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Biogeochemistry of intertidal sediments

T.D. Jickells and J.E. Rae

In some places the boundary between land and sea is in the form of abrupt and often spectacular cliffs but, elsewhere, the boundary can take the form of a complex environment of intertidal sediments. These environments include shingle banks, sandy beaches, mud flats, saltmarsh and mangrove (or mangal) communities. In some cases one or other of these environments will occur, in others they will be associated with one another. For example, on many North Sea and North American East Coast shorelines, mud flats grade into saltmarshes behind the shelter of shingle spits and sand dunes. In general, saltmarshes and mangroves occupy similar ecological niches with mangroves at lower latitudes (winter temperatures greater than 10 °C) and saltmarshes at high latitudes, though in some locations both communities coexist (Chapman, 1977).

The considerable global significance of these intertidal systems is evident from Figure 1.1. Around the coast of Britain alone there are 44 370 hectares (ha) of saltmarsh (Allen & Pye, 1992) and 589 429 ha on the US East Coast (Reimold, 1977) with a total global area of 3.8×10^7 ha (Steudler & Peterson, 1984 and references therein). There are 365 500 ha of mangal forest around the Indian subcontinent and another 250 000 ha in the Mekong delta (Blasco, 1977). The total global area of mangal is about 2.4×10^7 ha (Twilley, Chen & Hargis, 1992). The total area of intertidal sediments is likely to be similar to that of adjacent saltmarshes and mangals.

These intertidal environments afford very effective coastal protection (Brampton, 1992). The importance of such coastal protection is increasing as a result of two processes. Firstly, the growth in world population is increasing the pressure on land in general. Moreover, the increase in populations in coastal areas is disproportionately large, compounding this pressure (Hinrichsen, 1994). Secondly, the process of sea level rise is threatening low lying land with increased risk of flooding. Sea level rise is

