NUTRIENT RELEASE AND NITROGEN TRANSFORMATIONS RESULTING FROM RESUSPENSION OF GREAT BARRIER REEF SHELF SEDIMENTS

Thesis submitted by
Pornsook CHONGPRASITH BSc (Chulalongkorn, Thailand)
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Marine Biology Department, School of Biological Sciences
at James Cook University of North Queensland

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ABSTRACT

The Great Barrier Reef (GBR) province is subjected to a range of episodic physical disturbances, the most dramatic of which are tropical cyclones. On average, two tropical cyclones cross the coast between 15° S and 21° S per year. These disturbances of the shelf system result in the elevation of the concentrations of suspended solids, particulate and dissolved nutrients in the water column. This study attempts to quantify the potential input of nutrients into GBR waters as a result of resuspension of shelf sediments by cyclones, to describe shelf area differences in the magnitude of this process, to assess the changes in nutrient concentrations within the water column following a sediment resuspension event and in particular the processes contributing to the elevation of dissolved inorganic nitrogen concentrations following a cyclone.

Experiments were carried out in the laboratory to investigate temporal trends in nutrient concentration and speciation after the initial prompt release of nutrients from resuspended sediment. Subsequent daily changes in the initially enhanced concentration were not large (< 2-fold range). The pattern of temporal changes in nutrient and chlorophyll concentrations differed between individual experiments. Concentrations of particulate nitrogen (PN) and phosphorus (PP) were largely constant for a few days during the experimental periods after being released from sediments. For the most part, dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations in seawater with suspended sediment and controls were similar and stable through time. Ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) concentrations fluctuated over time. Inorganic phosphate (PO_4^{3-}) and silicate ($Si(OH)_4$) concentrations decreased after the initial release from the sediment. Chlorophyll *a* (chl *a*) released from sediment increased after about a week of the experimental period while phaeophytin concentrations were stable throughout the experimental period. Thus, the immediate effect of cyclonic sediment resuspension on nutrient concentrations and speciation can be assessed by the measurement of water samples taken up to several days after the passage of a cyclone.

Comparison of amounts of nutrient release from both the inner and outer shelf sediments was carried out. The amounts of suspended solids ($r^2 = 0.8$), PN ($r^2 = 0.7$), total dissolved nitrogen (TDN, $r^2 = 0.6$), DON ($r^2 = 0.4$), PP ($r^2 = 0.4$), PO_4^{3-} ($r^2 = 0.8, 0.6$), $Si(OH)_4$ ($r^2 = 0.4$), phaeophytin ($r^2 = 0.4, 0.6$) released were directly related to the mass of sediment resuspended into the water column. However, not all nutrient species followed this pattern, most likely due to vertical patchiness of NH_4^+, NO_2^- and DOP in the sediment column and the high variability in these nutrient stocks between sediment

sites.

Laboratory resuspension experiments showed that shelf sediments contributed significant amounts of total N, total P, PN, PP, NH_4^+, total oxidized nitrogen (NO_3^- plus NO_2^-), PO_4^{3-}, $Si(OH)_4$, chl *a* and phaeophytin to the water column as a result of sediment resuspension. The amounts of total phosphorus, chl *a* and total pigments promptly released differed between sediment types ($P < 0.05$). Amounts of chl *a* and total pigments derived from resuspended inner shelf sediments were greater than from outer shelf sediments. More phosphorus was promptly released from outer shelf sediments. The prompt releases of the remaining nutrient species (total N, PN, DON, NH_4^+, $NO_3^- + NO_2^-$, PP, DOP, PO_4^{3-}, $Si(OH)_4$, phaeophytin) were unrelated to sediment type.

DON, DOP, individual NO_3^- and NO_2^- concentrations in the water column, were not significantly increased as a result of simulated shelf sediment resuspension events. This was due to the difficulty of detecting small changes in concentrations of NO_3^- and NO_2^- which were low in sediment stocks and remained close to analytical detection limits and high existing DON and DOP concentrations in the water column.

A comparison was made of the amount of nutrients released promptly by resuspension of sediment from sites within inner, mid- and outer shelf areas. The estimates of nutrient release are presented in three groups, normalized to volume of wet weight of sediment, volume of water-free sediment and estimated porosity of the sediment. The calculated amounts of 10.5 - 28.0 μmol of total N, 0.1 - 0.6 μmol of total P and 0.2 - 2.6 μmol of $Si(OH)_4$ promptly released from cubic centimetre of wet sediment. The calculated amounts of 0.1 - 3.8 μg of chl *a* and 0.7 - 5.7 μg of phaeophytin were accumulated by stimulation of sediment resuspension.

Ammonium and nitrite oxidation rates in sediment-amended seawater were compared using two techniques: dark ^{14}C-bicarbonate uptake with and without added nitrification inhibitors (Nitrapyrin, Allylthiourea, Hach2533) and the oxidation of ^{15}N labelled tracers. Nitrapyrin (N-serve) was found to be the most efficient inhibitor of ammonium oxidation. Higher concentrations of nitrapyrin (50 mg l^{-1})were required as compared to previous studies, because sediment particles adsorbed nitrapyrin and also hindered the isotope measurements. The high concentration of nitrapyrin required may have affected nitrification rate, resulting in an apparent high rate of N-serve sensitive dark carbon bicarbonate uptake.

Ammonium oxidation rates measured by ^{15}N techniques ranged from 0.4 to 6.0 nmol N l^{-1} h^{-1}. Ammonium oxidation rates in seawater with either freshly collected sediment (range 1.2-6.0 nmol N l^{-1} h^{-1}) or frozen-thawed sediment (0.9-4.7 nmol N l^{-1} h^{-1}) were significantly higher than rates in the control seawater (range 0.4-3.9 nmol N l^{-1} h^{-1}) ($P < 0.05$). Ammonium oxidation rates in the seawater with frozen-thawed sediment did not differ from rates measured in seawater mixed with freshly collected sediment.

Nitrite oxidation rates were measured in experiments involving both $^{15}NH_4^+$ and $^{15}NO_2^-$ additions. The nitrite oxidation rates obtained from experiments with $^{15}NO_2^-$ additions were always higher than the rates obtained with $^{15}NH_4^+$ addition. The differences resulting from $^{15}NO_2^-$ additions compared to $^{15}NH_4^+$ additions were likely due to contamination of the nitrate samples by pre-existing nitrite. Nitrite oxidation rates measured in samples with freshly collected sediment added were 2- to 3-fold higher than rates in seawater with frozen-thawed sediment added where $^{15}NO_2^-$ was used as the ^{15}N source.

Nitrite oxidation rates measured in experiments with $^{15}NH_4^+$ additions (range = 0.2 to 1.5 nmol N l^{-1} h^{-1}) in seawater with sediment added were significantly higher than rates in control seawater (0.2 to 1.2 nmol N l^{-1} h^{-1}). Nitrite oxidation rates (with $^{15}NH_4^+$ addition) measured in seawater with freshly collected sediment differed from rates measured in seawater with frozen-thawed sediment (by a factor of 0.1-1.2).

Uptake rates of ammonium, nitrite and nitrate were measured by ^{15}N techniques. Overall, ammonium uptake rates were higher (2.6-82.2 nmol N l^{-1} h^{-1}) than uptake of either nitrate (0.3-16.8 nmol N l^{-1} h^{-1}) or nitrite (0.1-9.8 nmol N l^{-1} h^{-1}). Ammonium uptake rates in seawater with freshly collected sediment added (37.7-82.2 nmol N l^{-1} h^{-1}) were significantly higher than rates measured in seawater with frozen-thawed sediment (4.3-57.0 nmol N l^{-1} h^{-1}) and in the control (2.6-39.1 nmol N l^{-1} h^{-1}) ($P < 0.05$). Likewise, nitrate uptake rates in seawater with the freshly collected sediment added were significantly higher than rates measured in the control (0.3-1.0 nmol N l^{-1} h^{-1}). The nitrate uptake rates measured in seawater with freshly collected sediment (9.7-16.8 nmol N l^{-1} h^{-1}) did not differ from rates measured in seawater mixed with frozen-thawed sediment (8.7-16.5 nmol N l^{-1} h^{-1}). In contrast, nitrite uptake rates in seawater with frozen-thawed sediment added (0.3-9.8 nmol N l^{-1} h^{-1}) were significantly higher than control seawater (0.1-1.33 nmol N l^{-1} h^{-1}), but did not differ from rates measured in seawater with freshly collected sediment added (2.8-3.0 nmol N l^{-1} h^{-1}).

Measured anaplerotic ^{14}C uptake/^{15}N oxidation ratios (0.5-0.7) were high compared to ratios reported from previous studies (0.06-0.2). This was due to potential differences between tropical and temperate systems, the differences between behaviour of bacteria populations in culture media and natural seawater, or side effects of the nitrification inhibitor. Therefore, to estimate nitrification rates in any systems by ^{14}C method, calibration of the C uptake/N oxidation ratio for that system is required.

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DECLARATION

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. In formation derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

Pornsook Chongprasith
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CHAPTER 1

GENERAL INTRODUCTION

1.1 NUTRIENT CYCLING IN MARINE ECOSYSTEMS

Nutrients (e.g. carbon-C, nitrogen-N, phosphorus-P, silicon-Si) are the primary structural constituents of plants and animals in oceanic waters (Furnas, 1991a). Marine phytoplankton takes up C, N, and P at atomic ratios of approximately 106:16:1 (Redfield, 1958; Redfield, *et al.*, 1963). Based on this ratio and the proportion of dissolved C, N and P in oceanic waters, it is considered that phytoplankton biomass is generally limited by N rather than P and it has been suggested that the supply of nitrogen largely regulates the magnitude of primary production (Ryther and Dunstan, 1971; Eppley *et al.*, 1979).

It has long been recognized that nitrogenous nutrients are essential for marine phytoplankton production (reviewed by McCarthy and Carpenter, 1983; Glibert, 1988). Nitrogen is the macro-nutrient which generally becomes depleted most rapidly and completely in surface seawater. Ambient levels of fixed inorganic nitrogen in surface waters are often inadequate to support a single doubling of phytoplankton biomass (Thomas, 1966, 1970; Ryther and Dunstan, 1971). The concept of nitrogen as the principal limiting nutrient in most marine pelagic ecosystems has become central to our understanding of marine primary productivity (but see Smith, 1984). However, the degree and manner to which nitrogen actually limits phytoplankton growth in surface ocean waters is not straight forward (Hecky and Kilham, 1988; Glibert, 1988).

Calculated nitrogen turnover rates in the water column indicate that nitrogen is rapidly recycled (e.g. Paasche and Kristiansen, 1982; Ward, 1985; Hopkinson *et al.*, 1987). Ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) occur in seawater as intermediates in the N cycle. These ions are important as substrates for assimilation by phytoplankton and bacteria, and for oxidation by nitrifying bacteria. Particulate organic nitrogen and dissolved organic nitrogen are also mineralized and recycled to supply the ongoing nitrogen needs of growing phytoplankton and bacterial communities (Eppley and Peterson, 1979; Jackson and Williams, 1985).

Planktonic autotrophs account for virtually all of the primary organic production in the world's ocean (Menzel, 1974). The requirement for light restricts their growth to the upper 100-150 m of water column, where essential macro-nutrient reserves are normally only sufficient for sustaining growth over short periods of time (Harrison, 1980). As a consequence, a continuous resupply of nutrients from external and internal sources is required to maintain primary production.

The surface waters of tropical and subtropical oceans characteristically contain low dissolved nutrient concentrations and plankton biomass levels (Eppley *et al.*, 1973) especially when viewed against to comparable temperate oceanic waters, estuaries and rivers (Hatcher *et al.*, 1989; Longhurst and Pauly, 1987). However, high biomass-specific rates of primary production occur in tropical aquatic systems, therefore active and constant recycling of nutrients must take place (Furnas, 1991a).

In order to gain a comprehensive understanding of the productivity of marine ecosystem, it is essential that the sources of nutrients to that system are identified. Dugdale and Goering (1967) introduced the now widely used concept of "new" and "regenerated" primary production to differentiate between sources of nutrient supply. "New" production refers to production based on inputs of nutrients from sources external to the ecosystem while "regenerated" production is maintained by the biological recycling of nutrients that are present within the ecosystem. For example, in tropical oceans, ammonium, urea and amino acid stocks are largely "regenerated" *in situ* by zooplankton and bacteria (e.g. Glibert, 1982; Garber, 1984a). "New" supplies of nutrients are either sourced from the atmosphere via precipitation, from the land via river discharge or from water that has been mixed upward from below the thermocline[1] (Figure 1.1)(Eppley *et al.*, 1979; Eppley and Petersen, 1979; King and Devol, 1979; Nixon, 1981; Nixon and Pilson, 1983; Furnas, 1991a). Nutrients released from sediments (e.g. Fisher *et al.*, 1982a; Nixon and Pilson, 1983) are generally considered to represent regenerated nutrients (Figure 1.1).

While coastal systems may be affected by riverine discharges (e.g. Meybeck, 1982; Mitchell, 1988; Mitchell *et al.*, 1990) and direct rainfall inputs (e.g. Menzel and Spaeth, 1962; Arenas and Lanza, 1983; Klein, 1985; Knap and Jickells, 1986; Paerl *et al.*, 1990), most required nutrients are regenerated *in situ* (Smith, 1984). In almost all

[1] A layer of water with a more intensive vertical gradient in temperature than that found in the layer above or below it. In the ocean, this high-gradient layer usually forms the division between surface and deeper water.

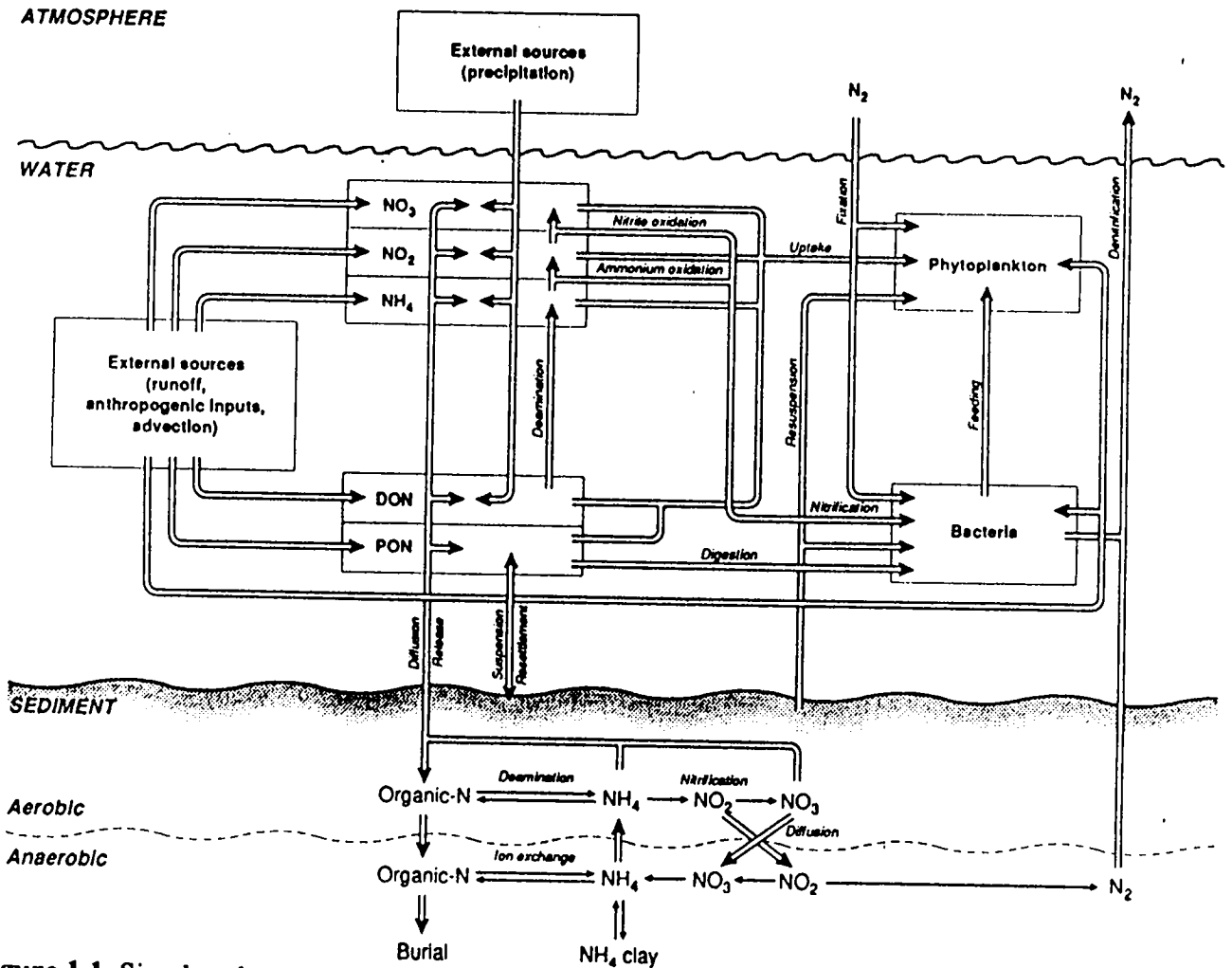

Figure 1.1 Simple schematic diagram of nitrogen cycling processes in both the water column and sediment mediated by bacteria and phytoplankton.

cases, regeneration is the major source of nitrogen and phosphorus for oceanic primary producers (McCarthy, 1972; Eppley, *et al.*, 1973; McCarthy *et al.*, 1977; Harrison, 1978; Glibert, 1982). Eppley and Peterson (1979) estimated that approximately 20 % of the phytoplankton nutrient requirement comes from allochthonous[2] sources, requiring 80 % to be derived from regeneration *in situ*.

In the ocean, nitrate (NO_3^-) and ammonium (NH_4^+) are considered to be the principal inorganic forms of new and regenerated nitrogen, respectively (Dugdale and Goering, 1967). Ammonium is preferred by phytoplankton for assimilation as compared to the oxidized N forms: nitrate (NO_3^-) and nitrite (NO_2^-) (McCarthy *et al.*, 1975; 1977). This preference arises because of the high energy requirements to reduce nitrate to ammonia prior to biochemical assimilation (e.g. Eppley and Rogers, 1970; McCarthy *et al.*, 1977; Glibert *et al.*, 1982). Nitrate uptake and reduction by marine phytoplankton in coastal systems appears to be suppressed at ammonium concentrations > 1 μM (McCarthy *et al.*, 1977, Packard *et al.*, 1971). Nitrite, urea and free amino acids can also be directly taken up, but concentrations of these nitrogen species are usually considerably lower than those of ammonium and nitrate in most marine systems (e.g. Eppley and Petersen, 1979; Paul, 1983).

Nitrate, the end product of sequential ammonium and nitrite oxidation, represents the main source of new nitrogen for the surface mixed layer (Ward, 1987) and for driving the phytoplankton population in the major upwelling regions of the world's oceans (Dugdale and Goering, 1967). The 'new production' based on nitrate is estimated to account for 10-20% of total global marine primary production (Eppley and Peterson, 1979). Calculated nitrate budgets (e.g. Walsh *et al.*, 1981) suggest that *in situ* regeneration processes are also responsible for the appearance of oxidized nitrogen in the sea. Nitrate can be released directly from the sediment after the nitrification process occurs or may be produced in the water column via rapid oxidation of regenerated NH_4^+ (Kemp *et al.*, 1982) such as that released from the sediment (Figure 1.1).

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[2]Plankton or other particulate matter that is imported into the ecosystem (Parsons *et al.*, 1984).

Primary production in tropical aquatic ecosystems is lowest in open oligotrophic[3] ocean regimes (< 0.2 g C m^{-2} day^{-1})(Ryther, 1969; Chavez and Barber, 1987). The productivity of tropical shelf ecosystems is higher, ranging between 0.5-6.3 g C m^{-2} day^{-1} (Chavez and Barber, 1987). Higher levels of phytoplankton biomass on tropical continental shelves are often associated with upwelling events (Walsh, 1976; Zeitzschel *et al.*, 1987; Pati 1980; Andrews and Gentein, 1982; Andrews, 1983; Andrews and Furnas, 1986; Furnas and Mitchell, 1986b) and river runoff (e.g. Brodie and Mitchell, 1992). Very low concentrations of phytoplankton biomass characterize tropical continental shelves where upwelling does not occur and where river outflows are small (e.g. Kidd and Sander, 1981; Bienfang *et al.*, 1984; Tranter and Leech, 1987). In the shallow tropical continental shelf waters, nutrient regeneration is the most important process contributing nutrient inputs to the nutrient cycle.

