}$ values in the upper reaches of the input arms are similar to each other but less positive than the subtidal areas of the

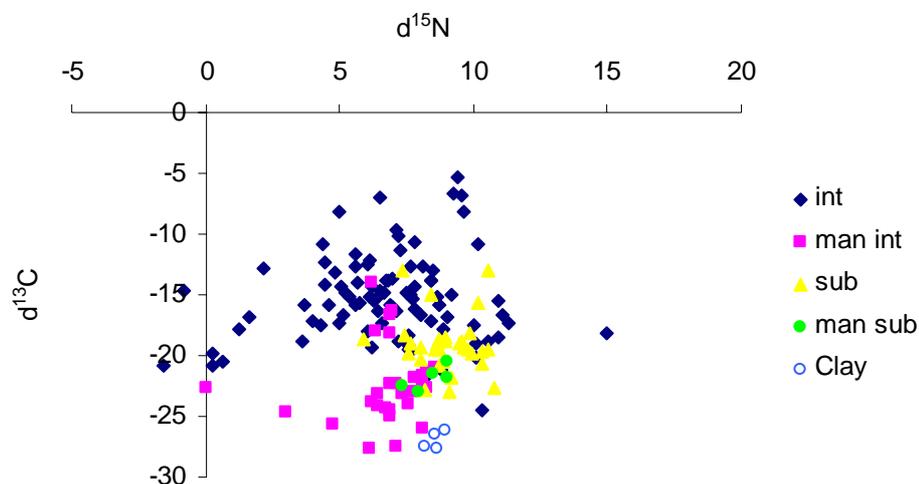
embayment. Sediment with $\delta^{15}\text{N}$ values of around 3 to 4 ‰ across much of the intertidal sand flats is consistent with marine and estuarine sediments (Fig. 1) and can be considered to be the background $\delta^{15}\text{N}$ levels for sediment in Whitford embayment.

Sediment with $\delta^{15}\text{N}$ values more negative than background may be associated with fixation of atmospheric nitrogen by benthic microphytes across the sand flats or nitrogen fertiliser inputs, such as urea or nitrate, in land drainage, e.g. on the western and eastern side of the estuary.

Sediments with $\delta^{15}\text{N}$ values more positive than background are likely to be associated with biological processes including microbial decomposition of buried organic matter. Very positive $\delta^{15}\text{N}$ values along the shoreline adjacent to urban areas of Howick and some farm land around the shores of the estuary correlate with the less negative $\delta^{13}\text{C}$ values, consistent with these inflows being contaminated with animal excrement and possibly domestic sewage. High $\delta^{15}\text{N}$ values in benthic algae have been used elsewhere as an indicator of waste-water contamination of an estuary via the ground water (McClelland & Valeia 1998).

In contrast to the close linear correlation between %C and %N, there was no significant relationship between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ although the data could be grouped by location (Fig. 6).

Fig. 6 Relationships between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediment from intertidal (int), intertidal mangroves (man int), subtidal (sub), subtidal mangroves (man sub), and the source clay. (d = ‰).



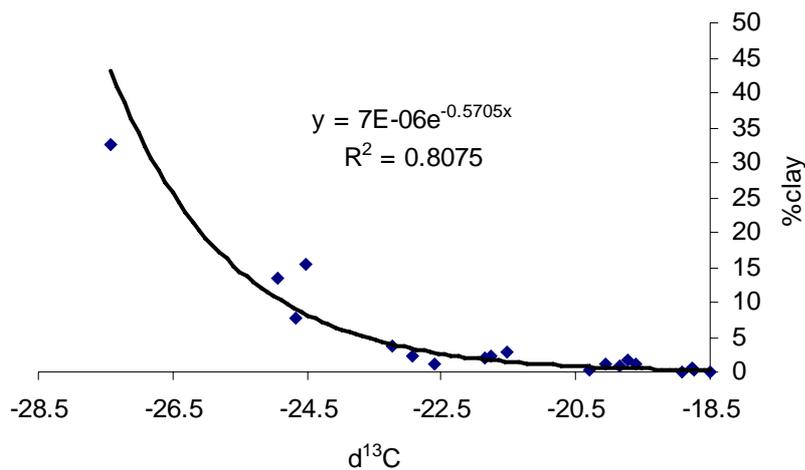
Although these groupings tend to overlap between intertidal and subtidal, the sediment from mangrove areas and the clay are generally well separated by their $\delta^{13}\text{C}$ values. The separation between the clay and the mangrove signatures, however, is more difficult to resolve. The clay signature is more negative than the boundary for the mangrove sediment signature, indicating that sediments from within the mangroves is likely to be a mixture of terrigenous clay and background estuarine sediments. Given

that the clay is trapped in the mangrove areas such a correlation is not unexpected and does not preclude using isotopic signatures to discriminate the presence of clay.