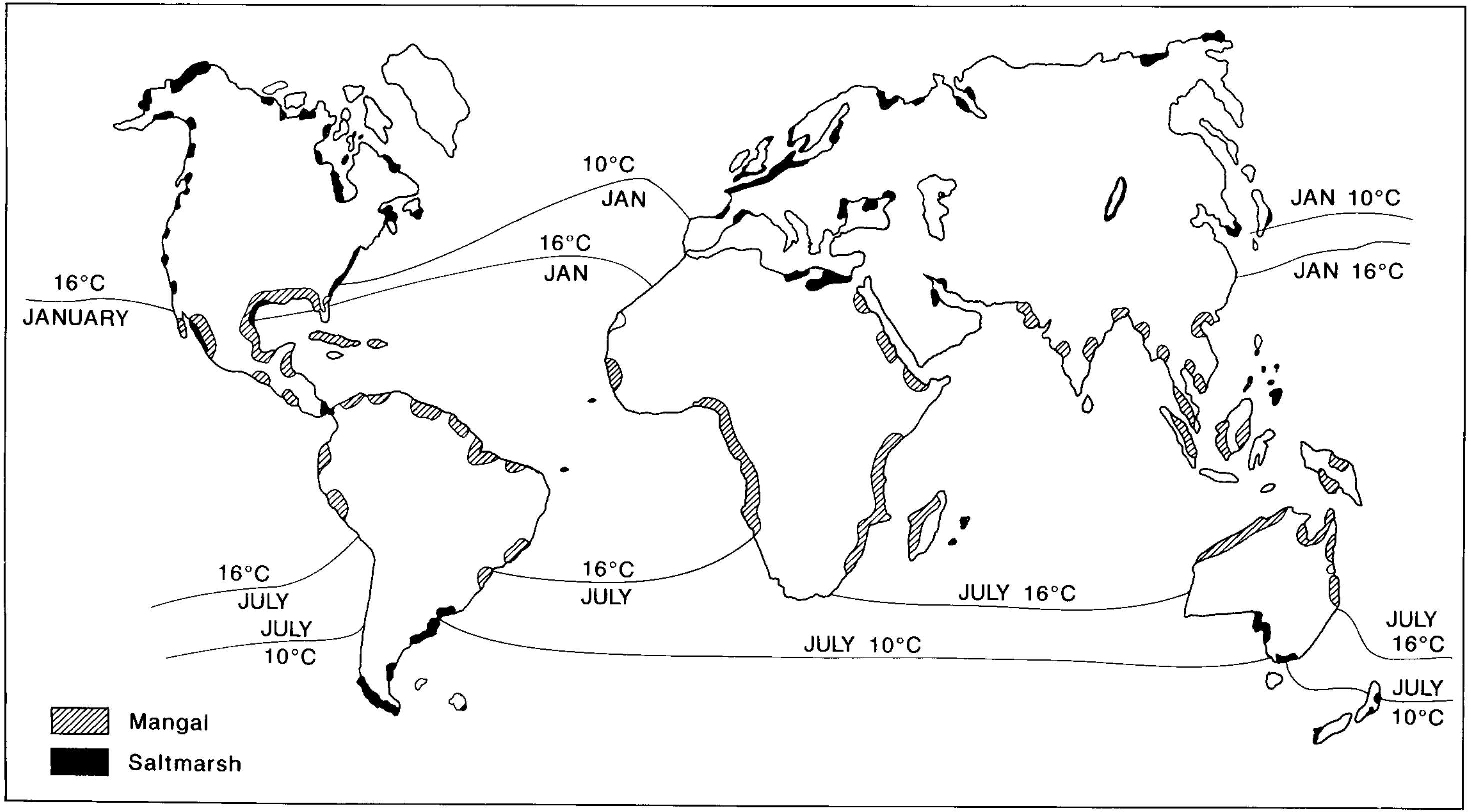

Figure 1.1 Map showing global distribution of saltmarshes and mangroves (mangal) in relation to average temperature, redrawn from Chapman, 1977.

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in part a natural process, as the coastal system slowly responds to the end of the last glaciation, but is now being exacerbated by anthropogenically induced climate change – the greenhouse effect (e.g. Wigley & Raper, 1992). The threat to coastal areas from climate change arises not just from sea level rise associated with global warming, but also potentially from changes in weather patterns and hence wave and current patterns (Tooley, 1992).

In addition to providing a valuable sea defence, intertidal sediments offer an important habitat for wildlife, food and recreation. The very nature of intertidal areas has left them relatively undisturbed by human activity compared to inland areas. This coupled with the rich food supply in the muddy sediments means that many intertidal areas are now very important wildlife sanctuaries and nursery grounds for fish and invertebrates (Adam, 1990). Thus, for example, up to 12 million birds of 50 different species live for at least part of the year on the vast shallow water or intertidal muds of the Wadden Sea off the north Dutch and German coast (North Sea Task Force, 1993). Beside these quantifiable environmental roles as wildlife habitats and coastal defences, these intertidal areas have an intrinsic beauty that has always attracted people.

For all these reasons, intertidal sedimentary environments are important areas for scientists to study, and there is a long history of such work. This has often focused on the geomorphology of these areas and how this can be used to interpret the geological record (e.g. Nummedal, Pilkey & Howard, 1987; Allen and Pye, 1992) and the ecology of these areas (e.g. Adam, 1990; Chapman, 1977; Mathieson and Nienhuis, 1991). In addition many studies have concentrated on one type of ecosystem (e.g. saltmarsh or mangal). This book aims to take a different and complementary approach. Firstly, it focuses on the chemistry of these systems as modulated by and interacting with the geological and biological environment – hence the term biogeochemistry. Secondly, we have drawn no distinction between the different types of intertidal ecosystem since we believe the fundamental biogeochemical processes are the same in all the systems, though of course the final chemical system observed by our measurement varies as a function of the ecosystem. Thus the biogeochemical environment of a mangal swamp and an arctic mud flat may be very different, but the fundamental principles regulating these environments will be similar. Some of the authors in this book have even drifted out into more open waters to illustrate their points; something that only serves to emphasise both the generality of the biogeochemical principles and also the limited research effort expended into some aspects of the biogeochemistry of intertidal areas.