1.2 THE REGENERATION OF NUTRIENTS ON CONTINENTAL SHELVES: ROLE OF THE BENTHOS

In shallow shelf and coastal systems, nitrogen in sediments constitutes the most important storage reservoir per unit area (Billen and Lancelot, 1988). Where water depths are shallow (< 50 m), benthic fauna and microflora contribute significantly to nutrient cycling (Davies, 1975; Hartwig, 1976a; Longhurst and Pauly, 1987; Rowe *et al.*, 1975; Rowe and Smith, 1977; Alongi, 1989a,b&c; Nixon, 1981; Val Klump and Marten, 1983; Capone *et al.*, 1992). Benthic nutrient inputs can contribute a substantial part of the nutrients required for primary production (Kristensen, 1988). Benthic nitrogen regeneration has been estimated to supply between 26-101% of phytoplankton N demand in coastal environments (Rowe *et al.*, 1975; Nixon *et al.*, 1976; Smith *et al.*, 1978; Fisher *et al.*, 1982b; Blackburn and Henriksen, 1983). However, in the all but shallowest coastal waters, water column remineralization supplies most of the short-term nitrogen demands of phytoplankton (Harrison, 1978; Glibert, 1982; Furnas *et al.*, 1986). Harrison *et al.* (1983) showed that nitrogen-based productivity is mainly sustained by microplankton and zooplankton in the water column. Despite the importance of nutrients derived from the benthos to water column primary production, few studies have examined benthic nutrient fluxes in tropical shelf systems such as the Great Barrier Reef (Hansen *et al.*, 1987; Ullman and Sandstrom, 1987; Alongi, 1989c, 1990c).

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[3]Eutrophic, mesotrophic and oligotrophic waters are classified according to a decreasing order of plankton abundance from the former to the latter.

In waters overlying continental shelves, turbulence generated by tides, currents and wind stress produces vertical mixing of the water column. Under such circumstances, sediments play an important part in ecosystem processes, and are closely associated with the planktonic environment (Paasche, 1988; Blackburn, 1988) as nutrients regenerated by the benthos are recycled with little delay to the plants of the photic zone. In addition to their role as sinks of mineral nutrients for the water column, sediments are the major site in coastal marine ecosystems in which anaerobic processes such as denitrification occur. For example, denitrification may remove up to 25 % of the nitrogen sedimenting to the benthos (Billen, 1978; Seitzinger *et al.*, 1980; Blackburn and Henriksen, 1983).

The amount of nutrients returned from sediments to the overlying water column depends upon various processes occurring both within the sediments and at the sediment-water interface. Benthic nutrient fluxes vary with temperature (Nixon *et al.*, 1976), rates of organic deposition (Nixon, 1981) and the composition of deposited organic matter (Suess, 1981), integrating both surficial (Kelly and Nixon, 1984), subsurface mineralization (Krom and Berner, 1981), denitrification (Seitzinger, 1987) and inorganic exchange/solution processes occurring above and below the oxycline (Mackin *et al.*, 1988; Suess, 1981) and burial (Walsh, 1988). Most of the organic material decomposes in the interstitial water before being released to the overlying water (Yamada *et al.*, 1987).

Particulate organic nitrogen in the water column falls to the sediment surface and returns to water column largely by mineralization to ammonium (NH_4^+). The proportion of benthic-regenerated ammonium that is not taken up by phytoplankton has three fates: (i) it may remain in the sediment ammonium pool, either in porewater solution or adsorbed to particles; (ii) diffuse back to the overlying water; (iii) or be oxidized to nitrite and nitrate. In aerobic sediments, nitrate produced by nitrification in the oxic layers either defuses to the overlying water or into anaerobic sediments where it is converted to diatomic nitrogen gas by denitrification (Figure 1.1; Vanderborght and Billen, 1975; Val Klump and Martens, 1983).

In coastal waters, time scales of benthic-pelagic interaction are short, the physical regimes are variable, and the loading of organic matter to the benthos is greater in both amount and complexity as compared to oceanic waters (Val Klump and Martens, 1983). Microorganisms in the uppermost sediment layers influence nitrogen cycling by incorporating and remineralizing nitrogen compounds (Revsbech *et al.*, 1988).

1.3 NUTRIENT STATUS OF THE GREAT BARRIER REEF CONTINENTAL SHELF

The Great Barrier Reef (GBR) of north-eastern Australia (Figure 2.1 inset) extends latitudinally over 15 degrees (10-25° S, 2000 km). It comprises of 2904 individual reefs and it is by far, the largest complex of coral reefs in the world, most of which lie on the outer continental shelf (Hopley *et al.*, 1989). The continental shelf south of Cape York has an area of 225,000 km^2 (Hopley *et al.*, 1989). An outer "barrier" matrix of reefs encloses the GBR lagoon, a more open strip of shallow coastal water which varies between 30-150 km in width.

Winds over the GBR generally blow from the southeast or northeast (Wolanski and Pickard, 1985). Southeasterly trade winds dominate throughout most of the year (Scoffin and Tudhope, 1985; Wolanski and Pickard, 1985; Andrews and Furnas, 1986). Modal wind speeds throughout the whole reef region range between 11 and 20 km h^{-1} (Scoffin and Tudhope, 1985). On average, 1.5 cyclones, with wind speeds in excess of 120 km h^{-1} and associated heavy rainfall, affect the Queensland coast each year (Lourensz, 1981). Annual rainfall along the Queensland coast varies with latitude (Pickard, *et al.*, 1977). The average mean annual rainfall is usually between 1000 and 2000 mm (Pickard, *et al.*, 1977).

Waters of the GBR shelf are usually well mixed vertically with regard to temperature and salinity during the austral winter (April-September)(Wolanski and Bennett, 1983; Furnas, 1990). The water masses of the continental shelf are influenced by the oceanic waters of the Coral Sea to the east. During the summer months, intrusions of colder Coral Sea water onto the shelf have been identified from changes in temperature. These intrusions do not usually extend further inshore than the inner edge of the reef matrix and rarely come within 10 m of the surface (Andrews, 1983; Wolanski and Bennett, 1983; Furnas and Mitchell, 1986b). Some stratification generally occurs following periods of calm weather in the austral summer (Andrews and Furnas, 1986; Wolanski and Bennett, 1983). The shelf waters are also affected by terrestrial inputs. River runoff occurs episodically, principally in the austral summer (King and Wolanski, 1990) and introduces freshwater into the inner shelf area, reducing the salinity of water masses in this area (Wolanski and Jones, 1981a; Wolanski and van Senden, 1983). Water temperature varies from 21-30° C over an annual cycle (Pickard *et al.*, 1977).

Currents in the central GBR are predominately barotropic[4] and are influenced by three phenomena (Wolanski and Pickard, 1985): diurnal and semi-diurnal tides, wind stress; and the poleward flowing ocean current seaward of the reef known as the East Australian Current (EAC). Longshore currents, which vary at frequencies with periods greater than two days, have greater velocities than cross-shelf currents (Wolanski and Pickard, 1985; Burrage *et al.*, 1991). Tidal current velocities on the shelf are generally small with peak current speeds < 30 cm s^{-1} (Wolanski and Pickard, 1985). King and Wolanski (1990) suggested that in the central GBR the reef matrix enhances velocity shear within the coastal zone, in both long-shore and cross-shore directions. This shear hinders the exchange of water across the shelf; thus, land-derived matter entering the coastal area remains trapped in the coastal zones under most weather conditions (King and Wolanski, 1990).

The biological productivity of the Great Barrier Reef Lagoon is supported from: river runoff (Walker and O'Donnell, 1981; Wolanski and Jones, 1981b; Mitchell *et al.*, 1990); export from tidal creeks and mangrove swamps (Boto and Bunt, 1981; Robertson *et al.*, 1988; Alongi *et al.*, 1989b; Boto *et al.*, 1990; Alongi, 1990b); upwelled outer shelf waters (Orr, 1933; Andrews and Gentien, 1982; Wolanski and Thomson, 1984; Andrews and Furnas, 1986); and sediments (Walker and O'Donnell, 1981; Ullman and Sandstrom, 1987; Wolanski *et al.*, 1988; Alongi, 1989a).

Phytoplankton biomass in GBR shelf waters, as indicated by chlorophyll *a* and nutrient concentrations, is typically low (Wolanski and Jones, 1981a; Andrews and Gentien, 1982; Mitchell, 1982; Revelante and Gilmartin, 1982; Revelante *et al.*, 1982; Andrews, 1983; Furnas and Mitchell, 1986b, Liston, 1991). Based on respirometry studies in coral reef flat environments, it has often been assumed that the phytoplankton contribution to productivity in coral systems is small (Revelante and Gilmartin, 1982) compared with benthic communities.

Seasonal variations in the physical, chemical, and biological environment of the GBR lagoon are influenced by seasonal precipitation patterns, with nutrient inputs by land drainage appearing to be of primary importance (e.g. Revelante and Gilmartin, 1982). Analysis of dissolved inorganic nutrient concentrations in GBR waters has revealed

[4]Barotropic means the surface of constant pressure is parallel to the surface of constant density. When the density of a fluid is a function of pressure only, as in fresh water of uniform potential temperature, the hydrostatic pressure (which is constant) and the density of the fluid (which is constant), are parallel to each other.

variations at event, regional, seasonal and cross-shelf scales (Walker and O'Donnell, 1981; Revelante and Gilmartin, 1982; Andrews, 1983; Furnas and Mitchell, 1986b; Furnas, 1991b; Liston, 1991). Ammonium is usually the most abundant dissolved inorganic nitrogen species in GBR waters (Furnas, 1991b). Nitrite and nitrate concentrations are generally low to very low, with the former at or close to instrumental detection limits (approximately 0.01 μM). Episodic exceptions to this general trend occur at the outer shelf which is affected by the seasonal shelfbreak upwelling, and near the coast, where local areas receive river runoff directly and are strongly mixed by tidal currents (Furnas, 1991b).

1.4 CYCLONIC EVENTS AND NITROGEN CYCLING IN THE GBR

In general, GBR shelf waters contain low levels of dissolved nutrients and plankton biomass (e.g. Furnas and Mitchell, 1986b). During "normal" conditions (non-cyclonic periods) benthic nutrient regeneration contributes only a small proportion of the nutrient demand of phytoplankton (Alongi, 1989c). Alongi (1989c) calculated benthic nutrient fluxes contribute 13% of the daily nitrogen and 24% of daily phosphorus requirements of phytoplankton production on the central shelf. It can therefore be assumed that there are other processes contributing nutrients to meet the ongoing demand related to primary production in the pelagic system. These other processes include runoff from the land (Mitchell *et al.*, 1990), upwelling at the shelfbreak (Andrews and Furnas, 1986; Furnas and Mitchell, 1986b), rainfall (Furnas *et al.*, 1993), water column mineralization (Hopkinson *et al.*, 1987) and resuspension events (Furnas, 1989). Most tropical coastal systems are affected by episodic, seasonal or inter-annual fluctuations with nutrient inputs from freshwater systems (Forsberg *et al.*, 1988) and by physical disturbances (e.g. Furnas, 1988), with the coupled release and remineralization of substantial stocks of nutrients incorporated into sediments and biomass (Furnas, 1991a).

Resuspension of sediments by physical and biological processes, whether in the short term, but over a large spatial area (cyclones, energetic storms), or for longer terms with a more confined area (waves or currents, bioturbation), occurs across wide areas of continental shelves such as the GBR shelf (Gagan *et al.*, 1987, 1988; Riddle, 1988; Sandstorm, 1988). Although occurring within short time periods, cyclonic events have a big impact on the short lived organisms that exploit these enhanced conditions.

Cyclones have long been recognized as a major influence on the GBR region (Dutton,

1986). Tropical cyclones occur seasonally between December and April, crossing the 600 km length of coast centered at Innisfail, Queensland (16°S to 21°S) about once every 1.5 years (Figure 1.2, Lourensz, 1981). Cyclones which have affected the central GBR region in recent years include "Winifred" (1986), "Charlie" (1988), "Aivu" (1989), "Ivor" (1990) and "Joy" (1990).

Wind stress and waves associated with tropical cyclones generate enhanced turbulent mixing in the ocean under the cyclone's path, altering the ocean's thermal structure (Chang and Anthes, 1979). Complete mixing extends to depths of at least 100 m, cooling the surface temperature by as much as 5° C after the passage of tropical cyclones (e.g. Leipper, 1967; Black and Whithee, 1976). Cyclones commonly produce sustained wind speeds of >120 km h^{-1} and generate waves to 6 m in height on the inner shelf (Belperio, 1978). For comparison, waves exceeding 2 m in height are capable of resuspending fine-grained sediment of water depths of 25 m under steady state wind conditions (Belperio, 1978; Wolanski *et al.*, 1981).

Energetic storms such as cyclones are found to affect marine, shallow water benthic and coral reef communities (Glynn *et al.*, 1964; Goreau, 1964; Ball *et al.*, 1967; Stoddart, 1970; Porter, 1974; Ogg and Koslow, 1978; Woodley *et al.*, 1981; Rogers *et al.*, 1982; 1983). Hurricanes "David" (1979) and "Allen" (1980) killed large amounts of benthic algae of the southwest coast of Puerto Rico (Ballentine, 1984). In contrast, Kirby-Smith and Ustach (1986) found that Hurricane "Diana" had little effect on the mid-continental shelf benthic communities (30 m depth). Not much is known about the effect of cyclones on communities in deeper waters. In the GBR region, cyclone "Winifred" affected shallow water corals (Done *et al.*, 1986; Harriott and Fisk, 1986) and soft sediment communities in reef lagoons (Riddle, 1988) under its path. Cyclone "Ivor" (1990) severely altered corals over a 50 km section of the outer GBR but with a patch work pattern of alteration (Done, 1991, Van Woesik, *et al.*, 1991).

Cyclonic storms directly affect oceanographic conditions in shelf systems. The passage of Hurricane "David" (1979) caused a brief sea level rise of 60 cm above normal high water level thorough Florida shelf waters, an increase in current speed to over twice the normal maxima and a decrease in near-bottom water temperature (Smith, 1982). After cyclone "Winifred" (1986) in the GBR, the greatly increased turbidity resulting from river plumes, resuspended lagoon and reef sediment and blooming plankton, reduced measurable light penetration to less than 5 m inshore, and

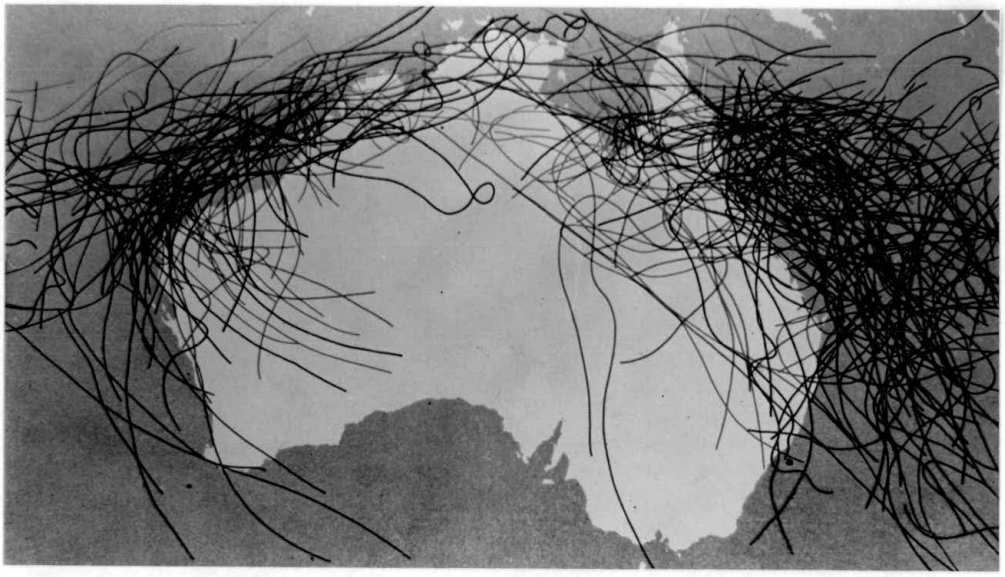


Figure 1.2 Cyclone paths around the Australian region from July 1909 to June 1980. (courtesy of the Australian Bureau of Meteorology).

less than 35 m on the outer shelf (Furnas and Mitchell, 1986a). Normally, GBR and lagoon waters are characterized by low turbidity, with 0.5 to 5% of the surface light penetrating to the bottom (60 to 80 m) on the mid and outer shelf (Furnas and Mitchell, 1986a).

In addition to water column physical properties (e.g. light intensity, salinity, temperature), cyclones affect nutrient levels across the shelf (Furnas, 1989, Figure 1.3). Following cyclone "Winifred", an extensive ($>10^3$ km^2) phytoplankton bloom extended from the shore to at least the shelf break. Chlorophyll *a* concentrations were frequently 5 to 10 times higher than normally measured in mid-shelf waters (Furnas, 1988). Dissolved inorganic nitrogen concentrations increased up to 20-fold, while dissolved inorganic phosphorus and silicate levels in the water column changed less than 2-fold when sampled 4 to 8 days after the cyclone.

Changes in water column nutrient concentrations following cyclones or other energetic storm events can be the result of a number of processes, including increased rainfall, terrestrial runoff and resuspension of sediment. Regional increases in nutrient stocks and phytoplankton biomass in Chesapeake Bay were measured following tropical storm "Agnes" in 1972 (Zubkoff and Warinner, 1976; Loftus and Seliger, 1977; Schubel, 1976; Schubel, *et al.*, 1976) largely resulting from an influx of floodwater (Loftus and Seliger, 1977). Similarly, Liston (1991) suggested that river discharges were the most important source of nutrients in inshore waters after cyclone "Charlie" (1988) on the GBR. As there are a number of major rivers located along the GBR coast (Figure 1.4), the input of nutrients and organic matter following cyclonic events (which produce high rainfall in river catchment areas), provide a large amount of nutrients associated with runoff into coastal waters (Mitchell, 1982, Mitchell *et al.*, 1990; Brodie and Mitchell, 1992).

Cyclonic disturbances affect the structure and distribution of shelf sediments. Shelf sediment movements during cyclonic events depends on the intensity, approach path and oceanographic conditions prevailing at the time of passage (Ball *et al.*, 1967; Perkins and Enos, 1968). Cyclone "David" (1976) affected the sediment structure and distribution patterns on Heron Reef, in the southern GBR (Flood and Jell, 1977). The percentage of coarser grain sizes in the sediments were increased as the finer sediments were removed to inter-reef areas (Gagan *et al.*, 1988).

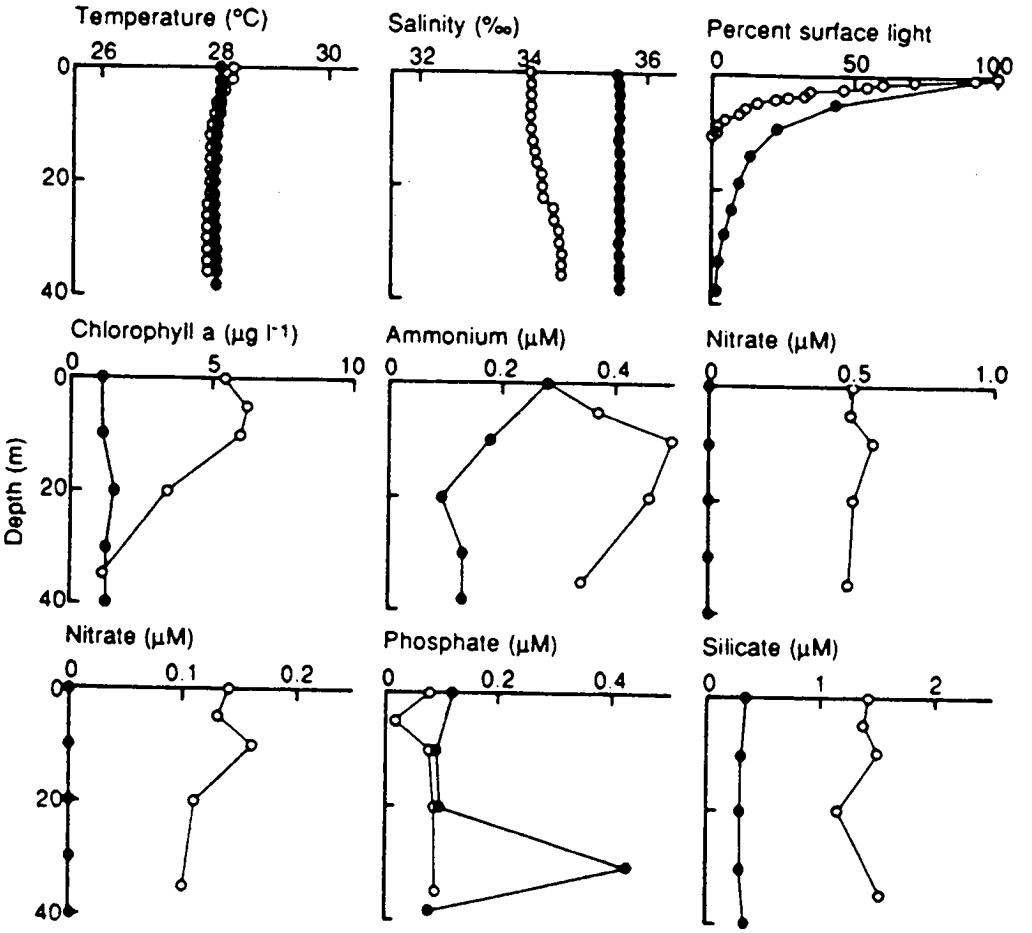


Figure 1.3 Vertical profiles of temperature, salinity, percent surface light, nutrients and chlorophyll in water column at mid-shelf sites between 17° 20' to 18° 30' S four days after cyclone "Winifred" (O) and one year later (1987) under normal conditions (●) (from Furnas, 1989).