4.1.3 Clay

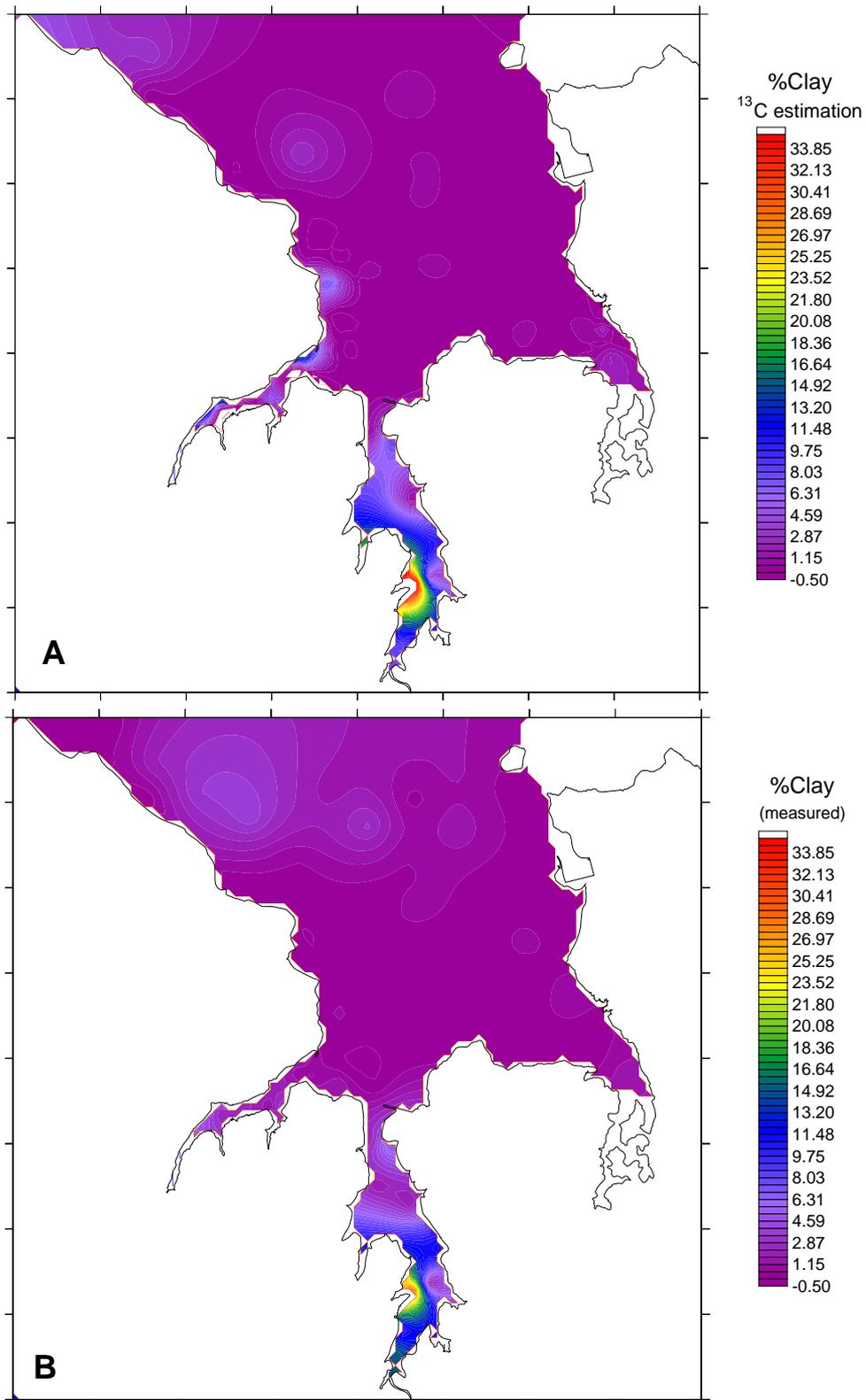
On the premise that clay makes up the bulk of the sediment beneath the mangroves compared with the %C content of those sediments, it is reasonable to assume that the dominant isotopic signature will come from the clay rather than the mangrove detritus. Assuming that the very negative $\delta^{13}\text{C}$ values were attributable to clay mineral content, the amount of clay present in each sediment core was estimated by using all the data more negative than background. The $\delta^{13}\text{C}$ data was transformed using a regression equation against data for clay content measured by particle size analysis (Fig. 7), with a mean background $\delta^{13}\text{C}$ value of -18.5 ‰. $\delta^{13}\text{C}$ values more positive than -18.5 ‰ were set to zero.