The detrital mineral phases of the intertidal sediments (e.g. clays and quartz) are of limited geochemical interest in the context of this book. Rather it is the organic matter and the chemicals adsorbed *to* the mineral phases of the sediment and to one another that drive most of the geochemical processes. Adsorption to sediments is a function of sediment surface area and hence particle size, with the finest sediments adsorbing the most material, as illustrated in the chapters by McDonald & Jones, Zhou & Rowland, and Rae. This means that in a geochemical (and also an ecological) sense the coarse sediments of high energy environments like shingle and sand beaches are of limited interest. The fine-grained organic matter which feeds the flora and fauna and fuels the geochemical reactions is washed out of these areas, to accumulate in the low energy environments such as the mud flats, mangals and saltmarshes that are the main focus of this book. Hence, the sunbathers can keep the sandy beaches and leave the geochemists to wallow in the mud!

These areas of fine sediment accumulate in both estuarine and open coast environments, though in the latter case they usually form in areas of reduced tidal and wave energy, such as behind barrier island complexes or in embayments (Allen & Pye, 1992). As noted earlier, in such environments there may be a continuum from sand dune through saltmarsh to mud flats, and the relative sizes of these can vary greatly. The marshes of Sapelo Island Georgia (USA) occupy 75% of the available coastal lagoon (Wiegert, Pomeroy & Wiebe, 1981) and in the 'big swamp' phase (6000 yr BP) many Australian estuaries were almost completely filled with mangal forest, to be replaced more recently by a mixture of mangal and mud flats (Woodroffe, 1990). By contrast in the sheltered embayment of the Wash coast in England (Malcolm & Sivyer, this volume) about 4000 ha of saltmarsh (Doodey, 1992) are fronted by about 30 000 ha of intertidal mud flats (S.J. Malcolm, pers. comm.).

These areas of sediment accumulation are transitory features on a whole range of time scales. They have migrated dramatically over the Holocene period (last 10 000 years) as relative sea levels have risen globally due to deglaciation, though this pattern of sea level change has varied locally (Allen & Pye, 1992). This is illustrated for the North Sea in Figure 1.2, and similar changes occurred in other coastal areas. As noted earlier, increases in sea level over the next 100 years may accelerate as a result of the greenhouse effect. Intertidal systems have responded to these changes by migrating where this is practical or accreting sediment sufficiently quickly to retain their position relative to sea level (e.g. Funnell & Pearson, 1989; Tooley, 1992). Maximum marsh vertical accretion rates appear to be 10–20 mm y^{-1}, similar to maximum predicted rates of sea level rise, so, provided sediment supply is maintained (which may depend on policies of coastal defence in sediment supply regions), marshes should be able to keep pace with sea level rise (Boorman, Goss-Custard & McGrorty, 1989; Reed, 1990). Because of the longer life span and slower growth rates of mangrove trees, mangals may not be able to respond so readily (Woodroffe, 1990).

Predicting the exact response of the whole intertidal sedimentary ecosystem to sea level rise is extremely difficult, though progress is being made, often with surprising results. Thus in the Wadden Sea, a rise in sea