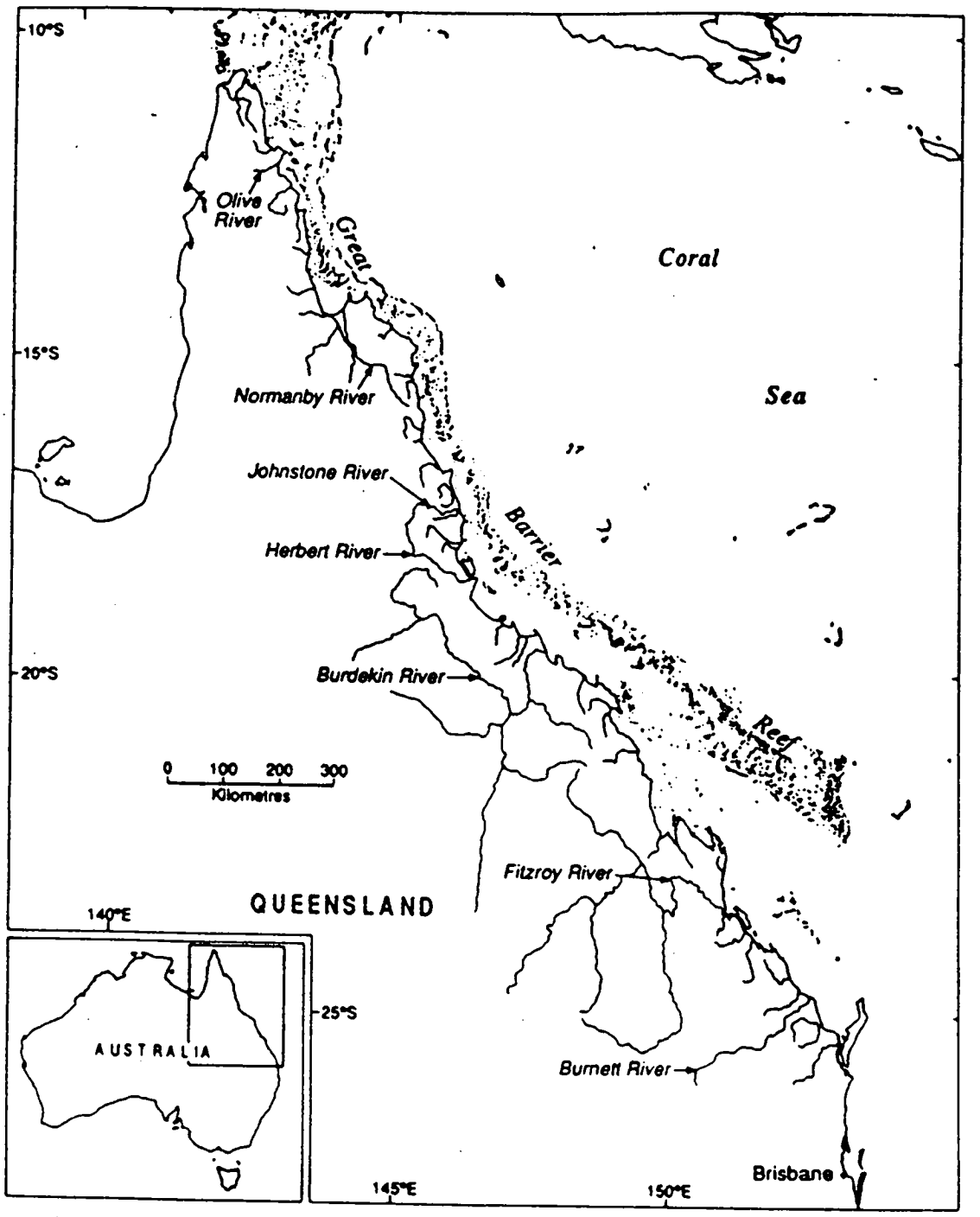


Figure 1.4 Location of major rivers along GBR coast.

Observations made shortly after cyclone "Winifred" indicated a widespread redistribution of the shelf sediments derived from local rivers (Gagan *et al.*, 1988). Fluvial sands from the Johnstone River estuary, near Innisfail, were largely retained within the coastal zone by the prevailing wave conditions, whereas finer terrigenous mud associated with buoyant freshwater plumes were dispersed over much greater distances (up to 12-15 km offshore), forming a thin veneer over much of the inner shelf (Gagan *et al.*, 1988). Carbonate reef detritus was moved up to 1.5 km shoreward to the mid-shelf areas and resuspended mid-shelf sediment was driven at least 15 km shoreward (Gagan *et al.*, 1988).

Despite the obvious importance of large disturbance, the quantities of nutrients released into the water column by mechanical disturbance of bottom sediments in open shelf areas of the GBR has not been examined. Observed increases in nutrient levels have been suggested as being related to large scale reworking of nutrient-loaded sediments (Sandstrom, 1986; Furnas, 1989). In nearshore areas, Walker and O'Donnell (1981) reported episodic nutrient release (nitrate, phosphate and silicate) from nearshore sediments during periods of bottom sediment resuspension. Ullman and Sandstrom (1987) calculated that resuspension of 1 cm of sediment at a nearshore site in the central GBR would lead to moderate increases in water column nutrient concentrations, particularly for nitrogen species.

Preliminary water column nutrient budgets calculated from measurements following cyclone "Winifred" (Furnas, 1989) suggested that most of the phosphate and silicate added to the water column could be accounted for by inputs from rainfall, porewater from resuspended shelf sediment, and river runoff. However, existing nitrogen stocks plus inputs from the above sources accounted for less than 25 percent of the nitrogen present in the post-cyclone water column (Furnas, 1989). Intrusion events conciding with cyclones may contribute additional nutrients (Furnas *et al.*, 1993). Microbial mineralization of organic nitrogen released from disturbed shelf sediments has been suggested as an additional source (Furnas, 1989). The high concentrations of nitrite in shelf waters are indicative of water receiving enhanced loadings of ammonium and organic nitrogen (McCarthy *et al.*, 1984). The ammonium released from sediment and mineralized from organic nitrogen could provide a substrate for nitrifying bacteria which convert to nitrite and nitrate.

1.5 STUDY OBJECTIVES

GBR shelf waters are generally nutrient-poor. Following cyclones or energetic storms which episodically pass through the region, high nutrient levels and productivity can be found over wide areas. Preliminary shelf nutrient budgets calculated for cyclone "Winifred" (Furnas, 1989) suggested that enhanced concentrations of dissolved inorganic nitrogen resulted from enhanced remineralization and subsequent nitrification following resuspension of bottom sediments (Furnas, 1989). Several specific questions arise from this observation. On the most general level, does shelf-scale cyclone or storm generated resuspension of sediments lead to significant short-term inputs of nutrients to GBR waters?

The continental shelf of the Great Barrier Reef province is characterized by a cross-shelf gradient of sediment types ranging from terrigenous sediment on the inner shelf to carbonate sediments on the outer shelf. Sediment characteristics which may affect the amount of nutrients released are addressed in Chapter 2.

In order to resolve the extent to which resuspended sediments contribute nutrients to the water column, a number of specific questions had to be resolved. Preliminary studies (Fanning *et al.*, 1987) indicated concentration of particular nutrient species (eg. ammonium) increase in the water column after storm events. What then happens to these nutrients following a brief resuspension event? There is no information available on the subsequent fate of nutrients. What are the temporal changes in nutrient levels and species after an initial release of nutrients into the water? In order to determine the amount of nutrients released as a result of the sediment resuspension processes, it is necessary to relate the amount of sediment added with the amount of nutrient released. As there may be variability in nutrient release associated with sediment types and distribution and analytical factors such as sediment site type, the source of water and sediment subsampling methods. What are the levels of variability occurring within experiments and analyses? These above questions are addressed in Chapter 3.

Bacteria and phytoplankton are known to play an important role in the recycling of nitrogen in all aquatic systems (Currie and Kalff, 1984; Vadstein *et al.*, 1988; Howarth, *et al.*, 1988; Wheeler and Kirchman, 1986). Both phytoplankton and bacteria use organic or inorganic forms of nitrogen as nitrogen sources (Brown, 1980; Wheeler *et al.*, 1974). Investigations of nutrient levels in GBR waters after cyclone "Winifred" indicated a dramatic change in nitrogen levels in particular (Furnas, 1989).

The very high nitrite and nitrate concentrations observed in the water column raises the question of where these species came from and the extent to which microbial uptake and mineralization processes in the water column contributed to observed water column nutrient concentrations? It may be hypothesized that the combination of elevated ammonium concentration and the presence of increased suspended particulate matter after a storm event produce conditions favouring bacteria which oxidize ammonium to nitrite and nitrate (Horrigan, *et al.*, 1981, Olson, 1981). This question is addressed in Chapter 4.

This study embraces eight discrete objectives:

1. To determine whether cyclone or storm generated resuspension of sediments lead to significant short-term inputs of nutrients to GBR water.

2. To quantify characteristics of inner and outer shelf sediments which affect the amount of nutrients released.

3. To quantify temporal changes in nutrient concentration and speciation following simulated sediment resuspension event.

4. To determine the relationship between sediment mass and the amount of nutrients promptly released by resuspension.

5. To assess the levels of variability associated with subsampling of water and sediment.

6. To compare the amounts of dissolved and particulate nutrients (N, P, Si) which are released in aerobic seawater from inner-shelf (terrigenous) and outer-shelf (carbonate) sediments collected from the central GBR shelf following a simulated resuspension event.

7. To measure oxidation rates of inorganic nitrogen species ($NH_4^+ \rightarrow NO_2^-$; $NO_2^- \rightarrow NO_3^-$) in GBR water following simulated resuspension events and nutrient loading under aerobic condition.

8. To measure uptake rate of dissolved inorganic nitrogen (NH_4^+, NO_2^-, $NO_3^- \rightarrow$ PN) in GBR water following simulated resuspension events.

CHAPTER 2

SEDIMENT COLLECTIONS, CHARACTERISTICS AND PRELIMINARY SEAWATER ANALYSES

2.1 INTRODUCTION

Broad patterns of surficial sediment distributions in the Great Barrier Reef (GBR) have been described by Maxwell (1968, 1973). The central GBR (16-21° S; Figure 2.1 inset) is characterized by a cross-shelf gradient of sediment types, ranging from mixed terrigenous sediments along the coast to carbonate sediments offshore (Maxwell, 1968; Alongi, 1989c). This gradient has developed because of the differential influence of continental runoff and carbonate sedimentation (Johnson, *et al.*, 1986; Gagan, *et al.*, 1987, 1988). The outer shelf sediments of the central GBR are skeletal in origin, and are characterized by sand or gravel-sized grains formed by foraminiferans, algae (e.g. *Halimeda)*, molluscs and corals (Scoffin and Tudhope, 1985). The shelf of the central GBR ranges between 100 and 150 km in width with depth from 10 - 20 m near shore to 50 - 80 m at the shelf-break[5]. Hydrographic conditions (Maxwell and Swinchatt, 1970; Pickard *et al.*, 1977; Andrews, 1983; Wolanski and Pickard, 1985) and geological conditions (Hopley, 1982; Belperio, 1983; Scoffin and Tudhope, 1985; Johnson *et al.*, 1986; Gagan *et al.*, 1987, 1988; Alongi, 1989c) in the central GBR province have been described in detail.

For the purpose of this study, three shelf sediments zones will be recognized: the inner shelf (0-20 m depth), the mid-shelf (20-40 m depth), and the outer shelf (40-80 m depth) as described by Belperio (1978, 1983). Sediments of the inner shelf are largely comprised of terrigenous mud and quartz sand with low (< 20%) carbonate content (Maxwell, 1968). Terrigenous sediment is largely restricted to the inner shelf (except during storms; Gagan *et al.*, 1987, 1988) mainly through the influence of the southeast trade winds which distribute terrigenous matter in a narrow band along the coast (Gagan *et al.*, 1987; Alongi, 1989c; King and Wolanski, 1990). The bulk of fluvially discharged organic matter is also confined to sediment within 10 km of land,

[5]edge of the continental shelf.

although traces of this material are detectable in outer reef lagoon sediments (Johns, *et al.*, 1988; Gagan *et al.*, 1988).

Compared to mid- and outer shelf sediments, inner shelf sediments have higher organic carbon content (C), lower total nitrogen (N) and phosphorus (P), and a higher C:N ratio (due to terrigenous and mangrove debris)(Alongi, 1989c). Dissolved nutrient concentrations in porewater, and inorganic nutrient fluxes from the sediments are low compared to temperate sediments (Alongi, 1989c).

Infaunal communities on the inner shelf are dominated by polychaetes (Arnold, 1979; Carey, 1982). Epifaunal diversity is low. Epifaunal communities are dominated by bryozoans and echinoderms (Birtles and Arnold, 1988). Meiofaunal and macro-infaunal densities and biomass of inner shelf sediment are low compared to mid-shelf and outer shelf areas (Alongi, 1989c).

The mid-shelf zone is comprised of carbonate dominated sediments, with a carbonate composition of 30-60% (Maxwell, 1968). Gagan *et al.* (1988) described the mid-shelf zone as sediment-starved, having a 0-2 m thick veneer of poorly sorted terrigenous-carbonate sediment formed by the mixing of skeletal carbonate and relict siliciclastic sediment. Low concentrations of organic carbon and nitrogen are also found in mid-shelf sediments (Alongi, 1989c). The (organic) C:P ratio of sediment decreases across the shelf reflecting less terrigenous C and the binding of P to $CaCO_3$ (Alongi, 1989c).

Epibenthic communities on the mid-shelf area are abundant and diverse and are dominated by echinoderms (103 known species), molluscs (196 known species), bryozoans, large ascidians, sponges and large foraminifera (Birtles and Arnold, 1988; Cannon *et al.*, 1987). The meiofaunal densities (15-33 x 10^5 individuals m^{-2}) and biomass (1200-3000 mg DW {dry weight} m^{-2}) found by Alongi (1989c) are higher than those inshore. Infaunal biomass is still low (1600-3300 mg AFDW {ash free dry weight} m^{-2}).

Outer shelf sediments are chiefly comprised of carbonate sand. Deposits on outer shelf reefs are up to 30 m thick and are composed of both detrital and framework carbonates (Davies and Hopley, 1983; Johnson *et al.*, 1984). Meiofaunal numbers (15-22 x 10^5 individuals m^{-2}) and biomass (1300-2700 mg DW m^{-2}) are higher than inshore. Infaunal biomass is low (940 mg m^{-2}) compared to inner- (2500 mg m^{-2}) and

mid-shelf (3370 mg m^{-2}) areas (Alongi, 1989c).

Inter-reefal areas cover most (91%) of the continental shelf area within the GBR province (Hopley *et al.*, 1989). Observations by Scoffin and Tudhope (1985) indicate that much of the inter-reef area on the outer half of the shelf consists of barren, bioturbated sandy seabeds without conspicuous epifauna and flora. Some areas of the seabed at the shelf edge are scattered with coral outcrops, boulders and linear banks of the calcareous algae *Halimeda* (Johnson *et al.*, 1986).

STUDY OBJECTIVES

The GBR continental shelf is characterized by an across-shelf gradient of sedimentary facies ranging from terrigenous sediment along the coast to carbonate sediment offshore and previous studies showed differences in ecological communuties. Sediment collected from different shelf types may affect the differences in amount of nutrient release. Sediment characteristics collected from various sites in this present study were therefore investigated.

It is known that phytoplankton and bacteria are primarily responsible for natural *in situ* nutrient transformations. Nutrient concentration and speciation may change during storage time if the seawater can not be collected prior to the experiment commencement. If the seawater needed to be kept for a period of time before using in the experiment, the question arises as to that how long the seawater can be kept without any significant change in nutrient concentrations. Therefore, measurements for detecting any changes in nutrient concentration over time are needed to be carried out to check whether significant concentration changes occurred during storage.

2.2 MATERIALS AND METHODS

2.2.1 Sediment collection sites

Sediments to be used for experimental measurements of nutrient release and transformations were collected at 12 sites within the central GBR province (Figure 2.1; Table 2.1). Seven experiments were conducted and the sites at which the sediment was collected for each are shown in Table 2.2.

For a pilot investigation of temporal changes in nutrient speciation and concentration,

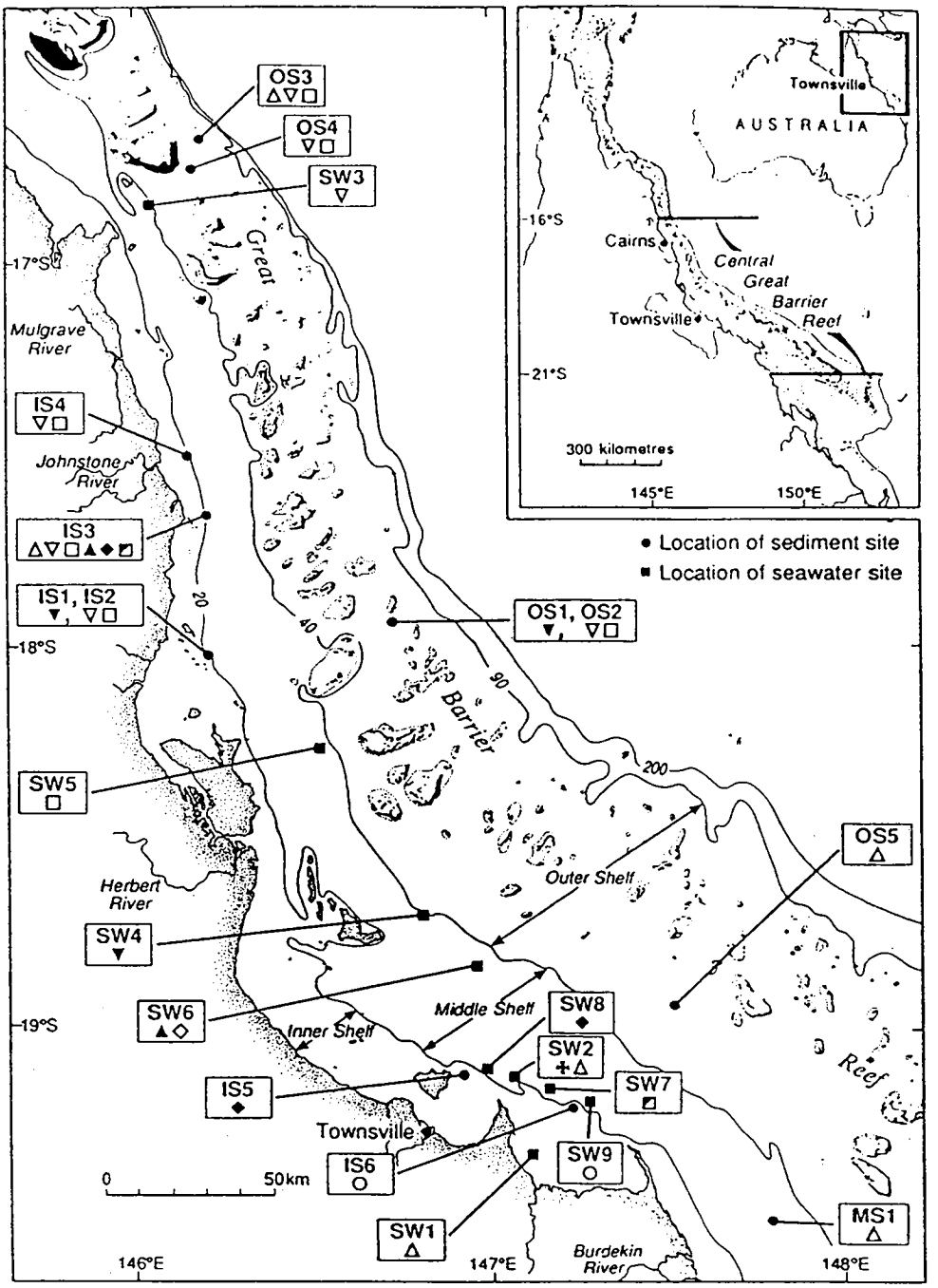


Figure 2.1 Sediment (●) and seawater (■) sampling sites. Symbols in boxes indicate the experiment in which sediment and seawater were used.