Fig. 7 Regression graph and equation used to transform $\delta^{13}\text{C}$ data into % clay. These data are taken from Whitford estuary sediments. ($d = \delta$).



The transformed $\delta^{13}\text{C}$ values were then contoured to give an estimated spatial distribution pattern for clay across the input arms and Whitford embayment (Fig. 8A) compared with the actual % clay content measured by particle size analysis (Fig. 8B).

Fig. 8 Spatial distribution of clay as estimated from the $\delta^{13}\text{C}$ data (A), and as measured by particle size analysis (B).



The contour plot of the % clay distribution estimated from the $\delta^{13}\text{C}$ data (Fig. 8A) is in relatively close agreement with the distribution of % clay measured by particle size analysis (Fig. 8B). There are some differences near the shore at Howick which may reflect anthropogenic inputs of fertiliser, as the $\delta^{15}\text{N}$ values were very negative in that area. The poor resolution at very low levels of clay (< 5%) in the subtidal zone may reflect the use of an exponential relationship for the data transformation or it may indicate a physical change in the subtidal sediments which affects the way clay particles are held in those sediments. Clay on the intertidal flats is exposed to dewatering and erosion or burial by wave action and hence may remain essentially isotopically unchanged. However, clay deposited subtidally is not exposed to these physico-chemical processes and may be more subject to transformation by deposit feeders. Further work is also required to refine the transformation algorithm. Nevertheless, these results suggest that the use of stable isotopes may be a valid technique for estimating the % clay in estuarine sediments.

Considering the potential for physical dispersion and/or burial of terrigenous clay within the sediments, the spatial distribution patterns (Fig. 8) represent the conditions over an undefined period of time before sampling. These data indicate very low levels of terrigenous clay contamination of the Whitford intertidal flats at the time of sampling, which means that it is likely that there has been sufficient time for the ecosystem to recover since the last substantial clay input.

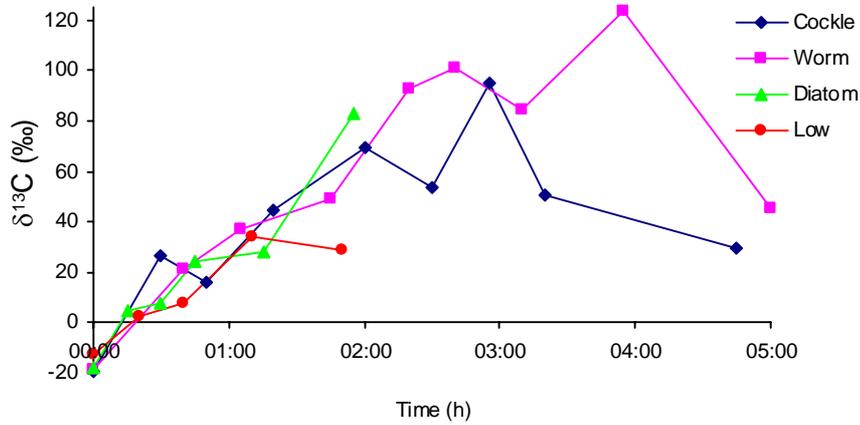
4.2 Clay impact experiments

The effects of thin smears of clay on benthic communities is described in a separate report (Berkenbusch et al. 2001). In this report we use bromide tracer and stable isotopes to determine the effect of the clay on the hydraulic conductivity of the sediments and the impact on the microphytobenthos in those sediments.

Microphytobenthos and microbial biofilms play critical roles in the mineralization of nutrients and primary production in intertidal ecosystems (Decho 2000). Microbial biofilms of extracellular polymeric secretions from these micro-organisms may also bind and thus stabilize sediments against resuspension. As primary producers these organisms also form the basis of the intertidal food chain. The application of ^{13}C labelled sodium bicarbonate on the exposed intertidal sand flats allowed the microphytobenthos to assimilate the ^{13}C label into their biomass and hence become a living indicator of storage and transfer through the food chain.