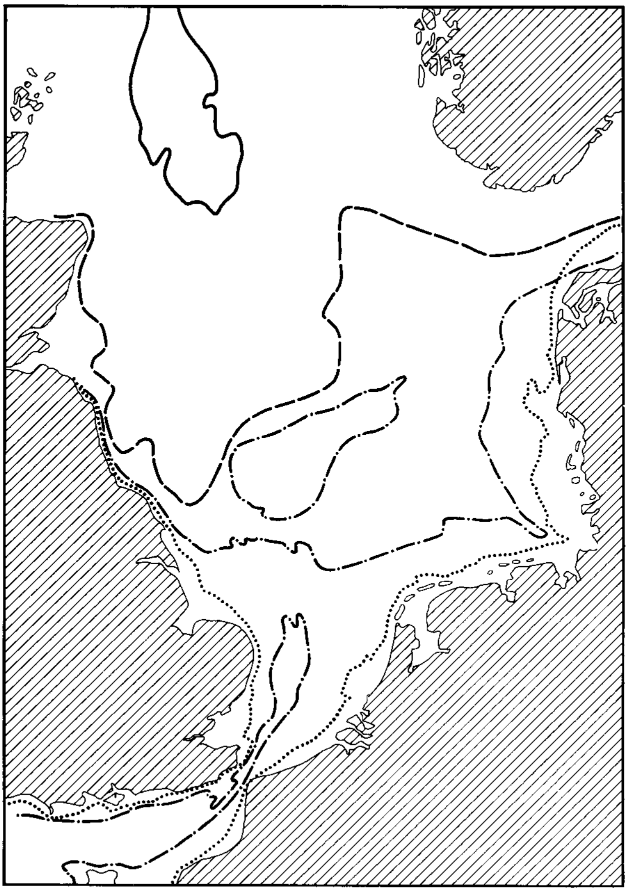

Figure 1.2 Map showing estimated locations of shore lines in the North Sea from 18 000 years ago to present, based on Jelgersma, 1979. ———— 18 000 yr BP, sea level 130 m below present day, — — — — 10 300 yr BP, sea level 65 m below present day, —·—·—·—·—·—·—· 8700 yr BP, sea level 36 m below present day, ... 7800 yr BP, sea level 20 m below present day.

level may result in increased exposure of intertidal areas and hence increased primary production (Peerbolte, Eysink & Ruardij, 1991). In areas where sediment supply is not maintained, loss of the intertidal ecosystems will occur. This is evident in areas such as the Nile and Mississippi deltas where damming has dramatically reduced sediment supply. This, combined with local subsidence, has meant that sea level rise exceeds sedimentation rates and contributes to marsh deterioration, at least in Louisiana (Reed, 1990), but probably also in the Nile delta, and indirectly in the Indus delta (Halim, 1991).

Other human impacts on intertidal systems are less subtle with a long history of drainage and protection from inundation to yield agricultural land. The data of Doodey (1992) imply that the UK has lost over 50% of its saltmarshes to reclamations that have gone on since Roman times and continue to the present day. In Holland, 40% of the present country is reclaimed land (Walker, 1990). In recent years in Europe, agricultural surpluses and rising sea levels have begun to encourage policies to reverse this trend and to allow recreation of marsh systems.

On shorter time scales intertidal systems are of course defined by the dramatic diurnal tidal cycles of inundation and drying out, and the saltmarsh ecological zonation by the spring/neap tidal cycles (Adam, 1990). On slightly longer time scales, storm events may cause dramatic short term erosion, though the systems can recover from this, often by exchange of sediments between the marshes and the adjacent intertidal mud flats (Pethick, 1992).

These short term changes present an enormous challenge to scientists studying intertidal systems as illustrated here in the chapters by Carpenter, Malcolm & Sivyer and Ruddy. Sampling at low tide in these systems is a relatively straightforward matter, though the terrain is often difficult and dangerous with the added requirement of returning to dry land before the tide returns. Sampling at high tide is more difficult but marine scientists have a wide range of tools for such tasks, and indeed for such expeditions the problem is one of retreating to sea before the tide falls and strands researchers. Mangal forests and swamps are difficult to penetrate at any state of the tide though some nutrient flux data from these systems are now becoming available (Boto & Robertson, 1990; Lugo, Brown & Bronson, 1988; Rivera-Monroy *et al.*, 1995). However, the real problem for scientists working in intertidal systems is coping with the dramatic and rapid changes from a system under water to one above water, and one where water flows reverse and change on very short time scales. The contrasting approaches of Carpenter, Ruddy and Malcolm & Sivyer in

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this volume illustrate two of the available strategies. These approaches are designed to address changes associated with diurnal tidal rhythms and also spring/neap tidal cycles. Pethick (1992), French & Spencer (1993) and Nyman, Crozier & de Laune (1995) present evidence that storm events may dominate sedimentation on saltmarshes. Such events are extremely difficult to study by direct observations because of their unpredictability, as well as the dangers of working in these environments under such conditions. We therefore have no direct measurements of fluxes during storm events, though they can be indirectly estimated (e.g. Nyman, Crozier & de Laune, 1995). Therefore we must be extremely cautious in extrapolating data from relatively low energy situations to such high energy conditions.