(✣ : Nutrient changes in seawater with storage time; Δ : Time-course changes of nutrients; ∇ : Relationships between sediment and nutrient; ▼ : Variability associated with sediment and water subsamples; □ : Nutrient release from inner and outer shelf sediment; ▲ : Dark ^{14}C uptake; Nitrogen transformations : ◇ : Trial N.1, ◩ : Trial N.2; ◆ : Trial N.3; O : Trial N.4).

Table 2.1

The location of sediment collection sites, shelf types, water depth and sampling dates.

Study site	Location	Shelf type	Water depth (m)	Sampling date
Near Family Islands (IS1)	18° 02.6'S 146° 15.4'E	Inner shelf	21	12/5/89
Near Family Islands (IS2)	18° 02.6'S 146° 15.4'E	Inner shelf	21	10/11/89
Near Barnard Islands (IS3)	17° 40.4'S 146° 12.0'E	Inner shelf	26	9/11/89
Near Johnson river mouth (IS4)	17° 30.0'S 146° 09.3'E	Inner shelf	21	9/11/89
Near Magnetic Island (IS5)	19° 10.0' S 147° 25.0' E	Inner shelf	20	2/9/91
Near Cape Ferguson (IS6)	19° 5.0'S 147° 30.0'E	Inner shelf	20	7/11/91
Near Old Reef (MS1)	19° 31.8'S 147° 48.0'E	Mid-shelf	30	7/5/88
Near Reef no. 17-065 (OS1)	17° 56.3'S 146° 43.3'E	Outer shelf	60	13/5/89
Near Reef no. 17-065 (OS2)	17° 56.3'S 146° 43.3'E	Outer shelf	59	10/11/89
Near Fin Reef (OS3)	16° 40.7'S 146° 12.3'E	Outer shelf	66	2/11/89
Near Arlington Reef (OS4)	16° 45.1'S 146° 11.7'E	Outer shelf	51	2/11/89
Near Davies Reef (OS5)	18° 57.25'S 147° 33.8'E	Outer shelf	50	5/5/88

Sites IS1, IS2 and OS1, OS2 are identical locations but sampled at different times.

Table 2.2

Sediment and mid-shelf water sampling sites in each experiment (IS: Inner shelf, MS: Mid-shelf, OS: Outer shelf sediment, SW: Seawater).

Experiment	Sediment site	Symbol in Figure 2.1	Mid-shelf water site	Experiment in text
1: Nutrient concentration changes in seawater with storage time	-	✠	SW2	Chapter 2
2: Time-course changes of nutrient concentration and speciation	MS1, OS5, IS3, OS3	△	SW1 SW2	Chapter 3
3: Relationship between sediment weight and nutrient concentrations	IS2, IS3, IS4, OS2, OS3, OS4	▽	SW3	Chapter 3
4: Variability of nutrient release related to sediment subsample and water subsampling	IS1 , OS1	▼	SW4	Chapter 3
5: Comparison of nutrient release from inner and outer shelf sediments	IS2, IS3, IS4, OS2, OS3, OS4	□	SW5	Chapter 3
6: Dark ^{14}C-bicarbonate uptake	IS3	▲	SW6	Chapter 4
7: Transformations of nitrogen using ^{15}N isotope				
Trial N.1	IS3	◇	SW6	Chapter 4
Trial N.2	IS3	◩	SW7	Chapter 4
Trial N.3	IS5	◆	SW8	Chapter 4
Trial N.4	IS6	○	SW9	Chapter 4

sediment was sampled from single sites on the mid-shelf (MS1) and outer shelf (OS5). Sediment and water samples within each zone were collected within regional where the research vessel was operating for other studies. In the experiment dealing with variability associated with subsampling, sediments were collected at sites IS1 and OS1 (Figure 2.1). These sites were resampled (IS2, OS2) and four additional sites (IS3, IS4, OS3, OS4) were sampled to compare potential nutrient release from inner and outer shelf zones. Sediment sites IS3 and IS4 were chosen because of their proximity to the Johnstone river which was directly affected by Cyclone "Winifred" (1986). Due to logistical problems, it was not possible to sample the outer shelf sites at equivalent latitudes to inner shelf sites. As a consequence the outer shelf sites were displaced approximately 100 km north of IS3 and IS4 (Figure 2.1). For the investigations of nitrogen transformation processes, fresh sediments were collected from sites IS5 and IS6 (Figure 2.1). These sites were chosen because of their proximity to the laboratory.

2.2.2 Sediment sampling and analysis

All sediment samples were collected with a stainless steel Smith-McIntyre grab. The sediment samples (MS1 and OS5; Table 2.2) collected for the first, preliminary experiments were stored frozen as bulk subsamples in plastic bags. For subsequent experiments (Table 2.2), intact subsamples of sediment, including porewater, were taken from undisturbed sediment in the Smith-McIntyre grab with cut-off plastic syringes used as piston corers. The subsamples of sediments were extruded into pre-weighed glass vials or bottles and frozen until used. This procedure minimized disturbance of the sediment and retained the porewater. Individual vials of sediment were thawed and re-weighed before starting experimental runs or sedimentological analyses.

a. Grain Size distribution: The grain size distribution of the sediment collected at five inner (IS2, IS3, IS4, IS5, IS6) and three outer (OS2, OS3, OS4) shelf sites was determined in duplicate following Folk (1974). Weight percentages of gravel, sand and mud were determined gravimetrically following wet and dry sieving. The clay composition of the mud fraction was determined by pipette analysis (Folk, 1974). Sediment type was classified following Wentworth (1922) as cited in Folk (1974). Discriminations were limited to mud (< 0.063 mm), sand (0.063-2 mm) and gravel (> 2 mm) size fractions. Sediment samples collected at four sites (IS1, MS1, OS1, OS5) were classified by visual appearance into mud, muddy sand or sand as there was no

sample to be classified by this procedure.

b. Carbon and nitrogen Composition: The total carbon (including $CaCO_3$) and nitrogen composition of sediments from inner (IS2, IS3, IS4, IS5, IS6) and outer shelf sites (OS2, OS3, 0S4) were determined by high temperature combustion using a Leco Carbon-Hydrogen-Nitrogen Analyser (Model CHN-600). Analyses were standardized against a reference sediment (BCSS-1, National Research Council, Canada).

c. Water content: Sediment porewater usually contain significant amounts of dissolved nutrients (e.g. Blackburn and Henriksen, 1983; Enoksson and Samaelsson, 1987; Capone *et al.*, 1992). In the central GBR, Alongi (1989c) found that concentrations of NH_4^+, NO_2^-, NO_3^-, $Si(OH)_4$ and PO_4^{3-} in porewater were significantly greater than concentrations measured in the overlying water. As a result, differences in the porosity (water content) of sediment would affect the amount of nutrients released as a consequence of resuspension. The porosity of sediment samples was estimated by weighing duplicate subsamples of sediment from each site before and after oven drying the sediment until constant weight (approximately 80° C for 24 hours).

2.2.3 Collection of seawater

The seawater used in most experiments was collected at the surface from mid-shelf sites. An exception was the initial trials using sediments from sites MS1 and OS5, where nearshore water collected from the Australian Institute of Marine Science (AIMS) jetty was used. Seawater was collected from mid-shelf sites to avoid higher amounts of suspended sediments and higher plankton concentrations found in inshore waters. Fresh seawater for individual experiments was collected from a number of mid-shelf sites (Table 2.1, Figure 2.1). Surface seawater was collected either with an acid-cleaned bucket, Nisken bottles, or by pumped into an acid-cleaned polyethylene drum. In all cases the water was filtered through a 20 μm nylon plankton net to exclude large zooplankton, but was not sterilized.

Mid-shelf seawater was used in all experiments for consistency because the nutrient content of mid-shelf seawater is less variable compared to inshore water and outer shelf water (Revelante and Gilmartin, 1982). Inshore water is seasonally affected by nutrient inputs from land while outer shelf water intermittently mixes with water from

the Coral Sea. During wet season, concentrations of some nutrient species ($Si(OH)_4$, chlorophyll, phaeophytin) in mid-shelf seawater are more variable, while some nutrient species such as NH_4^+, NO_2^-, NO_3^- and PO_4^{3-} are less variable when compared to outer shelf sediment (Furnas and Mitchell, 1984). Most of the water samples were collected during the dry season.

The use of seawater from the specific sites where sediment was collected (e.g. outer shelf seawater for outer shelf sediment and inner shelf seawater for inner shelf sediment), was avoided as it would have involved resolving whether the variability in chemical components of both seawater and sediments was the result of different sites of either the seawater or sediment. Inshore water was not used as it would be difficult to detect small nutrient releases following sediment resuspension, when control seawater (no sediment added) naturally contained higher concentrations of nutrients, chlorophyll and/or suspended solids. The use of seawater from the outer shelf area was deemed impractical because of the longer transportation and storage times involved.

2.2.4 Effects of storage on nutrient concentrations in seawater

Mid-shelf water was pumped through a plankton net (mesh size 20 μm) into a 60-litre polyethylene drum. The drum was stored closed in a shaded area and sampled at 0, 12, 24, 36, 49, 61 and 73 hours after collection. Before each sampling event, the drum contents were thoroughly mixed. At each sampling time four replicates were taken each for measurement of ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), silicate ($Si(OH)_4$), dissolved inorganic phosphorus (PO_4^{3-}), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), particulate organic nitrogen (PN), chlorophyll *a* and phaeophytin. After filtration, the sub-samples of water were frozen pending chemical analysis. Details of filtration and chemical analysis methods are given in Chapter 3.

The data were analyzed using a one-way analysis of variance (ANOVA; Zar, 1984) to determine whether nutrient concentrations sampled after different storage times differed. Prior to the ANOVA, Cochran's C Test (Dixon and Massey, 1969) was applied to test whether the variance was heteroscedastic. The data was found to be normally distributed. Tukey's multiple comparison test (Zar, 1984) was used to make *a posterior* comparisons of means.

2.3 RESULTS

2.3.1 Sediment characteristics

The sediment grain size distribution, carbon and nitrogen composition and water content at each site are summarized in Table 2.3. The highest percentage of the gravel size fraction in sediment was found at site IS3 (25%) compared to other sites. The sediments from IS4, IS5, IS6 and OS2 sites contained a high percentage of silt ($\geq$ 49%). Not surprisingly, outer shelf sediments contained a significantly higher percentage of total carbon than inner shelf sediments (T-test, $\underline{P} < 0.05$). Total nitrogen composition was similar in inner shelf and outer shelf sediments.

The water content of sediment collected from sites IS2, IS3, IS4, IS5, IS6, OS2, OS3 and OS4 were similar (approximately 60%). The initial sediment samples collected and stored in bulk (MS1 and OS5) were characterized by a lower water content (approximately 24%).

2.3.2 Effects of storage on nutrient concentrations in seawater

Temporal changes in the concentration of individual nutrient species are shown in Figure 2.2. The results of the ANOVA and the Tukey's tests indicated that water can be kept for up to 12 hours without significant change in nutrient concentrations. Concentrations of PO_4^{3-} and $Si(OH)_4$ did change significantly after 24 hours. PN, TDP and DOP changed significantly after 36 storage hours while the concentration of DON only altered significantly after 49 hours. Chlorophyll *a* concentrations changed after 73 hours. No significant changes in TDN, NH_4^+ and phaeophytin were measured during 73 hours of storage. Maximum recommended storage periods for individual nutrient species without significant change in concentration are indicated by arrow symbols in Figure 2.2.

2.4 DISCUSSION

2.4.1 Sediment characteristics

Sediment grain size characteristics varied among individual sites. There was no clear trend in grain size distribution between inner and outer shelf sediments. This may reflect the limited sampling within each zone. It is not surprising that the percentage of

Table 2.3

Sediment characteristics : water content, suspended solids concentrations released per gram wet weight, elemental composition and grain size distribution. Mean (SD), n = 2, nd = no data

Study Site	Water content % (w/w)	Suspended solids concentrations mg./l per gm. wet wt.	Elemental compositions		Grain size distribution				Sediment type
			%Total Carbon (+ CaCO3)	%Nitrogen	% gravel	% sand	% silt	% clay	
IS1	60.5(0.7)	23.2(8.7)	nd.	nd.	nd.	nd.	nd.	nd.	Sandy mud
IS2	56.0(0.0)	8.6(2.1)	4.95(0.2)	0.01(.001)	4.56	64.77	27.7	2.97	Muddy sand
IS3	60.0(2.8)	4.0(0.9)	3.33(0.5)	0.01(0.0)	25.09	44.98	27.27	2.66	Muddy sand
IS4	40.5(0.7)	8.3(2.4)	3.40(0.1)	0.02(.007)	1.55	40.33	49.4	4.52	Sandy mud
IS5	56.0(2.2	13.1(2.1)	3.87(0.5)	0.01(.001)	2.34	41.25	47.86	8.55	Sandy mud
IS6	65.0(1.2)	15.6(1.8)	4.06(0.3)	0.01(.004)	1.96	43.54	48.21	6.29	Sandy mud
MS1	24.0(2.8)	10.0(1.2)	nd.	nd.	nd.	nd.	nd.	nd.	Muddy sand
OS1	62.5(2.1)	11.9(2.4)	nd.	nd.	nd.	nd.	nd.	nd.	Sandy mud
OS2	60.0(1.4)	11.3(2.3)	9.47(0.1)	0.01(.001)	0.2	44.08	49.4	6.32	Sandy mud
OS3	59.0(2.8)	19.0(3.6)	9.95(0.1)	0.01(.001)	0.33	61.77	33.68	4.22	Muddy sand
OS4	57.0(1.4)	11.3(1.4)	10.15(0.2)	0.01(.001)	10.58	46.4	38.33	4.69	Muddy sand
OS5	24.0(1.4)	11.0(1.7)	nd.	nd.	nd.	nd.	nd.	nd.	Muddy sand

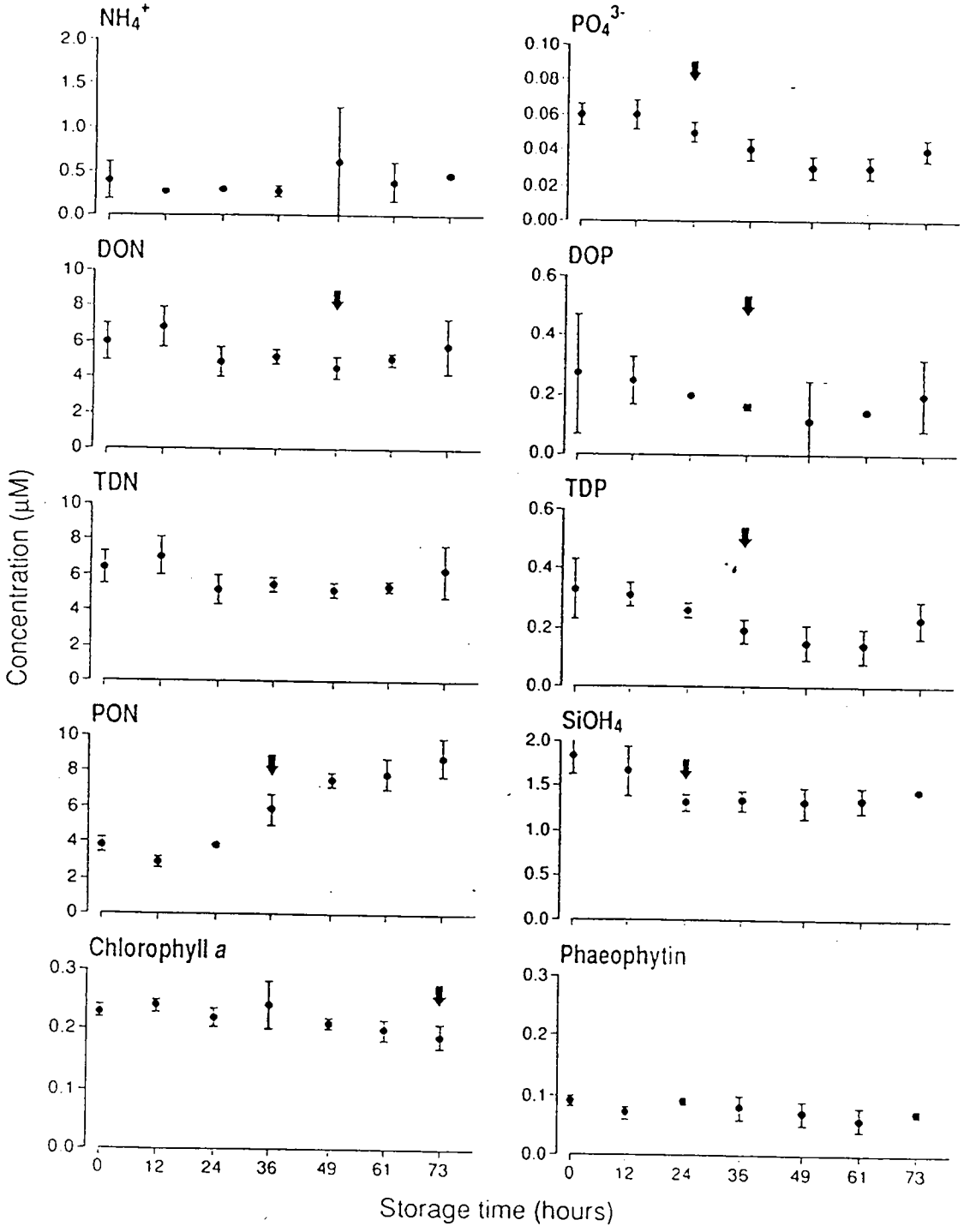


Figure 2.2 Changes in mean concentrations of nutrient with storage time. Bars show standard deviation and arrows indicate the first significant changes at $\underline{P} < 0.05$ level.

total carbon in outer shelf sediments was higher than inner shelf sediments since outer shelf sediment was largely comprised of calcium carbonate. The water content of sediment samples collected for this study were (24-62 %) similar to values samples reported by Alongi (1989c) (31-38 %). The lower water content of sediments from sites MS1 and OS5 is likely due to loss of porewater as bulk subsamples procedure which sediment may be disturbed.

2.4.2 Effect of storage on nutrient concentrations in seawater

Nutrient concentrations fluctuated with time during storage. However, over the longest periods of storage (73 hrs), concentrations of nutrients remained within normally encounter concentration ranges (Table 2.4). While nutrient concentrations in stored seawater from mid-shelf areas were variable, the small changes were deemed to be acceptable. Wherever possible, water was collected immediately prior to commencement of the main experiment. If this was not possible, water was stored for less than 12 hours before use.

2.5 CONCLUSIONS

1. Grain size distributions and water contents of sediment samples used for this study did not differ greatly between inner and outer shelf zones except for the higher percentage of calcium carbonate in outer shelf sediments.

2. Water to be used for experiments can be reliably stored for up to 12 hours with no significant change in nutrient concentrations. Changes in nutrient concentration over storage time remained within concentration ranges of normally encountered in seawater found at mid-shelf.

Table 2.4

Summary of the concentration ranges of nutrients previously measured in seawater collected from mid-shelf areas of the central GBR. All units in µM except chlorophyll *a* and phaeophytin which are in $\mu g\ l^{-1}$. (nd. = no data).

Nutrient species	Years						
	1975-1977	1977	1978	1976-1977	1979	1983	1983
PO_4^{3-}	nd.	0.06-0.80	0.07-0.53	0.06-0.80	nd.	0.13	0.09-0.27
NO_3^-	nd.	0.0-0.90	0.05-0.96	0.04-2.50	nd.	0.08	0.00-0.20
NO_2^-	nd.	0.0-0.65	0.07-0.36	0.00-2.04	nd.	0.03	0.00-0.03
NH_4^+	nd.	0.0-1.80	0.0-1.35	0.00-2.70	nd.	nd.	0.01-0.55
$Si(OH)_4$	nd.	0.0-35.3	3.20-15.14	0.00-29.20	nd.	1.42	0.30-4.85
DON	nd.	nd.	1.32-4.23	nd.	nd.	nd.	nd.
DOP	nd.	nd.	0.0-0.32	nd.	nd.	nd.	nd.
Chlorophyll *a*	0.08-2.43	nd.	0.10-1.29	0.52-0.62	0.0-3.10	0.39	.09-1.33
Phaeophytin	0.0-0.90	nd.	0-0.42	nd.	0-0.65	nd.	.01-1.17
References	Ikeda *et al.*, 1980			Revelante and Gilmartin, 1982	Wolanski and Jones, 1981b	Andrews, 1983	Furnas and Mitchell, 1984

CHAPTER 3

NUTRIENT RELEASE FROM RESUSPENDED SEDIMENTS

3.1 INTRODUCTION

The movement of dissolved substances across the sediment-water interface is an important process affecting the dynamics of nutrients in shallow water environments (e.g. Davies, 1975; Hartwig, 1976; Rowe *et al.*, 1975; Nixon *et al.*, 1976; Walker and O'Donnell, 1981; Fanning *et al.*, 1982; Ullman and Sandstrom, 1987; Yamada *et al.*, 1987; Capone *et al.*, 1992). Nutrient releases from sediments are affected by physical processes in the water column immediately above and within the benthic boundary layer and by biological, physical and chemical processes within the sediment (Berner, 1976).