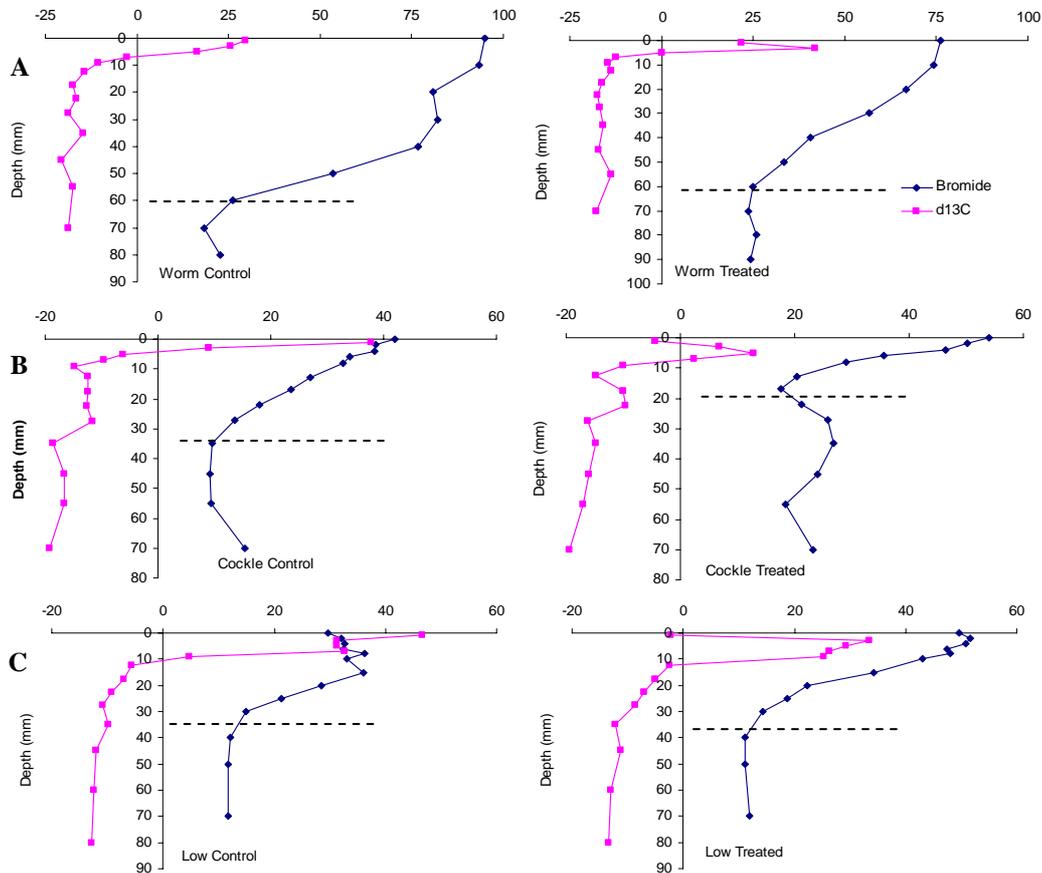
Uptake of ^{13}C -carbonate was measured in the control plots only and assumed to be the same in the adjacent designated treated plots. This was to ensure there were no holes in the surface of the treated plots which could alter the thickness of the clay smear and potentially affect subsequent sampling and results.

Fig. 9 Uptake rates of ^{13}C -bicarbonate by the benthic microphytes at the 4 experimental sites. Background ^{13}C levels were -18 to -15 ‰.



Time series samples from all sites showed a rapid uptake of the ^{13}C label over the first 3 hours after application, then a decline as the incoming tide approached the sites (Fig. 9). After 1 tidal cycle $\delta^{13}\text{C}$ values were about $+10$ to $+20$ ‰ and remained at about those levels in the upper 5 mm of sediment for the duration of the experiment.

Fig. 10 Initial bromide profiles showing infiltration depth (broken lines) against microphyte distribution depth as indicated by their $\delta^{13}\text{C}$ label profiles. (Keys as for Worm Treated).