The primary productivity of many of these intertidal communities is high relative to offshore communities – 200–500 gC m^{-2} yr^{-1} for saltmarshes and mangroves (Mann, 1982) and about 100 gC m^{-2} yr^{-1} for benthic algae on mud flats (Cadée & Hegeman, 1974). This high productivity is supported in part by very high rates of N_2 fixation. Capone and Carpenter (1982), for example, estimate that almost half of all marine N_2 fixation takes place in saltmarshes and mangroves, though more recent data (e.g. Howarth *et al.*, 1988; Boto & Robertson, 1990) suggests substantially lower rates. Very little of the productivity of marshes and mangroves appears to be grazed while alive, but is rather decomposed as detritus by micro-organisms (Mann, 1982; Adam, 1990) partly in or on the sediments, together with the products of benthic algal production, and partly after export to adjacent coastal waters. Based on studies of carbon isotopes in particulate organic matter in saltmarsh creeks, this export appears to be minor (Adam, 1990) though the subject of considerable debate (Carpenter, this volume). For nitrogen, even if net exchanges are minor, transformations may occur such as from dissolved to particulate forms (e.g. Rivera-Monroy *et al.*, 1995) or nitrate to ammonium (Carpenter, this volume). Thus much of this plant detritus, together with decomposing below-ground plant material and organic carbon associated with imported fine sediment, provides the sediments with a rich supply of organic matter. This organic matter ultimately feeds the invertebrates and birds of these areas and also drives the geochemical reactions in the sediments.

It is the decomposition of this organic matter which provides one of the unifying biogeochemical concepts in all these intertidal environments. In all areas subject to fine-grained sedimentation, organic matter content of sediments is relatively high. This organic matter is subsequently oxidised by bacteria using a variety of oxidising agents or terminal electron acceptors (TEA) which are themselves reduced, hence the term redox reactions. These different TEAs yield different amounts of energy from their reactions with organic carbon (Table 1.1), so the microbial community using the highest energy yielding system always dominates, assuming there is a significant amount of that TEA present. Thus, as long as there is oxygen present, this will always be the oxidising agent used, but, once this is exhausted, alternative oxidants are used in a fixed sequence beginning with nitrate (Coleman, 1985; Ruddy, this volume). It is for this reason that these intertidal sediments can consume large amounts of nitrate very quickly (Malcolm & Sivyer, this volume). In many systems nitrate levels are naturally low, but increasing concentrations of nitrate in rivers arising from human activity can mean that nitrate is an important electron acceptor in some coastal systems today. Once nitrate is exhausted in the sediments the readily available oxidised iron and manganese are reduced to their more soluble reduced form. Since phosphate in sediments is usually strongly associated with iron, this iron mobilisation can also

Table 1.1 Redox equilibria (based on Andrews *et al.*, 1995)

Aerobic respiration
$O_2 + CH_2O \rightarrow CO_2 + H_2O$
$\Delta G = -29.9$ kcal/mol

Denitrification
$\frac{4}{5}NO_3^- + CH_2O = \frac{4}{5}H^+ \rightarrow \frac{2}{5}N_2 + CO_2 + \frac{7}{5}H_2O$
$\Delta G = -28.4$ kcal/mol

Manganese reduction
$2MnO_2 + CH_2O + 2HCO_3^- + 2H^+ \rightarrow 2MnCO_3 + 3H_2O + CO_2$
$\Delta G = -23.3$ kcal/mol

Nitrate reduction
$\frac{1}{2}NO_3^- + CH_2O + H^+ \rightarrow \frac{1}{2}NH_4^+ + CO_2 + \frac{1}{2}H_2O$
$\Delta G = -19.6$ kcal/mol

Iron reduction
$4FeOOH + 4HCO_3^- + 4H^+ + CH_2O \rightarrow 4FeCO_3 + 7H_2O + CO_2$
$\Delta G = -12.3$ kcal/mol

Sulphate reduction
$\frac{1}{2}SO_4^{2-} + CH_2O + \frac{1}{2}H^+ \rightarrow \frac{1}{2}HS^- + CO_2 + H_2O$
$\Delta G = -5.9$ kcal/mol

Methane formation
$CH_2O \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2$
$\Delta G = -5.6$ kcal/mol

CH_2O is a simplified representation of organic matter

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result in phosphorus mobilisation (Sundby, Gobeil, Silverberg & Mucci, 1992). These reactions involving the important nutrients, nitrate and phosphorus, illustrate the ways in which intertidal sediment processes can influence the productivity of the intertidal ecosystems and potentially the adjacent coastal waters. These potential effects provide a rationale for flux studies such as those of Carpenter (this volume) and similar studies in mangals (e.g. Rivera-Monroy *et al.*, 1995). Once the reservoirs of available oxidised iron and manganese are depleted, sulphate reduction begins as discussed by Ruddy (this volume).