Processes involved in or affecting nutrient releases from sediments include: wave generated turbulence (e.g. Stephenson, 1949; Vanderborght *et al.*, 1977; Walker and O'Donnell, 1981), energetic storms (e.g. Fanning, *et al.*, 1982; Ullman and Sandstrom, 1987), molecular diffusion (e.g. Davies, 1975; Zeitzschel, 1980; Fisher, *et al*, 1982a), buoyancy displacement (e.g. Smetacek *et al.*, 1976), absorption (e.g. Stumm and Leckie, 1971; Forsberg, 1989), bioturbation (e.g. Rhoads, 1974; Smith *et al.*, 1978; Aller, 1980a,b; Henriksen *et al.*, 1980; Blackburn and Henriksen, 1983; Aller *et al.*, 1985), denitrification (e.g. Seitzinger *et al.*, 1980; Hattori, 1983; Kemp *et al.*, 1982), and nitrification (e.g. Aller *et al.*, 1985; Grundmanis and Murray, 1977). Nutrient transfers from sediments to the water column are affected by processes operating over a range of time scales. These processes are both continuous (e.g. diffusion, bioturbation, denitrification and nitrification) which contribute to steady-state nutrient exchanges with the water column occurring over long periods, and sporadic, event-related processes, such as resuspension or deposition events, which result in nutrient exchanges in short bursts. Nutrient release processes also depend on sediment type (Aller and Benninger, 1981; Fisher *et al.*, 1982a), vertical distribution of subsurface sediment (Rosenfeld, 1979, 1981; Grundmanis and Murry, 1977; Berner, 1974; Aller and Bernninger, 1981: Aller and Yingst, 1980; Aller, 1980b; Pomeroy *et al.*, 1965), temperature (Nixon *et al.*, 1976; Aller, 1980c; Aller and Benninger, 1981; Aller and Yingst, 1980) and organic matter input fluxes to surficial sediments (Billen, 1978; Kelly and Nixon, 1984; Aller and Benninger, 1981; Garber, 1984b).

Sediment resuspension has been identified as contributing to enhancement of nutrient inputs to both coastal and continental shelf waters (Fanning, *et al.*, 1982; Ullman and Sandstrom, 1987; Walker and O'Donnell, 1981). Wind-generated waves exceeding 2 m in height are capable of resuspending fine-grained sediment in water depths of 25 m (Wolanski *et al.*, 1981). Resuspension of sediments by energetic physical processes (e.g. cyclones, storms, wind waves or currents) can occur across wide areas of shallow continental shelves such as that on which the GBR is situated (Gagan *et al.*, 1987, 1988; Riddle, 1988a; Sandstrom, 1988).

Cyclones or energetic storms have been shown to resuspend large amounts of sediment (Ball, *et al.*, 1967; Perkins and Enos, 1968; Woodley, 1980; Gagan *et al.*, 1988). Tons of sediment were removed from shallow reef slopes and terraces by Hurricane "Allen", which traversed the Caribbian in 1980 (Woodley, 1980). Riddle (1988) reported that increases in the proportion of coarser materials in coral reef lagoon sediments following cyclone "Winifred" (North Queensland, 1986) were likely to be the result of the removal of fine particles. Hurricane "Donna" (Florida Keys, 1960) disturbed sand over an area at least 1.6 km wide by 32 km long (Ball *et al.*, 1967; Perkins and Enos, 1968).

Cyclone "Winifred" which affected the central GBR shelf in 1986 reworked shelf sediment over an area exceeding 10^3 square km (Gagan *et al.*, 1988). This effect extended at least 30 km offshore and resuspended surficial sediments in water depths greater than 40 m (Gagan *et al.*, 1988). Erosion depths were greatest on the mid-shelf averaging > 6.9 cm as compared to 5.1 cm on the inner shelf. Particles finer than medium sand (< 2 mm) were eroded and transported out of the mid-shelf region (Gagan *et al.*, 1990). Gagan *et al.* (1990) concluded that the storm layer formed by "Winifred" on the inner shelf resulted from a combination of three processes: 1) the seaward transport of terrigenous sediment in buoyant freshwater flood plumes, 2) the resuspension and settling of inner-shelf sediment, and 3) the resuspension and shoreward transport of mid-shelf sediment. At least 10-30 % of the inner shelf-storm layer was composed of mud removed from the mid-shelf area.

Cyclones and other energetic storms affect not only the sediments on shelves but also nutrients in the water column. Changes in nutrient concentrations in marine ecosystems following cyclones or other energetic storm events can be attributed to increased rainfall, vertical mixing, terrestrial runoff and resuspension of shelf sediments. The tropical storm, "Agnes" had a pronounced effect on nutrient and plankton concentrations in Chesapeake Bay (Schubel *et al.*, 1976). Rainfall from "Agnes" produced large floods, which increased the sediment runoff into Chesapeake Bay (Schubel, 1976). Nitrate and nitrite

concentrations increased 2 to 3-fold. Ammonia concentrations were also elevated, while phosphate concentrations changed only slightly. As a result, the mean chlorophyll *a* concentration in lower Chesapeake Bay nearly doubled, increasing from 8.8 $\mu g\ l^{-1}$ prior to the storm, to 14.3 $\mu g\ l^{-1}$ (Zubkoff and Warinner, 1976; Loftus and Seliger, 1977). Likewise, the phytoplankton standing crop in the Gulf of Mexico measured in surface water after Hurricane "Inez" (0.235 $\mu g\ l^{-1}$) was about double the level measured before the hurricane (0.125 $\mu g\ l^{-1}$) (Franceschini and El-Sayed, 1968).

Fanning *et al.* (1982) reported that nutrient concentrations in northern Gulf of Mexico shelf waters were significantly elevated after a winter storm. In contrast, however, Dagg (1988) found that a winter storm in the Gulf of Mexico moved coastal, chlorophyll-rich water offshore at the surface and caused upwelling of inner shelf water with low concentrations of nutrients and chlorophyll. Likewise, tropical storm "Dennis" produced changes in temperature and salinity off the coast of Georgia, but not in nutrient or chlorophyll concentrations (Zeeman, 1985).

Measurements of nutrient and chlorophyll concentrations before and after cyclonic events in the central GBR show a significant change in water column properties following cyclones. Cyclone "Winifred", in particular, produced up to 10-fold increase in chlorophyll concentration, and 20-fold increase in DIN concentration, but less than two fold in PO_4^{3-} and $Si(OH)_4$ concentrations (Furnas, 1989; M. Furnas unpubl. data). Following the passage of cyclone "Charlie" (1988), nutrients (NO_3^-, NH_4^+ and PO_4^{3-}) near Cape Bowling Green, Queensland (1988) rose to levels 2-4 times higher than those measured at other nearby inshore stations (Liston, 1991). Chlorophyll concentrations increased fourfold over pre-cyclone concentrations, though they remained within the range of concentrations measured at inshore stations unaffected by the cyclones (Liston, 1991).

Nutrients measured in the water column following cyclonic disturbance events can be derived from several sources. Nearshore increases in nutrients off South Carolina after tropical storm "Dennis" were attributed to river outflow (Zeeman, 1985). Likewise, the large nutrient increases within Chesapeake Bay measured after tropical storm "Agnes" were also attributed to river outflows (Loftus and Seliger, 1977). Laboratory resuspension studies on fine-grained shelf sediment, strongly suggest that increases of nutrient and suspended matter on the Florida shelf, were due to the resuspension of sediments during a winter storm (Fanning *et al.*, 1982). Floods (Wolanski and Van Senden, 1983) and the resuspension of bottom sediment (Walker and O'Donnell, 1981; Ullman and Sandstorm, 1987; Liston, 1991) are suggested to be important sources of

nutrients in inshore waters of the central GBR region. Preliminary nutrient budgets (Furnas, 1989) suggest that coastal runoff, rainfall and porewaters from disturbed shelf sediments following cyclone "Winifred" accounted for most of the additional phosphate and silicate dissolved in shelf waters and incorporated into the phytoplankton standing crop. Furnas also considered that most of the additional nitrogen came from microbial mineralization of organic nitrogen released from resuspended shelf sediments. However, the evidence for these sources of elevated nutrient were not able to be resolved at that time.

The occurrence of tropical cyclonic events in the GBR clearly affect the sediment, nutrient status and productivity of the normally oligotrophic GBR waters (Liston, 1991; Furnas, 1989). The regional impact of cyclonic events is likely to be high because marine sediments are often major sinks for nitrogen (Val Klump and Martens, 1983), and phytoplankton biomass in GBR waters appears to be nitrogen-limited (Furnas and Mitchell, 1986b). The unresolved question concerning nutrient sources following cyclonic disturbance, highlights the need for quantitative studies on the effect of sediment resuspension caused by cyclones or energetic storms on nutrient dynamics in GBR shelf waters. The amounts of nutrients released following resuspension of bottom sediments by mechanical processes (cyclones or other energetic storms, waves or currents) in open shelf areas such as the GBR have not been quantified. If resuspended sediments do contribute significant amounts of nutrients to the GBR shelf system, a further question that arises is: are there regional differences between the inner and outer shelf areas in the amount and speciation of nutrients released?

STUDY OBJECTIVES

The overall objective of the experiments described in this chapter is to quantify the amount of nutrients which are released from sediments and made available for biological processes in the water column of the central GBR as the result of a cyclonic resuspension event. To answer this general question, a number of related problems had to be resolved. First, do the concentration and speciation of nutrients in the water column change significantly over time following a sediment resuspension event? The nature of temporal changes in nutrient concentration and speciation would dictate the frequency of sampling needed to resolve the effects of resuspension and aid the interpretation of field data collected after natural events. Second, in order to determine the amounts of nutrients released as a result of sediment resuspension processes, it is necessary to relate the amount of nutrient released with the amount of sediment resuspended. From an experimental standpoint, what mass sediment must be added to get a definitive result? Third, what are the levels of variability associated

with local geographical sources of sediment and analytical factors such as water and sediment subsampling methods. Finally, because sediment character varies on a cross-shelf areas, it is necessary to determine whether regional differences in nutrient releases exist between inner (terrigenous) and outer shelf (carbonate) sediments.

This chapter embraces four specific objectives:

1. To investigate temporal changes in nutrient concentration and speciation following simulated sediment resuspension events.
2. To determine relationships between sediment mass and extractable nutrient mass.
3. To assess levels of variability associated with subsampling of water and sediment.
4. To compare the amounts of dissolved and particulate nutrients (N, P, Si) which are released in aerobic seawater from inner-shelf (terrigenous) and outer-shelf (carbonate) sediments collected from the central GBR shelf following a simulated resuspension event.

3.2 MATERIALS AND METHODS

3.2.1 General procedures

Definitive experimental measurements of nutrient release from resuspended shelf sediment and their speciation cannot be conducted *in situ* because confounding processes cannot be excluded or separated. Laboratory experiments using stirred or shaken sediments were therefore carried out to directly measure both the quantities and types of nutrients released from the two dominant sediment types occurring on the central GBR shelf: terrigenous sediments which characterize the inner shelf and carbonate sediments which typify the outer shelf. Because of differences in the physical and chemical nature of these two sediment types, the quantity and type of dissolved and particulate nutrients released from each sediment types were expected to be qualitatively and quantitatively different. The amount of nutrient released from the two sediment types should also provide an estimate of nutrient released from mid-shelf sediments, which consist of a mixture of inner and outer shelf sediments.

Changes in nutrient concentration arising from the dispersion of sediment samples into aerated seawater were measured by stirring known masses of sediments and water under controlled laboratory conditions. This approach was chosen in order to directly measure

the amount of nutrients which would be promptly released from the sediment into the water column by mechanical disturbance.

Four experiments were carried out. These experiments are in turn divided into individual trials. The first experiment measured nutrient concentration and speciation over time following simulated sediment resuspension events to investigate temporal changes in nutrient concentrations and compare these to natural seawater without sediment resuspension (control). This experiment was also used to describe temporal nutrient changes in general and to resolve aspect of the noise inherent in nutrient measurements. This experiment involved three individual trials using sediment from different sites. The second experiment assessed whether the degree of nutrient release was related to the sediment mass added to the water column. The experiment was also designed to assess whether there were different sediment mass-nutrient release relationships between sediment collected from different inner and outer shelf sites. The third experiment was conducted to determine whether variability associated with water and sediment subsampling affected estimates of nutrient release over and above the effects of the main factors (release mechanisms: promptly release vs nine-day interval release and treatment: seawater vs seawater with suspended sediment). Information gained from the first three experiments was necessary for the design of a more comprehensive experiment , the fourth experiment in which the amounts of nutrients released from resuspended inner and outer shelf sediments are compared.

3.2.2 Nutrient species and water parameter measurements

Dissolved and particulate nutrient concentrations in seawater to which sediments were added (hereafter called the "experimental carboy/bottle") were compared with concentrations in seawater with no added sediment (hereafter called the "control carboy/bottle"). Analysis of the data focused on quantifying concentration differences between experimental and control containers for the following variables:

1. Dissolved inorganic nitrogen (DIN comprising NO_2^-, NO_3^-, NH_4^+)
2. Dissolved inorganic phosphorus (DIP comprising PO_4^{3-})
3. Dissolved organic nitrogen (DON)
4. Dissolved organic phosphorus (DOP)
5. Particulate nitrogen (PN)
6. Particulate phosphorus (PP)
7. Dissolved inorganic silicate ($Si(OH)_4$)
8. Chlorophyll *a* (Chl *a*) and phaeophytin

9. Suspended solids

3.2.3 Preparation and analysis of nutrients and other properties of water samples

Procedures for water subsampling and the handling during experiments are described below. The associated analytical methods are summarized in Table 3.1.

a. Particulate Nitrogen (PN), Particulate Phosphorus (PP)

Four 100 ml subsamples collected from each container were filtered through pre-combusted (450 °C overnight) Whatman GF/F glass-fibre filters. Two filters, to be used for PP determinations, were stored frozen until analysis. Two filters to be used for PN analyses were frozen, freeze-dried and stored in a desiccator.

b. Dissolved Organic Nitrogen (DON), Dissolved Organic Phosphorus (DOP)

Duplicate subsamples of water were filtered through Whatman GF/F glass-fibre filters. Dissolved organic nitrogen and dissolved organic phosphorus in the filtrate was oxidised to inorganic forms of nitrogen and phosphorus by exposure to high intensity ultra-violet light for 7 h. DON and DOP concentrations were then calculated by subtracting DIN and DIP concentrations measured in unoxidized samples from the total dissolved nitrogen and phosphorus concentrations in oxidized samples.

c. Chlorophyll *a* and Phaeophytin

Duplicate 100 ml subsamples of water were filtered through Whatman GF/F glass-fibre filters which were then frozen. A few drops of a 1 % $MgCO_3$ suspension were added during filtration to stabilize the pigment during storage. Analyses were always completed within 4 weeks.

d. Dissolved Inorganic Nutrients

The remainder of the subsampled aliquot was filtered through the GF/F filters for analysis of dissolved inorganic nutrients (NH_4^+, NO_3^-, NO_2^-, PO_4^{3-} and $Si(OH)_4$). In the initial experiments (temporal changes in nutrient concentrations), analyses were carried out

manually (Strickland and Parson, 1972; n = 3 replicates). Thereafter, the subsamples were filtered, and frozen for later analyses by automatic segmented flow analysis (Ryle and Mueller, 1981; n = 2 replicates).

e. Suspended Solids

A well shaken 1-litre water sample was taken from each carboy and filtered through pre-weighed Nucleopore filters (0.4 μm pore diameter). The filters were rinsed with distilled water to remove salt from the filters and stored in a desiccator until dry. The concentration of suspended solids was determined by subtracting the weight of the filter before filtration of the water sample from the weight of the dried filter plus particulate material. This measurement was made to check the extent to which sediment added into the water column remained in suspension, and to assess the amount of fine suspensible material which was contained in a given weight of added sediment.

3.2.4 Environmental conditions and seawater handling

Experiments were carried out in a constant temperature room (27 °C). This temperature simulated natural seawater temperatures in the GBR during the summer (data from AIMS Weather Station, Australian Institute of Marine Science, Australia). Although near-bottom summer water temperatures (normally 26-29 °C) may across the shelf, especially as a result of upwelling events and surface heating, the experimental temperature was fixed to minimize confounding effects of variable temperature on rate processes. A fluorescent light fixture located either above or behind the experimental carboys or bottles provided 40-50 $\mu E\ m^{-2}\ s^{-1}$ of cool-white fluorescent light (12 h:12 h light-dark cycle). The intensity of light was approximately 2-3 % of the normal intensity of surface sunlight and simulated the conditions arising from reduced light penetration in seawater following a major resuspension event.

Table 3.1

Summary of analytical methods for determination of nutrients and chlorophyll

Variables	Method	Instrumentation	References
DIN	* Manual		
•Ammonium	colorimetric	-	Solorzono, 1969
•Nitrate	colorimetric	-	Strickland and Parson, 1972
•Nitrite	colorimetric	-	Strickland and Parson, 1972
•Phosphate	colorimetric	-	Strickland and Parson, 1972
•Silicate	colorimetric	-	Strickland and Parson, 1972
DIN (= $NH_4^+ + NO_3^- + NO_2^-$)	Auto analyser	Skalar Analytical SA 20/40 SFA analyser	Ryle and Mueller, 1981
DON and DOP	oxidation by UV radiation and Auto analyser	Ultra-Violet Photo oxidation unit Skalar analytical SA 20/40 analyser	Armstrong, *et al.*, 1966; Walsh, 1989 Ryle and Mueller, 1981
PN	High Temperature Combustion	Antek Chemiluminescent nitrogen analyser, Model 707C	Furnas *et al.*, 1990
PP	Colorimetric following acid-persulfate digestion	-	Furnas *et al.*, 1990
Chlorophyll *a*	Fluorometric	Fluorometry Turner Designs Model 10-005R	Strickland and Parson, 1972
Phaeophytin	Fluorometric	Fluorometry Turner Designs Model 10-005R	Strickland and Parson, 1972

* DIN was analysed by manual method only in the experiment 1 using mid shelf sediment.

3.3 EXPERIMENTAL PROCEDURE AND RESULTS

3.3.1 EXPERIMENT 1: Temporal changes of nutrient concentration and speciation following a resuspension event.

This experiment was conducted to simulate and observe changes in nutrient concentrations and speciation which might occur after a cyclone. Daily changes in nutrient concentration and speciation in carboys of seawater with a high load of fine suspended sediment were compared to parallel changes in seawater without added sediment.

a. Experimental design

The experimental design is shown schematically in Figure 3.1. Three trials were conducted using sediment from different sites. The sources of sediment used in individual trials are given in Table 2.1 and Figure 2.1. Experimental incubations were carried out using three 20 litre polycarbonate carboys (Nalge, USA), with one used as the "control carboy" and two as "experimental carboys". In trials 1.1 and 1.2, where mid-shelf sediment (MS1) and outer shelf sediment (OS5) were used, respectively, the sediment subsamples for resuspending in the two experimental carboys were obtained from the same site. For trial 1.3, one "experimental carboy" contained sediment collected from an inner shelf site (IS3) and the other sediment collected from an outer shelf site (OS3).

On the first day of each trial (called "Day 1"), 20 litres of freshly collected seawater were added to each of the three carboys. The water was collected from the AIMS jetty for trials 1.1 & 1.2 and from a mid-shelf site for trial 1.3. The large volume of seawater collected ensured that a representative sample of planktonic microorganisms was obtained and allowed the required number of replicate subsamples to be taken. Based on pilot trials using reef sediment (data not presented), motorized stirring paddles were used to provide constant, efficient circulation of the water in the carboys (Figure 3.2). As *in situ* turbulent velocities of water during cyclonic event are not known, the stirring speed in the laboratory was set arbitrarily to suspend all the small sediment particles. An air pump continuously aerated the water in each carboy following passage through a 1 % sulfuric acid solution to absorb ammonia and then through a trap to exclude any acid aerosol. Approximately 5 ml (7-10 gm wet weight) of pre-weighed, frozen-thawed[6] sediment

[6]Frozen-thawed (abiotic) sediment mean that the freshly collected sediment was frozen and then thawed before use in the experiment to ensure that sediment bacteria were not active.

were added to each of the "experimental carboys". This mass of sediment resulted in a suspended sediment concentration similar to that measured near the bottom after cyclone "Winifred" (4-5 days after) in 1986 (9.5 ± 3.9 mg l^{-1}, n=18, J. Blevin pers. comm.).