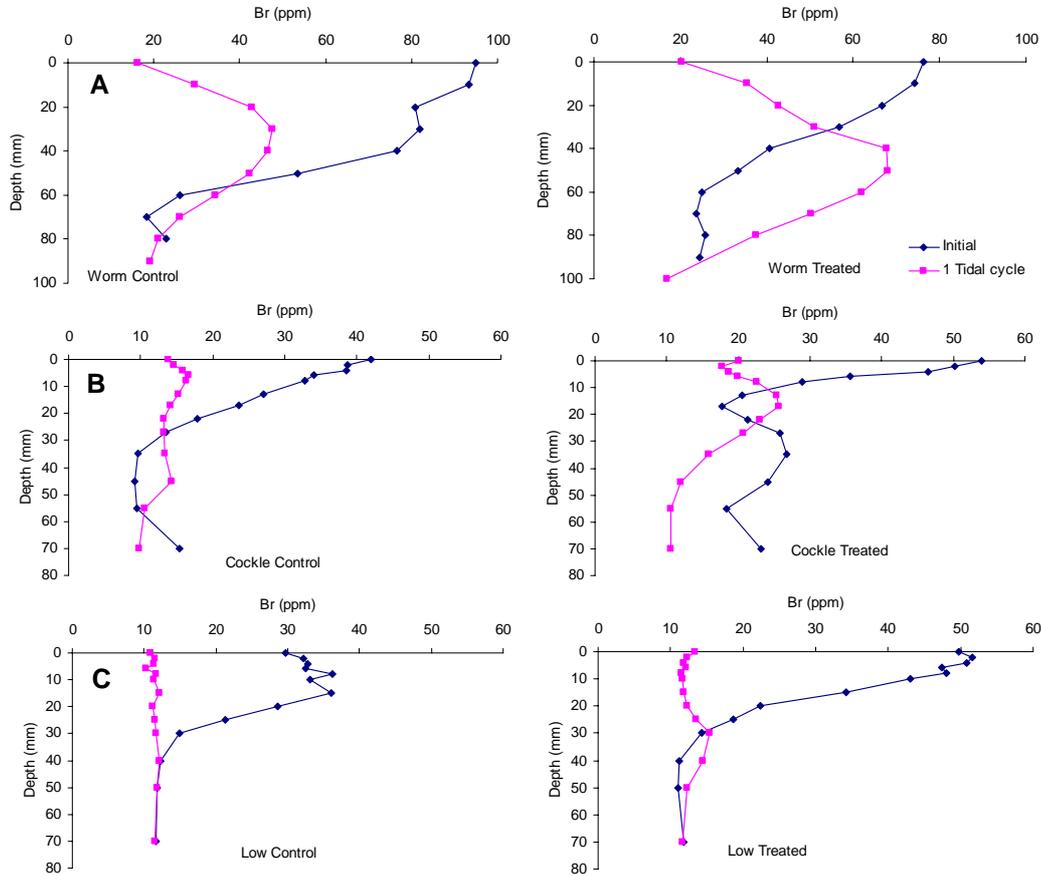


The impact of the thin clay layer was seen in the core profile data, and the depth of tidal flushing and its effect on the ^{13}C -labelled microphytes was seen in the bromide and $\delta^{13}\text{C}$ data (Fig. 10).

Initial core profiles showed that bromide infiltrated the worm site to a depth of about 60 mm with or without the clay layer (Fig. 10A). At the cockle site the bromide infiltration depth was about 30 mm without clay and <20 mm with the clay layer (Fig. 10B). At the low site, another site dominated by cockles, the initial bromide infiltration was similar to the cockle site at about 30 mm (Fig. 10C). At all sites the microphyte layer was confined to the upper 10 mm, as indicated by the $\delta^{13}\text{C}$ profiles.

The data from the worm and cockle treated plots (Fig. 10A,B) show that the 5 mm thick layer of clay was not a barrier to infiltration of a solute such as bromide. There was a small difference in the depth of penetration of the bromide due to the clay layer only on the Cockle site. However, there was a marked difference in bromide penetration between the Worm site and the sites dominated by cockles. This is likely to be related to sediment porosity with a higher porosity at the sandier worm site.