In deep ocean waters, organic carbon inputs, microbial activity, sedimentation and bioturbation rates are relatively low and the various TEA reaction zones occur as distinct vertical layers. As the chapter by Ruddy emphasises, this is not the case in these intertidal sediments where organic inputs are high and heterogenous, giving rise to high benthic bioturbation rates. Heterogeneity may be particularly important in mangal forests where there is evidence that the different physiology and biochemistry of tree species may result in markedly different patterns of accumulation and degradation of organic matter in sediments (Lacerda, Ittekkot & Patchineelam, 1995). Together these factors mean that the different sediment reaction zones will be concentrated around micro-environments, yielding complex sediment profiles of chemicals involved in these redox cycles and a variety of resultant diagnetic mineral assemblages (Coleman, 1985). Pye *et al.* in this book consider the mineralogical evidence for the mechanisms of carbon oxidation and further emphasise that the classic theories of clear transitions from one TEA zone to another with depth in the core are inappropriate. This chapter also emphasises that microbiological investigations can provide a useful insight into the controls on these processes.

Estimations of fluxes out of these intertidal sediment systems cannot be based solely on passive and diffusional flux measurement. Rather such flux estimates must take account of the active exchange arising from burrow irrigation, the effect of the tidal ‘pumping’ (arising from the drainage of sediment pore waters at low tide and their recharge at high tide which can affect both water and gas exchange, Nuttle & Hemond, 1988) and the effect of uptake by algal and nutrient communities at the surface of the sediments. Many of these biologically mediated processes (bioturbation, plant growth, benthic algae growth) will have a marked seasonality in temperate regions. In addition, redox reactions in sediments can show a seasonality both directly via the seasonal input of organic matter from the growth cycle of marsh plants (at least in temperate

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regions) and also via the seasonal production of organic ligands in pore waters by higher plants which can regulate the sedimentary iron cycle (Luther *et al.*, 1992). Redox and pH conditions can also change on short time scales (hours) as a result of tidal pumping and intrusion of air during the tidal drying of tidal flats (Kerner & Wallmann, 1992). All these complications mean that studies of fluxes from these intertidal systems tend to take one of two forms; either involving studies of individual sediment cores to assess rates of individual processes or alternatively fluxes from the whole system. Both are difficult and uncertain as the chapters by Carpenter and Malcolm illustrate. This means that we are a long way from currently being able to effectively quantify fluxes in and out of these intertidal sediment systems. The chapter by Malcom & Sivyer in particular does, however, illustrate the potential importance of these fluxes to coastal ecosystems in general.

A further consequence of the oxidation of organic carbon by a sequence of TEAs is the production of various gaseous products including reduced sulphur species such as dimethyl sulphide (Steudler & Peterson, 1984) and carbonyl sulphide (Chin & Davis, 1993), methane and N_2O. These gases all have potential climate modifying roles (Houghton, Callander and Vaney, 1992). For the sulphur gases, saltmarshes (and possibly all intertidal systems) appear to produce relatively high fluxes per unit area, though their contributions to global fluxes, in comparison to ocean and terrestrial soil sources which occur over much larger areas, is necessarily modest (Charlson *et al.*, 1987). Methane emissions from wetlands are also potentially important (Dacey, Drake & Klug, 1994) though saltmarshes are likely to be small sources compared to terrestrial wetlands because of the greater role in marine systems of sulphate reduction which precedes methanogenesis (Table 1.1; Harriss *et al.*, 1988). However, Barber, Burke & Sackett (1988) have reported very high methane fluxes from Florida mangrove environments which they suggest may reflect rapid consumption of sulphate in these organic rich environments. Malcolm & Sivyer (this volume) indicate the potential for large scale N_2O emissions from intertidal sediments as a biproduct of nitrate reduction.

Since all these gas emissions are byproducts of organic matter decomposition they are natural sources, but the magnitude of these fluxes may be altered by human intervention both directly, via destruction of intertidal sediments, and also indirectly, via increases in atmospheric CO_2 levels (Dacey, Drake & Klug, 1994) or changes in nitrate fluxes (Malcolm, this volume). Thus while intertidal sediments are very sensitive to climate change, they are not wholly passive since they can themselves influence