The suspended solids concentration in each carboy was measured at the start of the experiment. Following the first two trials (using sediment from sites MS1 and OS5), the amount of sediment added to the "experimental carboys" was increased to heighten the difference between nutrient concentrations in the control and the experimental carboys. Water sampling was started immediately after the addition of sediment. Thereafter, 1 litre subsamples were taken from each carboy at the same time each day for 7-10 days or until dissolved inorganic nutrient (NH_4^+, NO_3^-, NO_2, PO_4^{3-} and $Si(OH)_4$) concentrations had remained constant for several days. The sampling duration corresponded to the time period over which cyclonic events are known to influence nutrient concentrations (Furnas, 1989; Liston, 1991).

b. Data analysis

Temporal change in concentrations of nutrients and chlorophyll in seawater with suspended sediment were compared with the corresponding concentrations in control carboys (without added sediment). The statistical analyses of results from this experiment are necessarily constrained because only a single control was used.

c. Results

The pattern of temporal change for nutrient and chlorophyll concentrations differed in individual trials. Concentrations of PN and PP were constant during the experimental period after release from sediments. For the most part, DON and DOP concentrations in the experimental and control carboys were similar and stable through time. Ammonium, nitrate and nitrite concentrations fluctuated over time. Inorganic phosphate and silicate concentrations decreased after release from the sediment. Phaeophytin concentrations were stable throughout the experimental periods while the chlorophyll *a* released from sediment increased after about a week of the experimental period. Details of the temporal changes in each nutrient species and each trials are given below.

Temporal changes in and speciation of nitrogenous nutrient concentrations

Daily change in PN, DON, NH_4^+, NO_3^- and NO_2^-, concentrations in the trials 1.1, 1.2

and 1.3 are shown in Figures 3.3 through 3.8. In trials 1.1 (Figure 3.3) and 1.2 (Figure 3.5), PN concentrations in the experimental carboys did not differ greatly from those measured in the control carboys. In trial 1.3 (site IS3 and OS3, Figure 3.7) noticeably higher PN concentrations were measured in the two experimental carboys as compared to the control carboy. This is due to the greater amounts of wet sediment added in trial 1.3 (24.3 g w/w) as compared to trials 1.1 (7.8 g w/w) and 1.2 (10.3 g w/w). Background PN concentrations differed between the three batches of natural seawater used. Small changes in water column PN concentration contributed by suspended sediment in the first two trials may not have been detected against the high background PN concentration. DON concentration remained constant throughout the trials 1.1 and 1.3. In trial 1.2, temporal changes in total nitrogen concentration were largely related to changes in DON concentration. In trial 1.2, DON concentrations in the control were also slightly higher than those in the experimental carboys.

Ammonium (NH_4^+) concentrations decreased through time in the control carboys in all trials (Figures 3.4, 3.6 and 3.8) but fluctuated erratically in experimental carboys. Concentrations of NO_3^- and NO_2^- fluctuated near the limit of detection (0.02 μM) throughout the experimental periods in all trials (Figure 3.3-3.8). In trials 1.1 and 1.2 the concentrations of NO_3^- dropped to very low levels early in the trial run (2-5 days) whereas NO_2^- concentrations remained detectable. This pattern of NO_3^- depletion was not noticeable in trial 1.3, however, NO_2^- remained readily detectable throughout.

Temporal changes in and speciation of phosphorus concentrations.

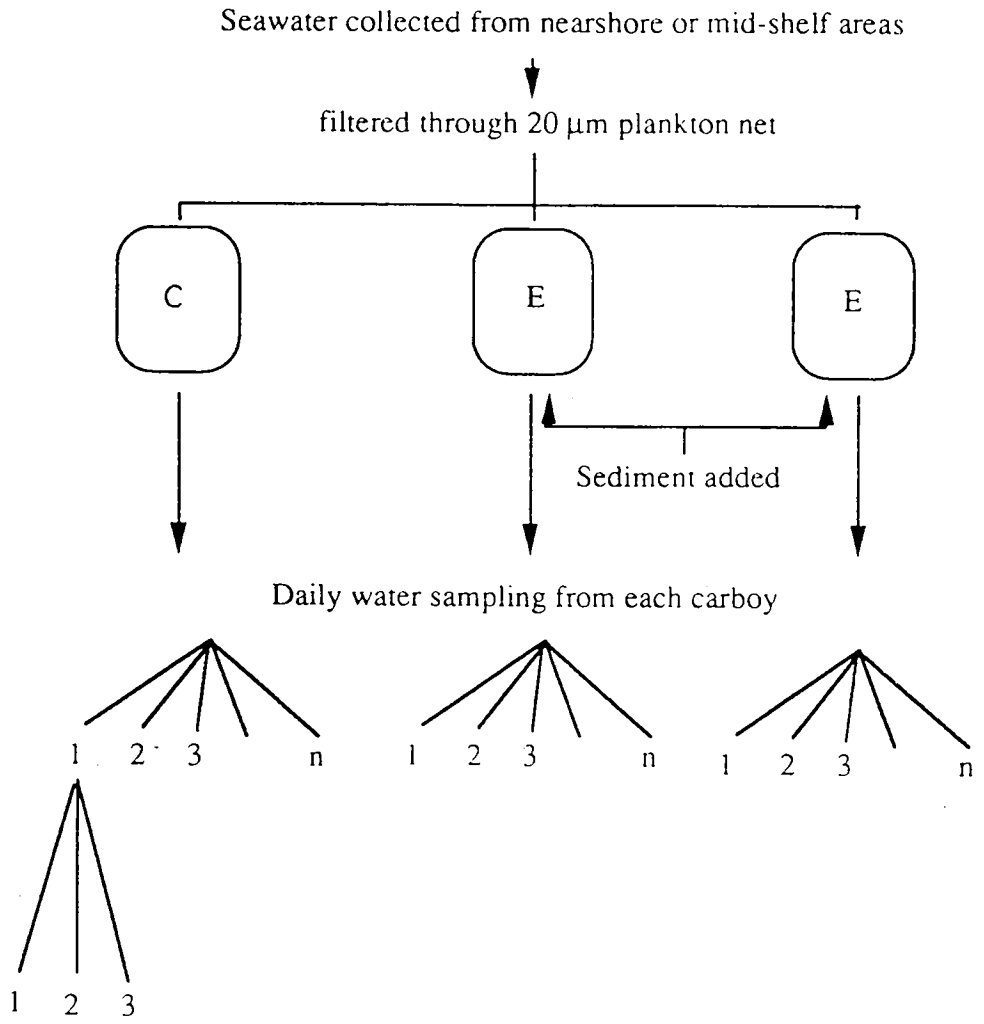
Changes of PO_4^{3-}, DOP and PP concentrations in the control and experimental carboys during the three trials (1.1, 1.2 and 1.3) are shown in Figures 3.9, 3.10, and 3.11, respectively. With the exception of the control carboy in trial 1.3, PO_4^{3-} concentrations decreased and DOP increased over time. In trials 1.1 and 1.2, PO_4^{3-} decreased and fell below detection limits within 3 and 11 days respectively, whereas in trial 1.3, PO_4^{3-} remained detectable in the water column at low levels throughout the experimental period (10 days). In trial 1.3, PO_4^{3-} tended to decrease faster in the water with inner shelf sediment than in the outer shelf sediment. In trials 1.2 and 1.3, PP concentrations were greater in the experimental carboys than in control carboys. No clear difference was apparent in trial 1.1. PP concentrations remained stable through time in trials 1.1 and 1.3. In trial 1.2, PP concentration increased for the first 6 days then varied. Varied results between the two replicates of experimental carboys from trial 1.2 were obtained after day 11.

Temporal changes of silicate concentrations.

With one exception, silicate concentrations in the control and experimental carboys exhibited the same temporal trend in individual trials. The overall temporal trends, however, differed among the three trials. In trial 1.1 (Figure 3.12), $Si(OH)_4$ concentrations remained stable for three days in all three carboys, then declined. In trial 1.2 (Figure 3.13), $Si(OH)_4$ concentrations in the three carboys showed no overall temporal trend. In trial 1.3 (Figure 3.14), $Si(OH)_4$ concentrations decreased in the control carboy and the carboy with offshore sediment throughout the experimental period. Higher $Si(OH)_4$ concentrations were found in the carboy with inshore (IS3) sediment. This higher $Si(OH)_4$ concentration on day 1 was obtained greater amounts of $Si(OH)_4$ in the porewater of the inshore sediment.

Temporal changes of chlorophyll a and phaeophytin concentrations.

Chlorophyll *a* (hereafter chl *a*) and phaeophytin concentrations exhibited different temporal trends within and between individual trials. Overall, chl *a* concentrations were higher in the experimental than in the control carboys. With the exception of the experimental carboys in trial 1.2 (where the phaeophytin concentration fluctuated through time), phaeophytin concentrations tended to be low and stable. Temporal trends in the concentrations of chl *a* and phaeophytin differed markedly between trials 1.1 (Figure 3.15) and 1.2 (Figure 3.16). In trial 1.2 concentrations of chl *a* and phaeophytin in the control carboy gradually decreased. Similar trends with high concentrations on day 2, day 7 and after day 11 were observed in both experimental carboys. In trial 1.3 (Figure 3.17), chl *a* and phaeophytin concentrations were considerably higher in the experimental carboys than in the control. Concentrations of chl *a* increased for several days in the experimental carboys, then declined, while phaeophytin concentrations remained stable. In the control carboy, chl *a* and phaeophytin concentrations remained constant.



Three replicate determinations for each nutrient species on each day

C : Control container = seawater without adding sediment
E : Experimental container = seawater with sediment

Figure 3.1 Design for experiment 1: Temporal changes of nutrient concentration and speciation following a resuspension event.

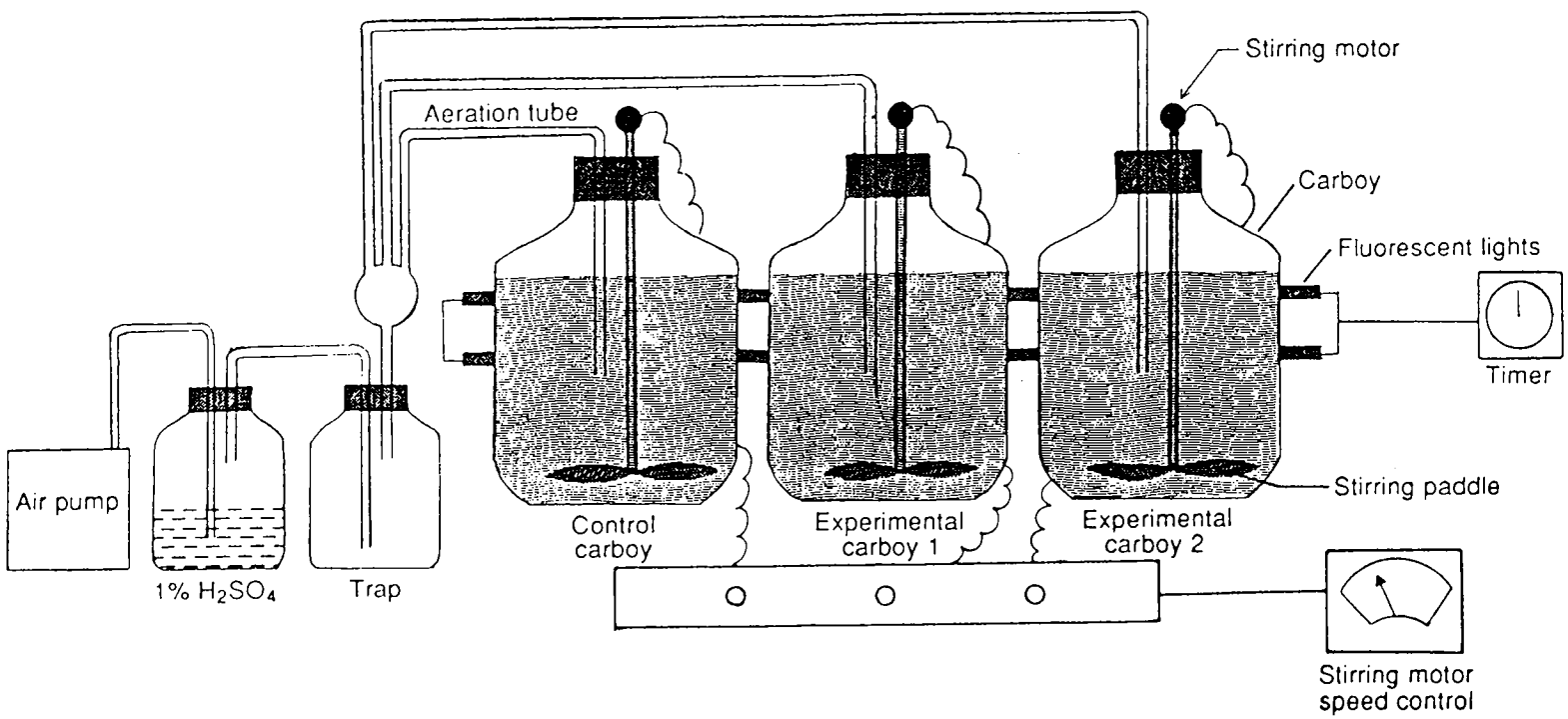


Figure 3.2 Experimental apparatus for experiment 1. Experimental carboys 1 and 2 contain seawater with added sediment. No sediment was added to the control carboy.

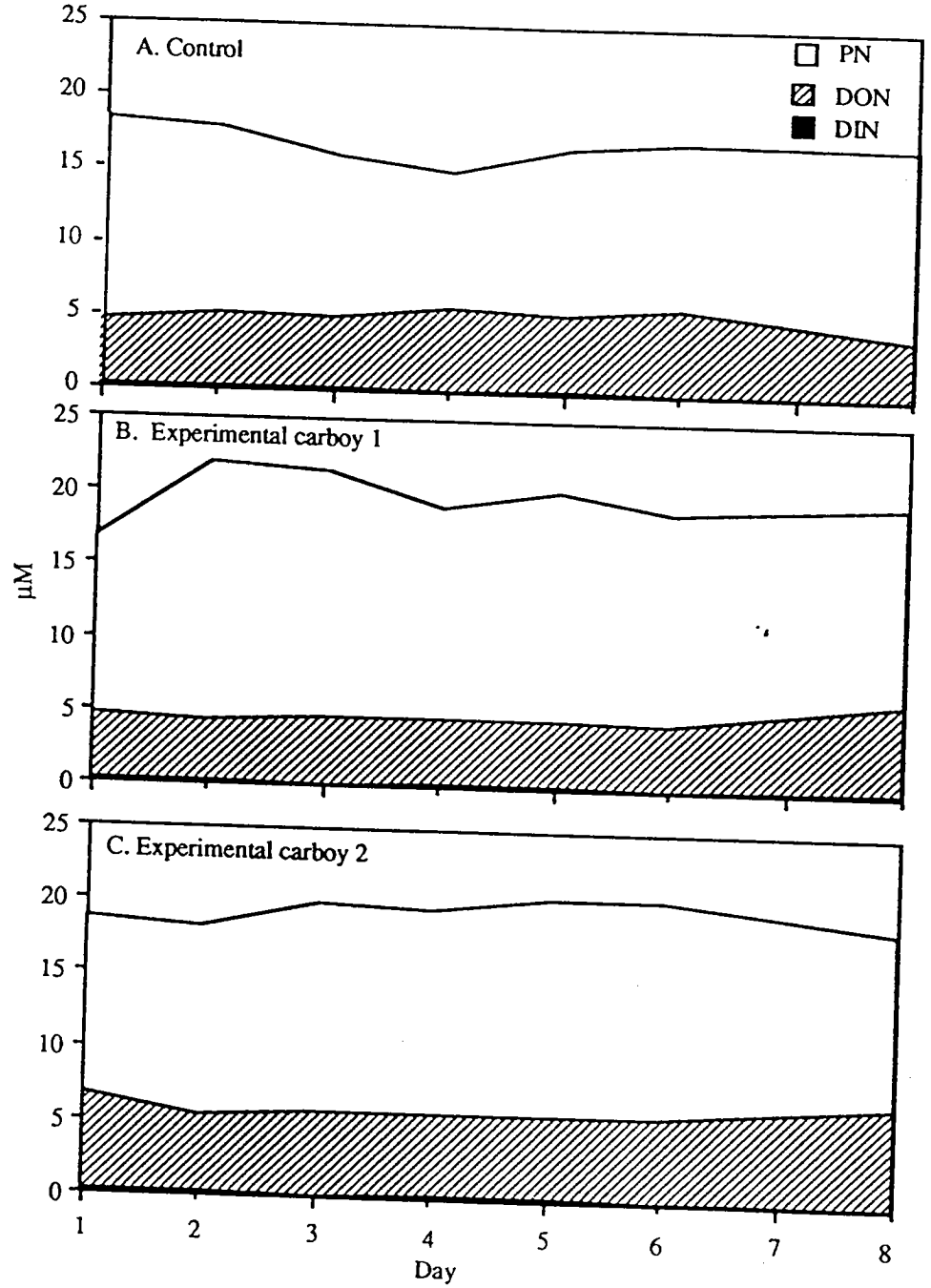


Figure 3.3 Temporal changes in total nitrogen concentration and the relative importance of N species in the control (A) and the experimental carboys with suspended sediment (B& C) during the trial 1.1, using mid-shelf sediment from site MS1. In this trial, 10.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

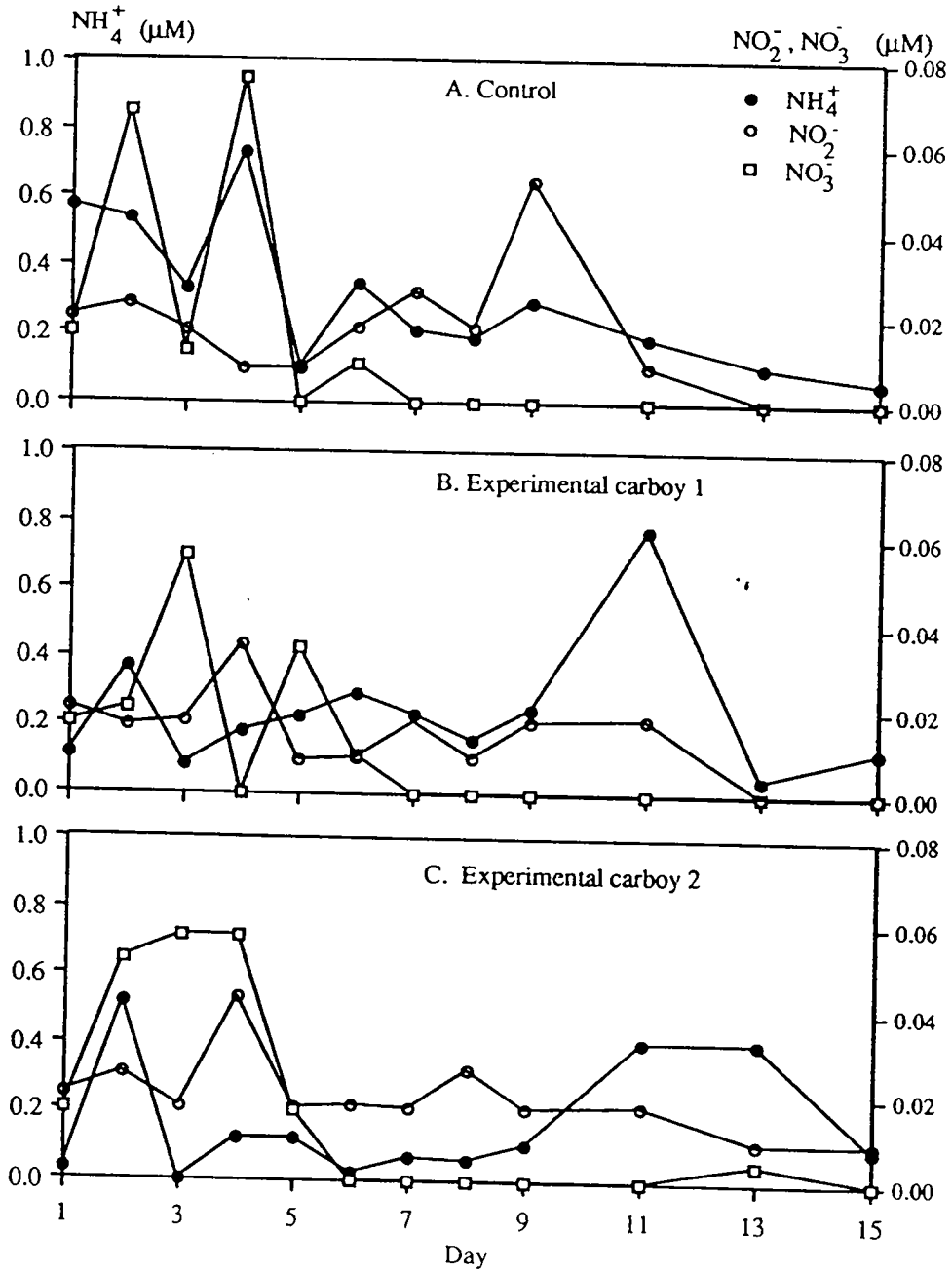


Figure 3.4 Temporal changes of DIN species (NH_4^+, NO_2^- and NO_3^-) in the control (A) and experimental carboys with suspended sediment (B & C) during the trial 1.1, using mid-shelf sediment from site MS1. Note that the vertical scales of the graphs are expanded from Figure 3.3.