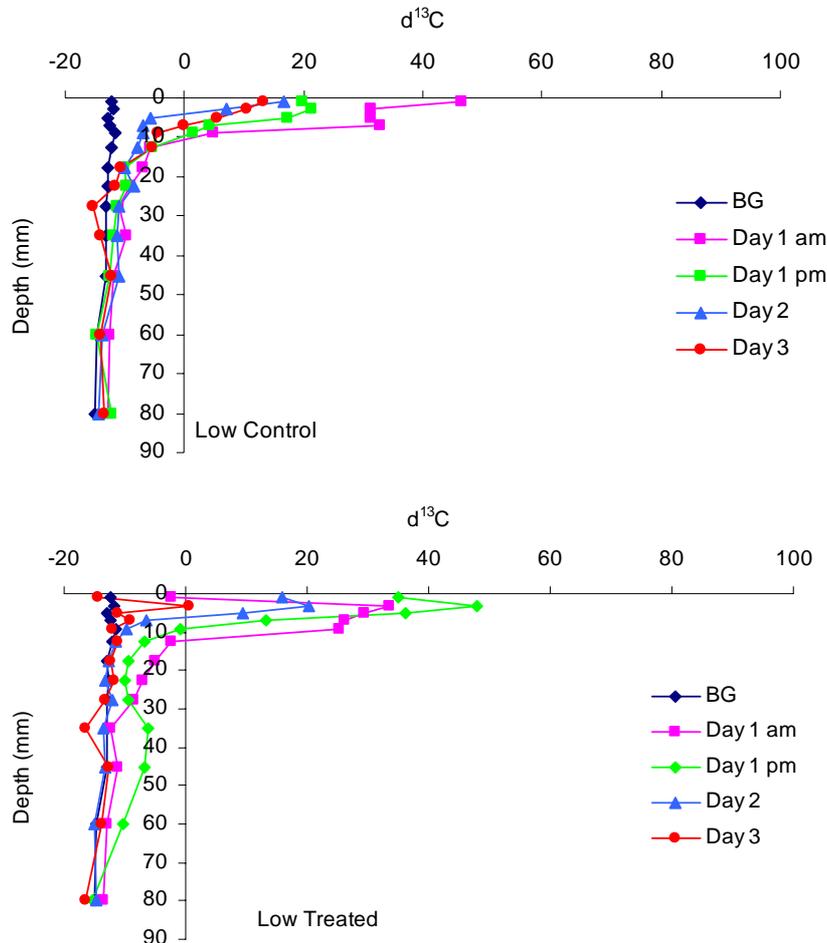
Fig. 11 Bromide concentrations in the pore water after initial infiltration and again after 1 tidal cycle. (Keys as for Worm Treated).



Hydraulic flushing of the sediments was indicated by the change in the bromide profiles after 1 tidal cycle (Fig. 11). At all sites, with and without clay, there was substantial flushing down to at least 30 mm into the sediments after 1 tidal cycle, as indicated by the loss of bromide from the upper core profile. At the worm site (Fig. 11A) the bromide reduction in the control was most likely caused by dilution and lateral flushing, whereas in the treated plot, the bromide appears to have been forced deeper into the sediments below the clay layer by the inundating tide. At the cockle site (Fig. 11B), the pattern was similar but less distinct. At the low site (Fig. 11C), the clay application over the bromide failed to prevent almost complete flushing.

Time series profiles of the $\delta^{13}\text{C}$ associated with the labelled microphytes at the Low site (Fig. 12) indicate that, whereas tidal flushing did not remove the microphytes from the control, beneath the clay the $\delta^{13}\text{C}$ signal declined indicating that the microphytes had died and subsequently decomposed.

Fig. 12 Time series profiles of the $\delta^{13}\text{C}$ labelled benthic microphytes at the Low site. The level of the $\delta^{13}\text{C}$ signal in the control plot appeared to stabilise after day 1 whereas the $\delta^{13}\text{C}$ signal in the treated plot declined from day 1 indicating a collapse of the microphytes population beneath the clay. (BG = background, d = δ).

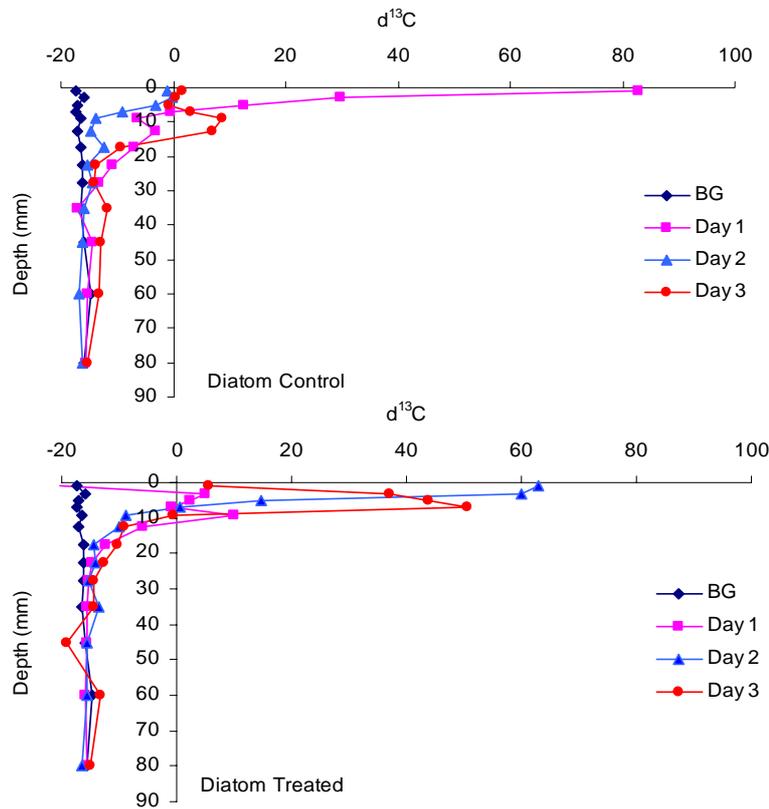


These results indicate that the thin (5mm thick) layer of clay was not a barrier to water and hence the solutes dissolved in that water. Consequently this indicates that fluxes of nutrients regenerated from the sediments would not be inhibited by a thin layer of clay. This is consistent with the results of the nutrient regeneration experiment conducted on the Low site in January (Berkenbusch et al. 2001).

The results of that experiment showed the nitrogen release flux increasing with the clay thickness up to the 5 mm tested. Oxygen production by the benthic microphytes still occurred under 1 mm clay but not under the 5 mm layer where dissolved oxygen concentrations decreased. This may be interpreted as a physical blocking of the microphytes from movement up through the clay at the Low site. The decline in the $\delta^{13}\text{C}$ signal beneath the clay over a period of 3 days is consistent with the microphytes dying, decomposing and the ^{13}C being lost from the system as CO_2 . The reduction in oxygen in the 5 mm treatment plots indicates sediment decomposition processes removing oxygen from the water above the sediments. This means that the clay layer

was not a block to gaseous exchange and the microphytes most likely died from lack of light.

Fig. 13 Time series profiles of the $\delta^{13}\text{C}$ labelled benthic microphytes at the Diatom site. ($d = \delta$).



In contrast to the Low site, time series data from the Diatom site (Fig. 13) indicated that the ^{13}C -labelled microphyte community rapidly declined or moved deeper in the control plot whereas it remained almost constant in the treated plot.

These results indicate that the microphyte community was probably eroded away by wave action flushing the coarse sands of the control plot while the clay stabilised the sand in the treated plot allowing the microphyte community to survive. This implies that the clay mixed with the sand and the resultant mixture was sufficiently porous for the microphytes to migrate up into the light for photosynthesis. The production of oxygen in the benthic chamber experiments from all clay treatments at the Diatom site (Berkenbusch et al. 2001) supports this conclusion.

5 Conclusions

While the primary objective of this study was to provide empirical evidence of the movement of terrigenous sediment (clay) through an estuary using stable isotope techniques and this was achieved, the results indicate that far more information about the estuary can be obtained from such data.

Spatial patterns of %C and %N indicate that much of the intertidal zone in Whitford embayment is low in carbon and nitrogen relative to the subtidal zones. Most of the inflow terrestrial carbon and nitrogen appears to be trapped in the upper reaches of the estuary arms by the mangroves. This trapping most likely occurs on the incoming or high tide. Slightly higher %C and %N content in the sediments of the subtidal channels from these arms indicates that sedimentation may occur in these zones at other stages of the tide.

Stable isotopic δ values of carbon and nitrogen also indicate a substantial trapping of terrigenous particulate material in the upper estuary arms by the mangroves.

Transformation of the $\delta^{13}\text{C}$ signature of the sediment allowed an initial estimate of the % clay distribution through the estuary arms and across Whitford embayment which was in good agreement with the % clay content measured by particle size analysis. Although further refinement of the algorithm used for the transformation is required, these results indicate that stable isotope techniques can be used to determine the input and movement of terrigenous clay in an estuarine setting.