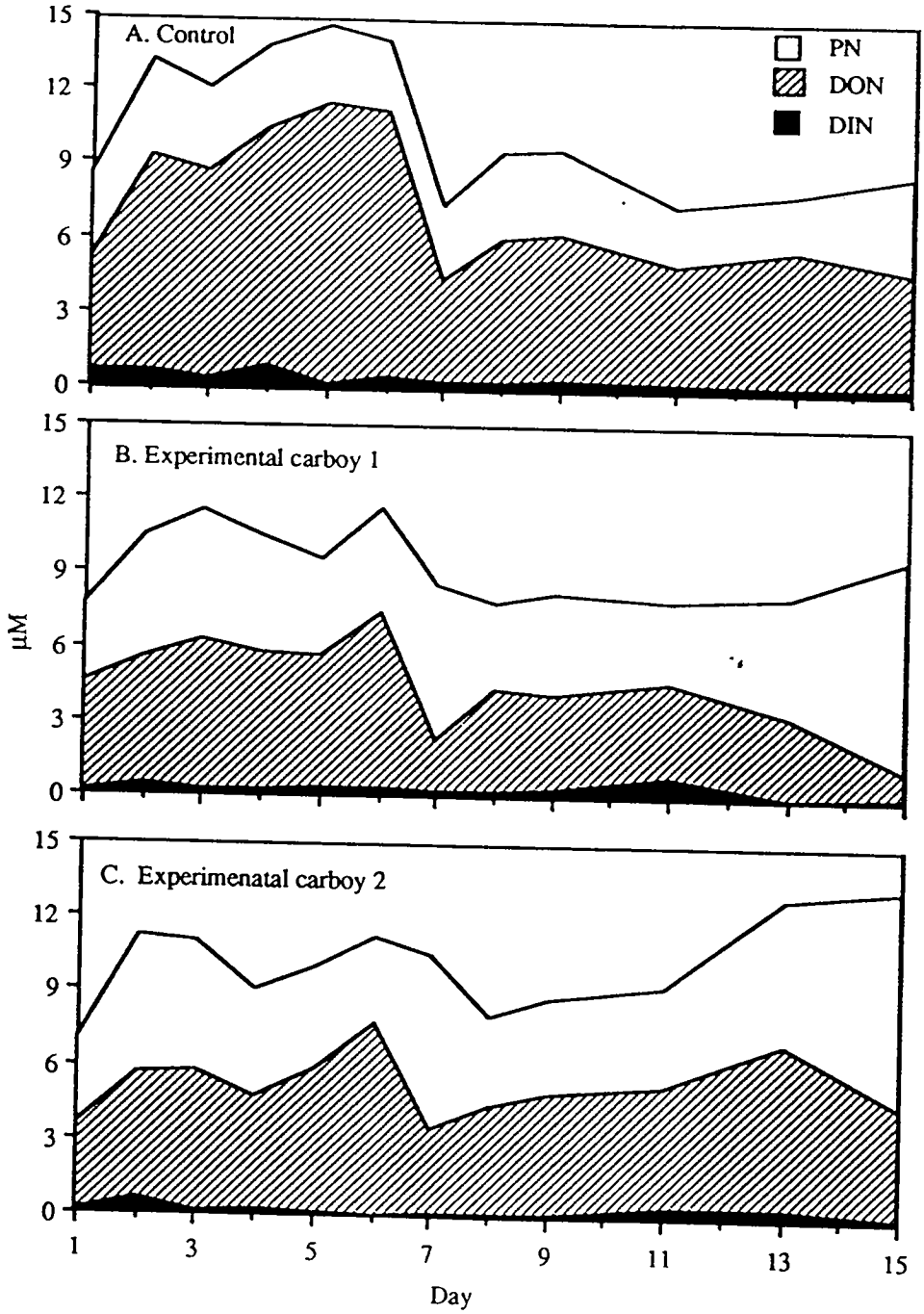


Figure 3.5 Temporal changes in total nitrogen concentration and the relative importance of N species in the control (A) and the experimental carboys with suspended sediment (B& C) during the trial 1.2, using outer shelf sediment from site OS5. In this trial, 7.8 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

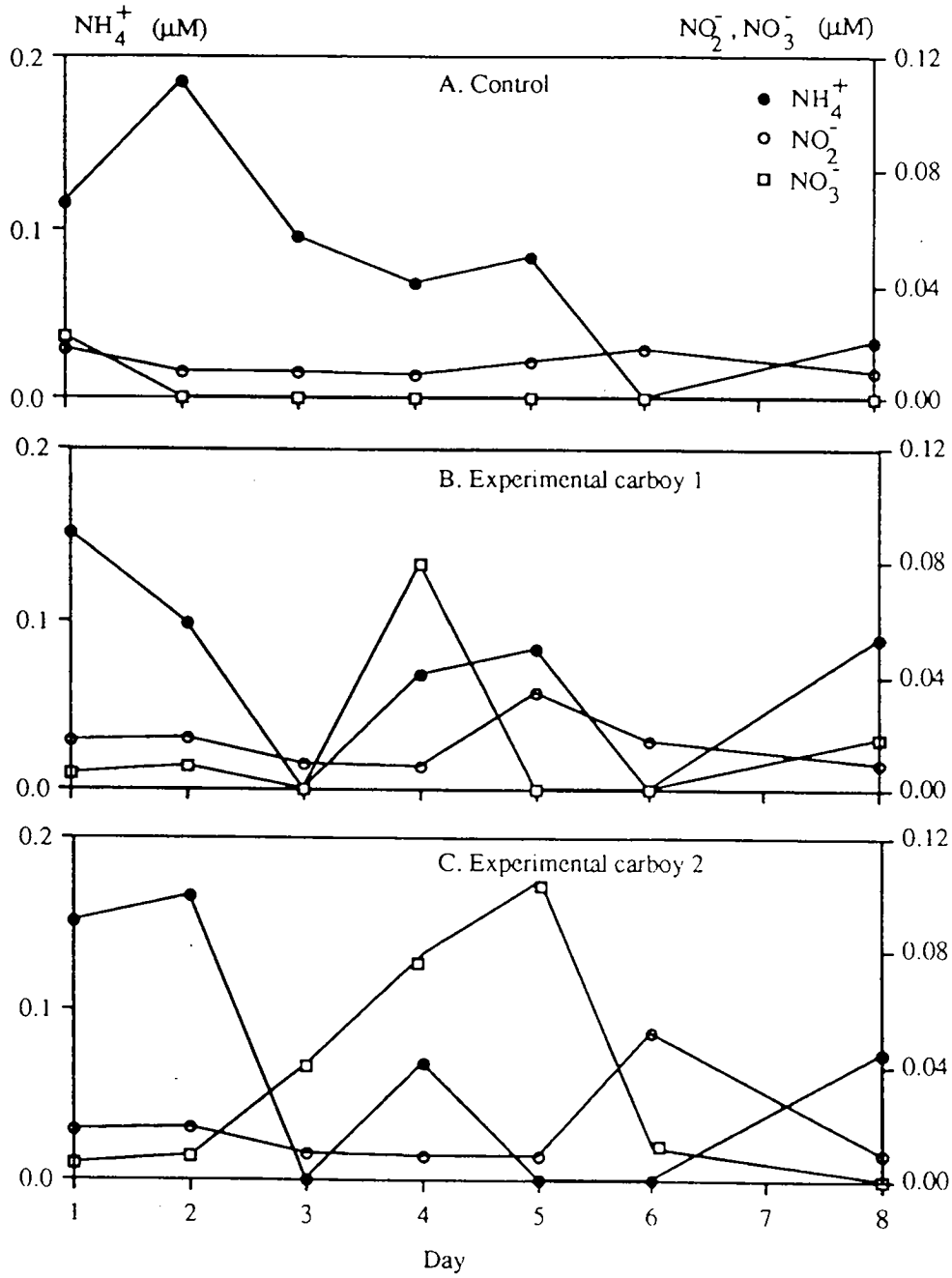


Figure 3.6 Temporal changes of DIN species (NH_4^+, NO_2^- and NO_3^-) in the control (A) and experimental carboys with suspended sediment (B & C) during the trial 1.2, using outer shelf sediment from site OS5. Note that the vertical scales of the graphs are expanded from Figure 3.5.

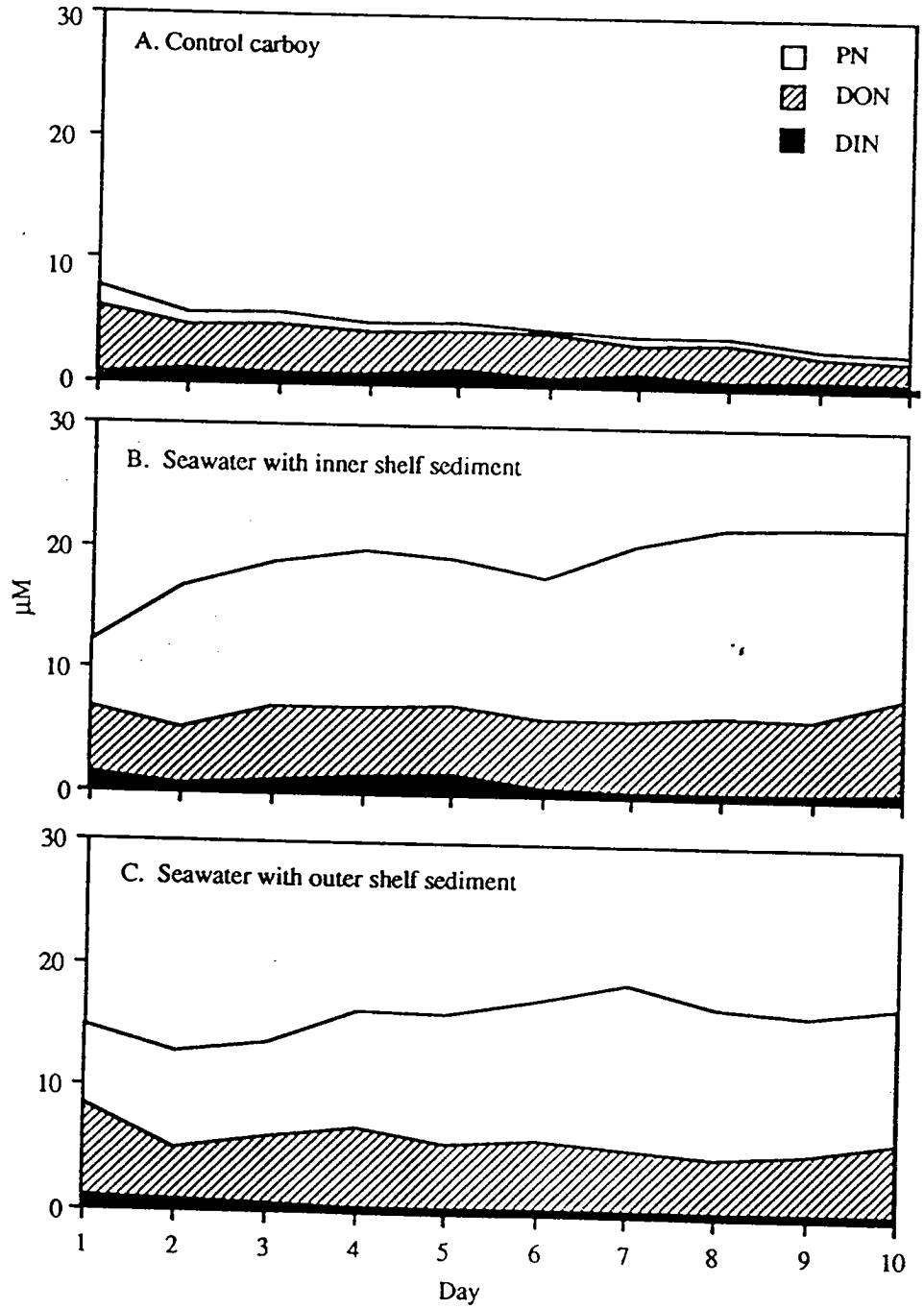


Figure 3.7 Temporal changes in total nitrogen concentration and the relative importance of N species in the control (A) and the experimental carboys with suspended sediment from the inner shelf site IS3 (B) and the outer shelf site OS3 (C) during the trial 1.3. In this trial, 24.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

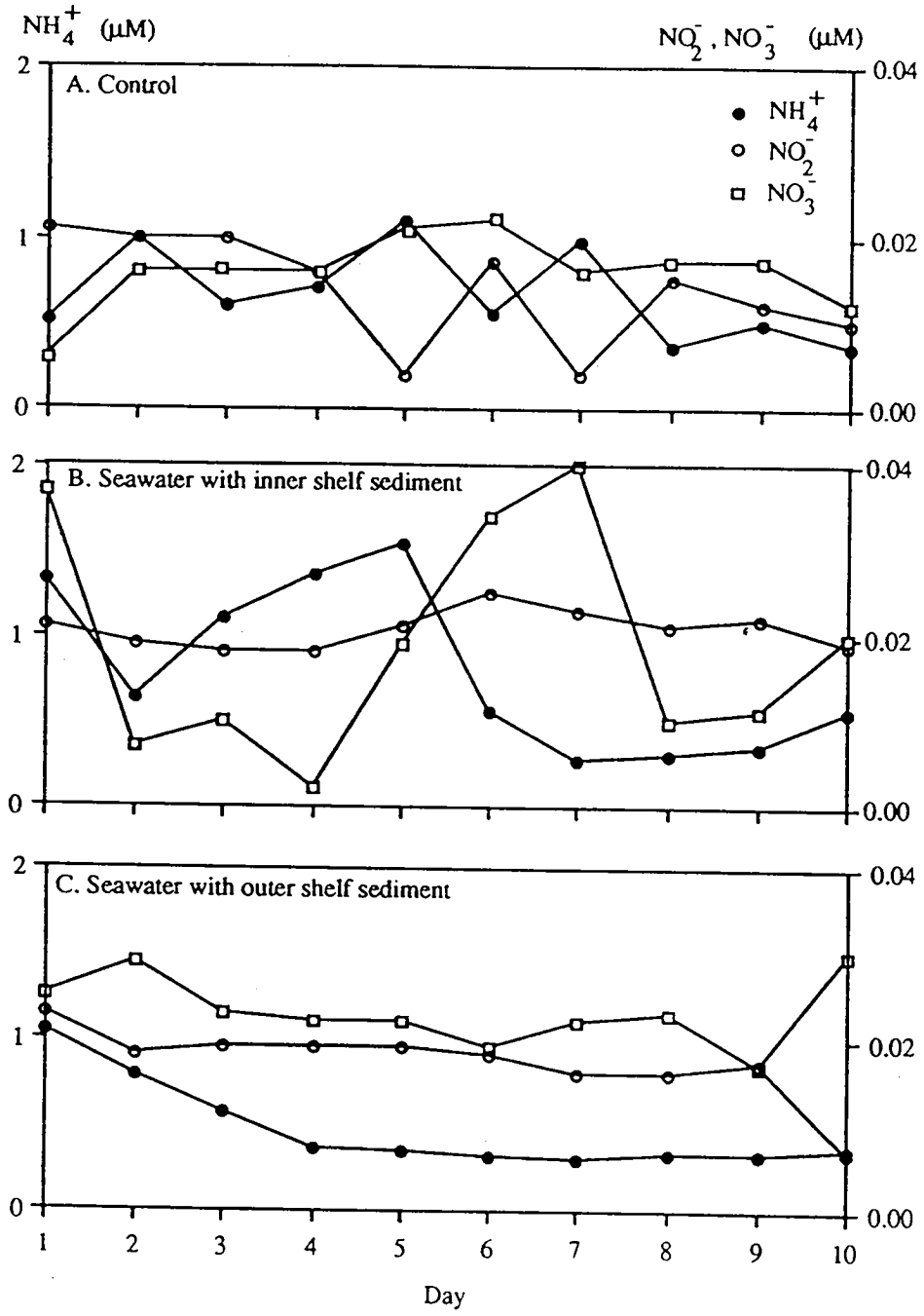


Figure 3.8 Temporal changes of DIN species (NH_4^+, NO_2^- and NO_3^-) in the control (A) and experimental carboys with sediment from the inner shelf site IS3 (B) and with outer shelf site OS3 (C) during the trial 1.3. Note that the vertical scales of the graphs are expanded from Figure 3.7.

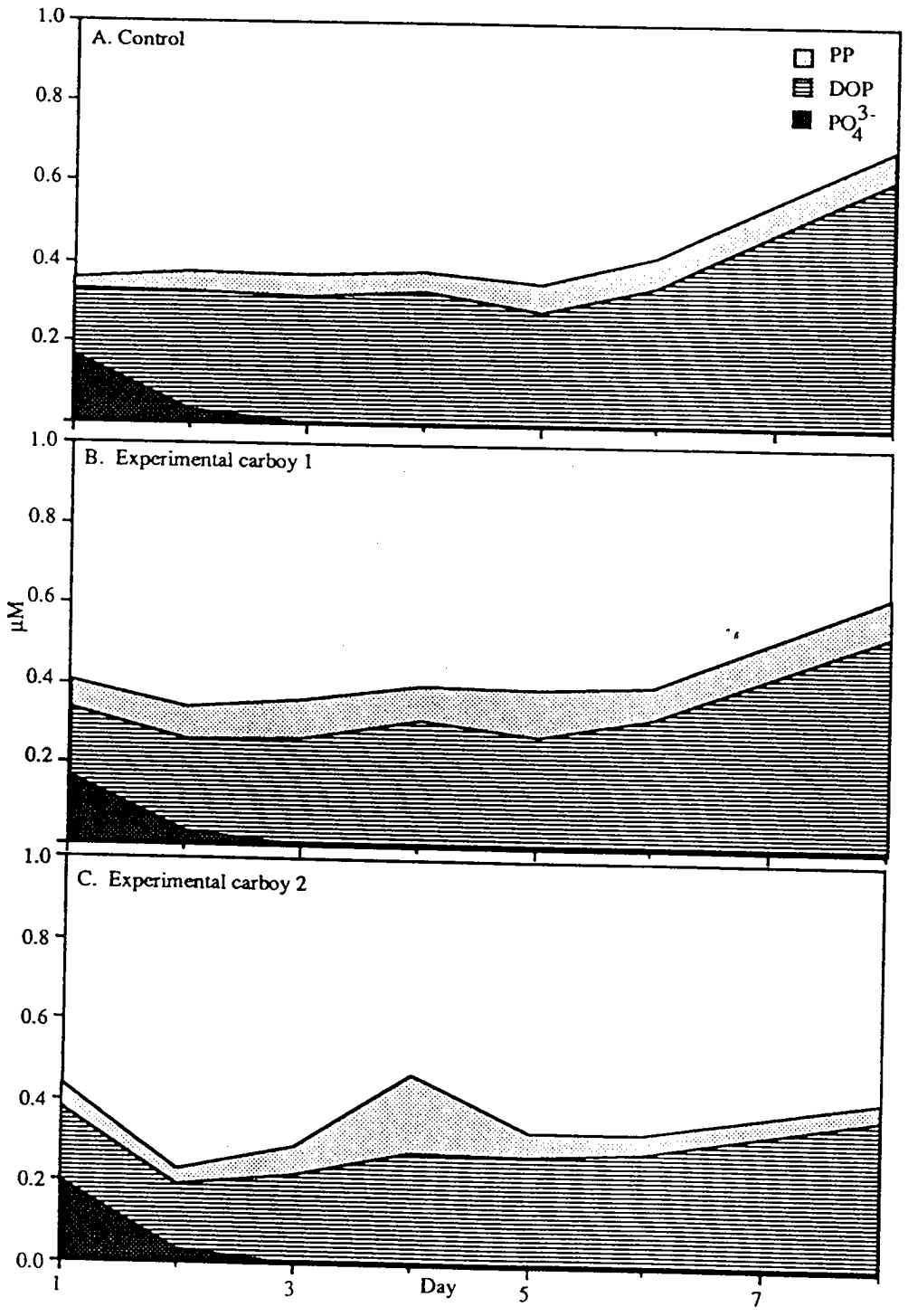


Figure 3.9 Temporal changes in phosphorus concentrations in the control (A) and the experimental carboys with suspended sediment (B& C) during the trial 1.1, using mid-shelf sediment from site MS1. In this trial, 10.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