The spatial distribution patterns obtained from the isotopic transformation and the measured data indicate that there was little terrestrial clay contamination of the Whitford intertidal flats at the time of sampling. This indicates that the intertidal flats have had sufficient time to recover since the last substantial input of terrigenous clay. The accumulation of clay in the estuarine arms of the embayment also means that mangroves may be an effective ameliorating agent to the present level of terrigenous clay inflow.

The untransformed natural abundance stable isotope data showed spatial distribution patterns that indicate terrigenous inputs other than clay may be impacting on Whitford embayment. There are clear indications of waste-water contamination of some stream and storm-water drain inflows from urban areas and areas under urban development. The natural isotopic abundance data also provided an indication of the dominant circulation pattern of water in the embayment and when sedimentation is most likely to occur, and indicated that there were likely to be correlations between benthic communities and their habitats.

The stable isotope enrichment experiments coupled with the bromide tracer study data showed that thin layers of terrigenous clay up to 5 mm thick did not block the movement of water, and hence nutrients or dissolved gases, through the sediment when the intertidal sandflats were submerged. Tidal flushing was deeper in the sandier sediments, as would be expected. However, whereas the tidal flushing could

penetrate to about 60 mm in the sand, the microphytobenthos communities remained in the upper 10 mm of the sediment.

The isotopically labelled benthic microphytes became markers for the effects of wave action on the sediments. In the sandy site, without clay wave action removed the labelled microphytes by sediment disturbance while the thin clay layer mixed into and stabilised the sand allowing the microphytes to survive. In contrast, at the more silty site dominated by cockles, the labelled microphytes survived in the sediment without the clay but died where they were covered by the 5 mm clay layer.

The results indicate that there is a very delicate balance between chemical fluxes across the sediment-water interface and primary production in the sediments for benthic communities. This balance can be affected by even small inputs of terrigenous clay. The degree of that effect is dependent upon the habitat impacted and the thickness of the clay layer. Significant ecological changes would depend on the frequency of clay deposition events.

6 References

- Berkenbusch, K.; Thrush, S.; Hewitt, J.; Aherns, M.; Gibbs, M.; Cummings, V. (2001). Impact of thin deposits of terrigenous clay on benthic communities. NIWA Client Report ARC01269. NIWA Hamilton, 56 pp.
- Bury, S. (1999). The Delta^{Plus} stable isotope mass spectrometer: advancing NIWA's research in environmental processes. *Water & Atmosphere* 7(2): 22-25.
- Decho, A.W. (2000). Microbial biofilms in intertidal systems: an over view. *Continental Shelf Research* 20: 1257-1273.
- Gibbs, M.; Thrush, S.; Ellis, J. (2001). Terrigenous clay deposition on estuarine sandflats: using stable isotopes to determine the role of the mud crab *Helice crassa* Dana, in the recovery process. *Isotopes in Health and Environmental Studies* 00: 1-19.
- Kaehler, S.; Pakhomov, E. A.; McQuaid, C.D. (2000). Trophic structure of the marine food web at the Prince Edward Islands (southern ocean) determined by $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis. *Marine Ecology Progress Series* 208: 13-20.
- Legendre and Legendre (1998). Numerical Ecology. Elsevier, Amsterdam. 853.
- McClelland, J.W.; Valiela, I. (1998). Linking nitrogen in estuarine producers to land-derived sources. *Limnology and Oceanography* 43(4): 577-585.
- Middleburg, J.J.; Barranguet, C.; Boschker, H.T.S.; Herman, P.M.J.; Moens, T.; Heip, C.H.R. 2000: The fate of intertidal microphytobenthos carbon: An *in situ* ^{13}C -labelling study. *Limnology and Oceanography* 45(6): 1224-1234.
- Nicholls, P.E.; Norkko, A.; Ellis, J.; Hewitt, J.; Bull, D. (2000). Short term behavioural responses of selected benthic invertebrates inhabiting muddy habitats to burial by terrestrial clay. NIWA Client Report ARC00258. NIWA Hamilton. 19 pp.
- Norkko, A.; Thrush, S.F.; Hewitt, J.E.; Norkko, J.T.; Cummings, V.J.; Ellis, J.I.; Funnell, G.A.; Schultz, D. (1999). Ecological effects of sediment deposition in Okura estuary. NIWA Client Report ARC90243. NIWA Hamilton. 41 pp.