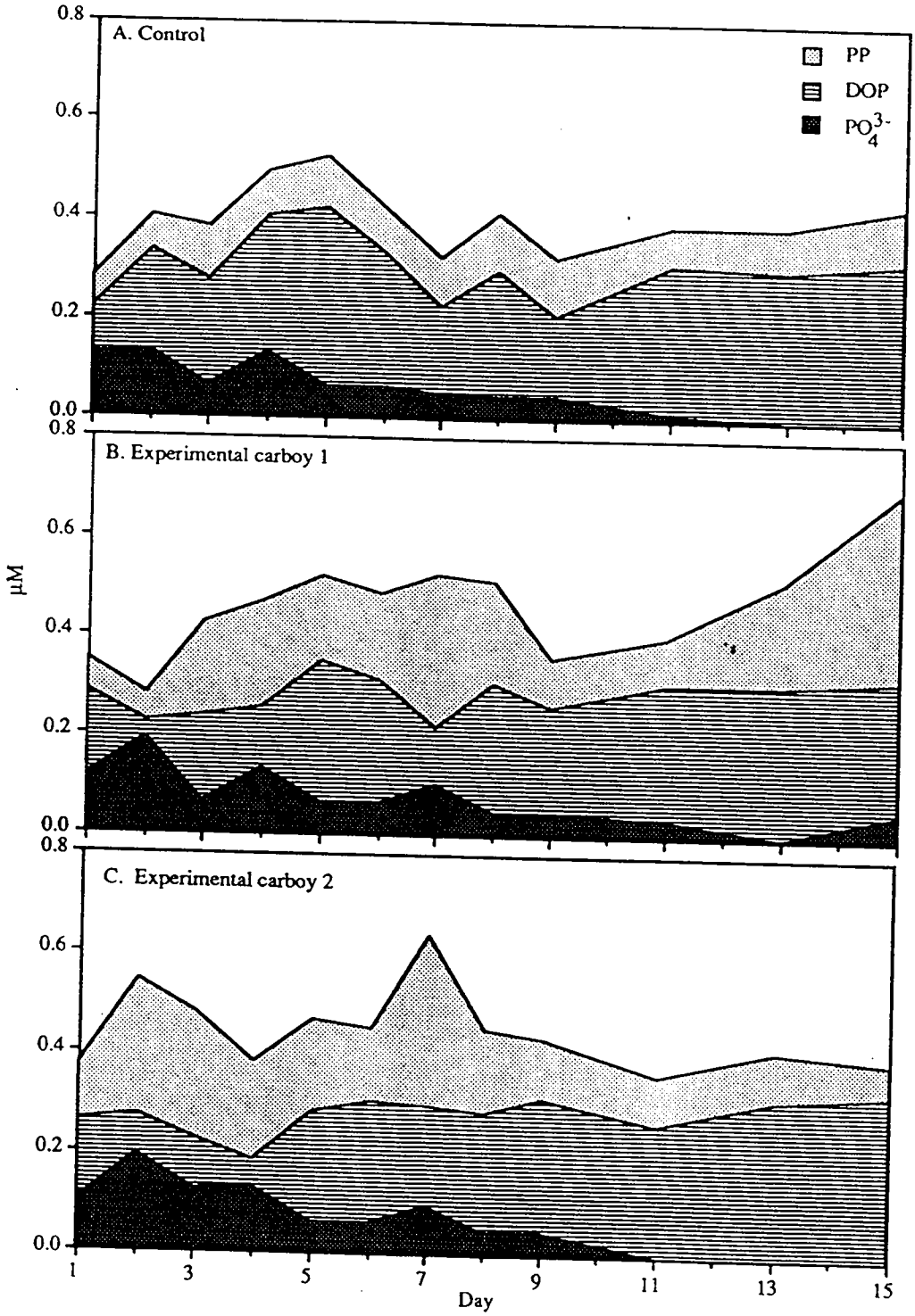


Figure 3.10 Temporal changes in phosphorus concentrations in the control (A) and the experimental carboys with suspended sediment (B& C) during the trial 1.2, using outer shelf sediment from site OS5. In this trial, 7.8 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

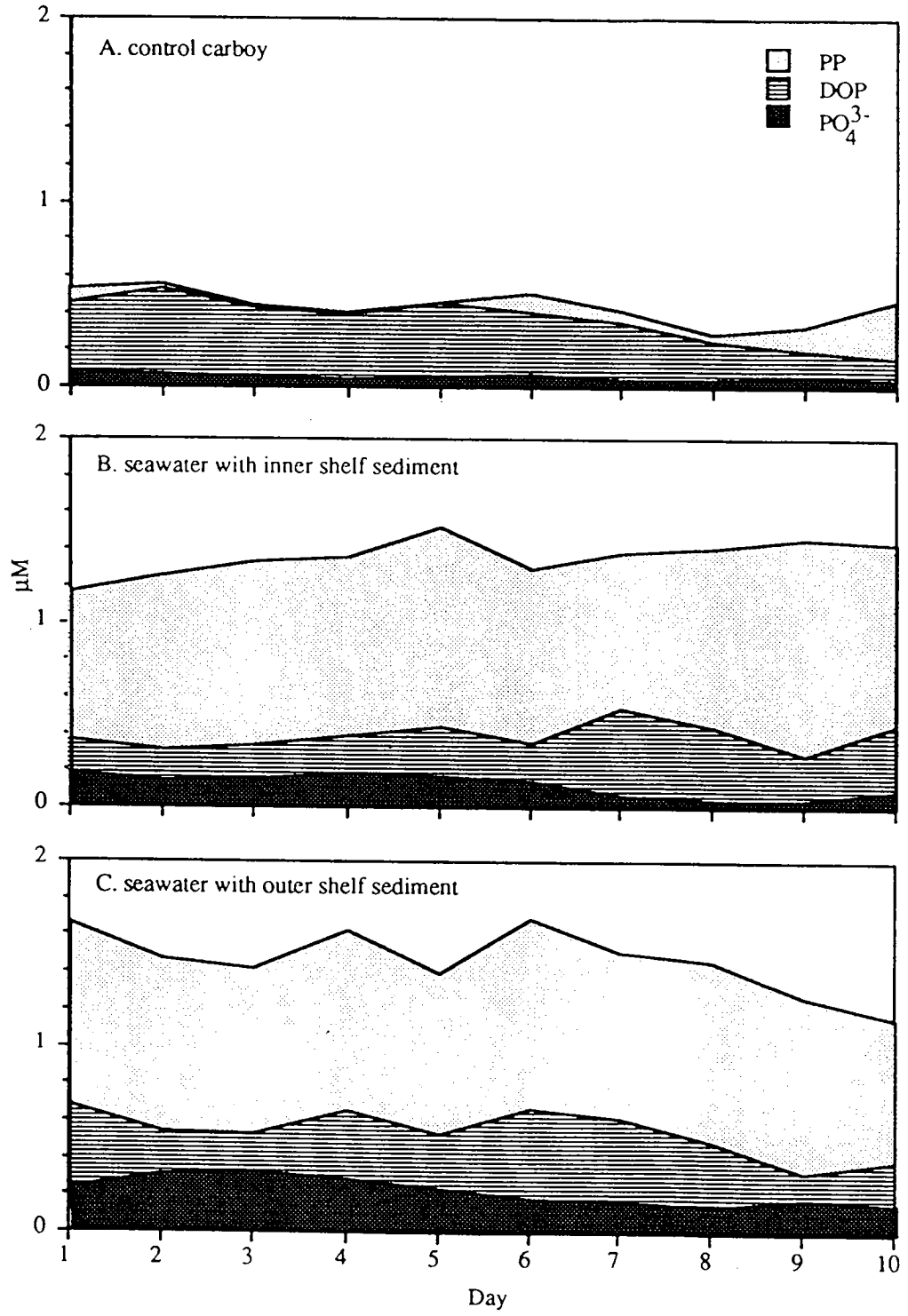


Figure 3.11 Temporal changes in phosphorus concentrations in the control (A) and the experimental carboys with sediment from the inner shelf site IS3 (B) and outer shelf site OS3 (C) during the trial 1.3. In this trial, 24.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

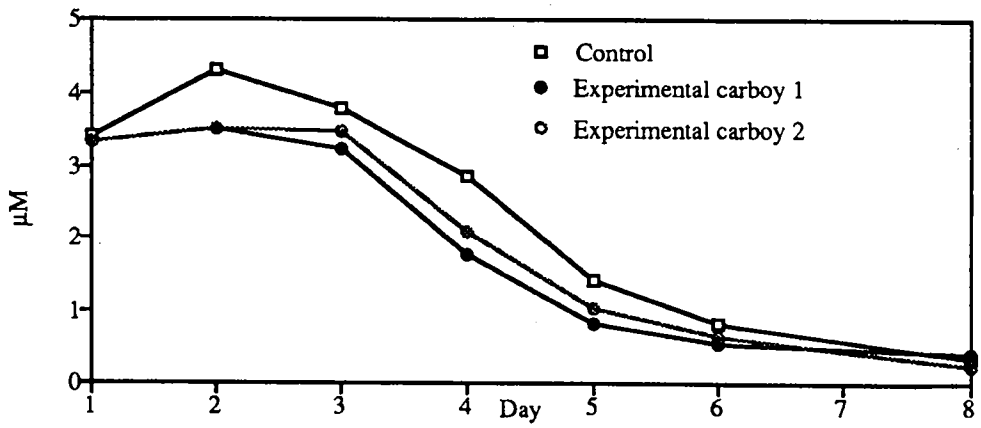


Figure 3.12 Temporal change in silicate concentrations in control and experimental carboys during trial 1.1 using mid-shelf sediment from site MS1. In this trial, 10.3 grams wet weight of sediment was added in each of the experimental carboys.

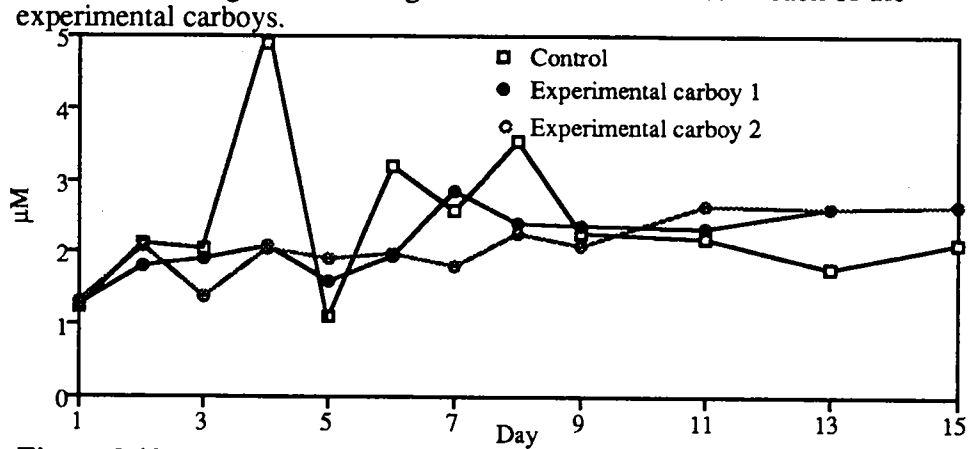


Figure 3.13 Temporal change in silicate concentrations in control and experimental carboys during trial 1.2 using outer shelf sediment from site OS5. In this trial, 7.8 grams wet weight of sediment was added in each of the experimental carboys.

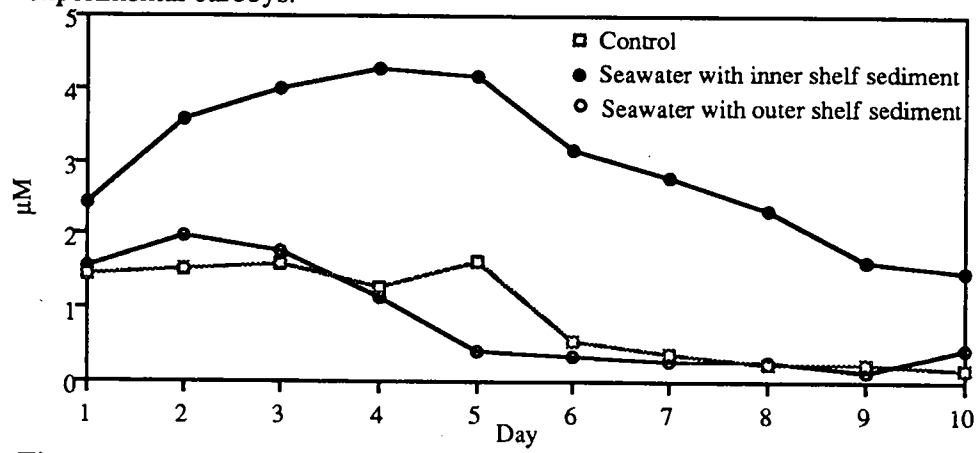


Figure 3.14 Temporal change in silicate concentrations in control and experimental carboys during trial 1.3 using inner shelf sediment from site IS3 and outer shelf sediment from site OS3. In this trial, 24.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

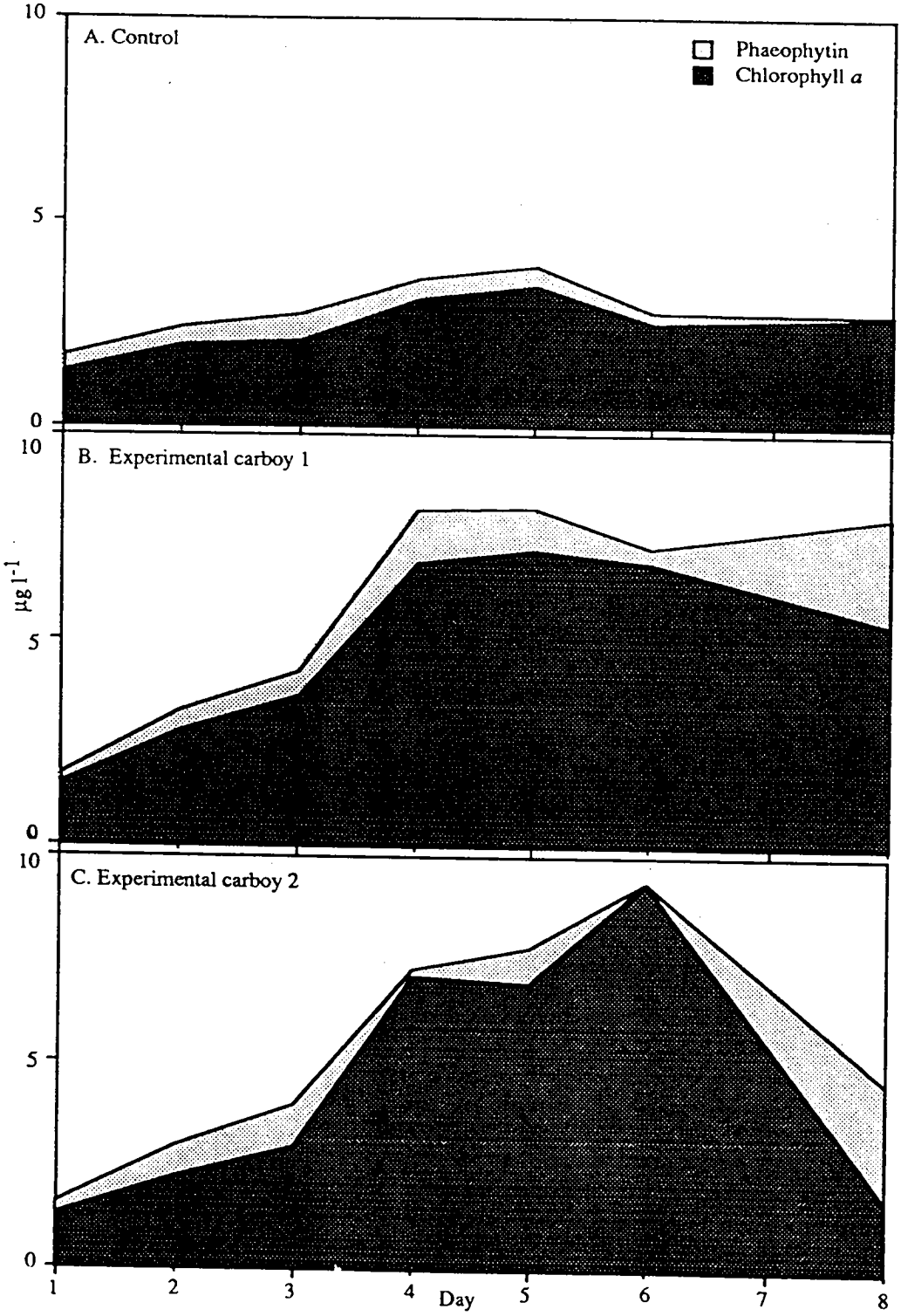


Figure 3.15 Temporal changes in chlorophyll *a* and phaeophytin concentrations in the control (A) and experimental carboys (B & C) during trial 1.1, using mid-shelf sediment from site MS1. In this trial 10.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

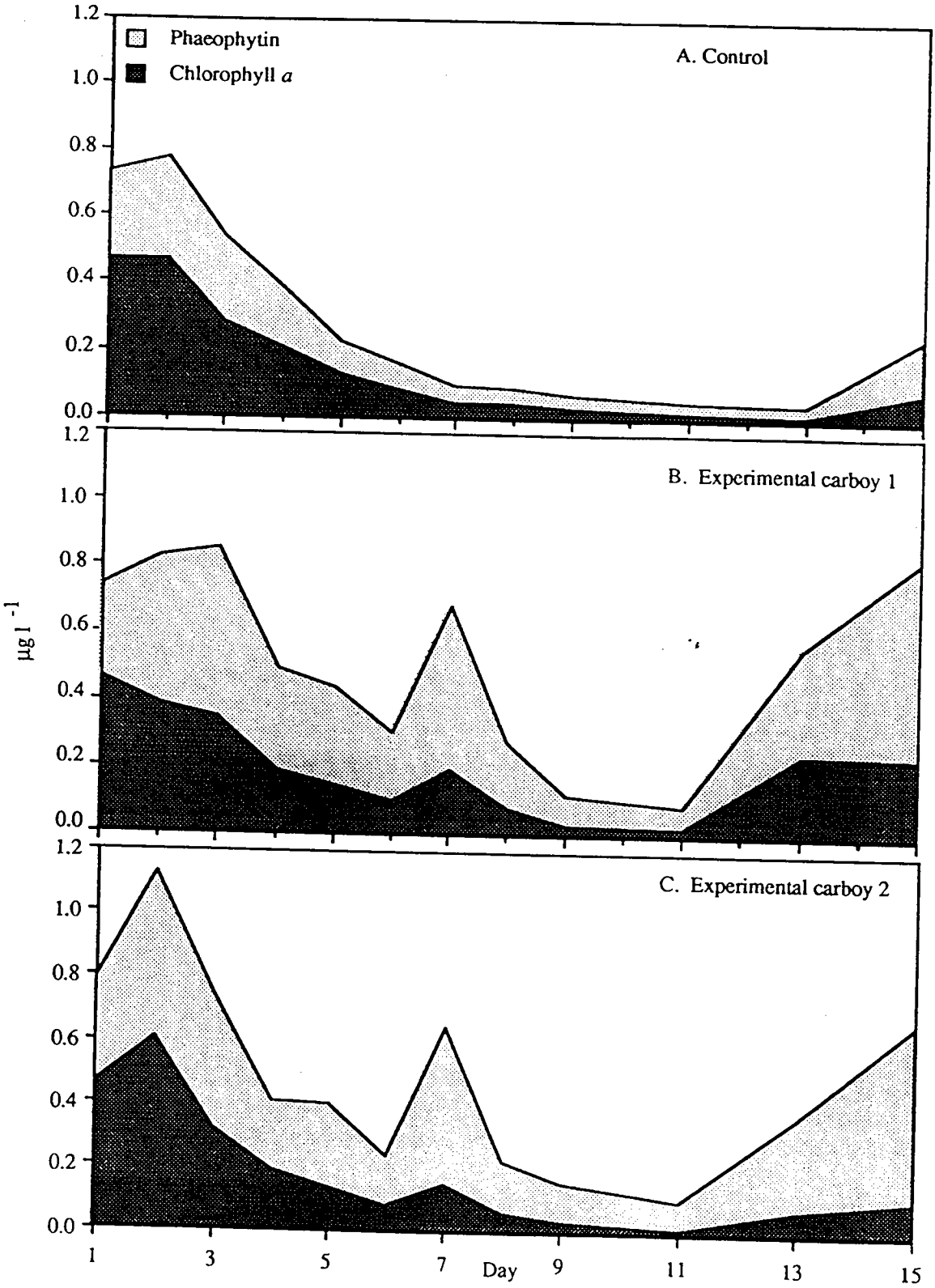


Figure 3.16 Temporal change in chlorophyll *a* and phaeophytin concentrations in the control (A) and experimental carboys (B &C) during trial 1.2, using outer shelf sediment from site OS5. In this trial, 7.8 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

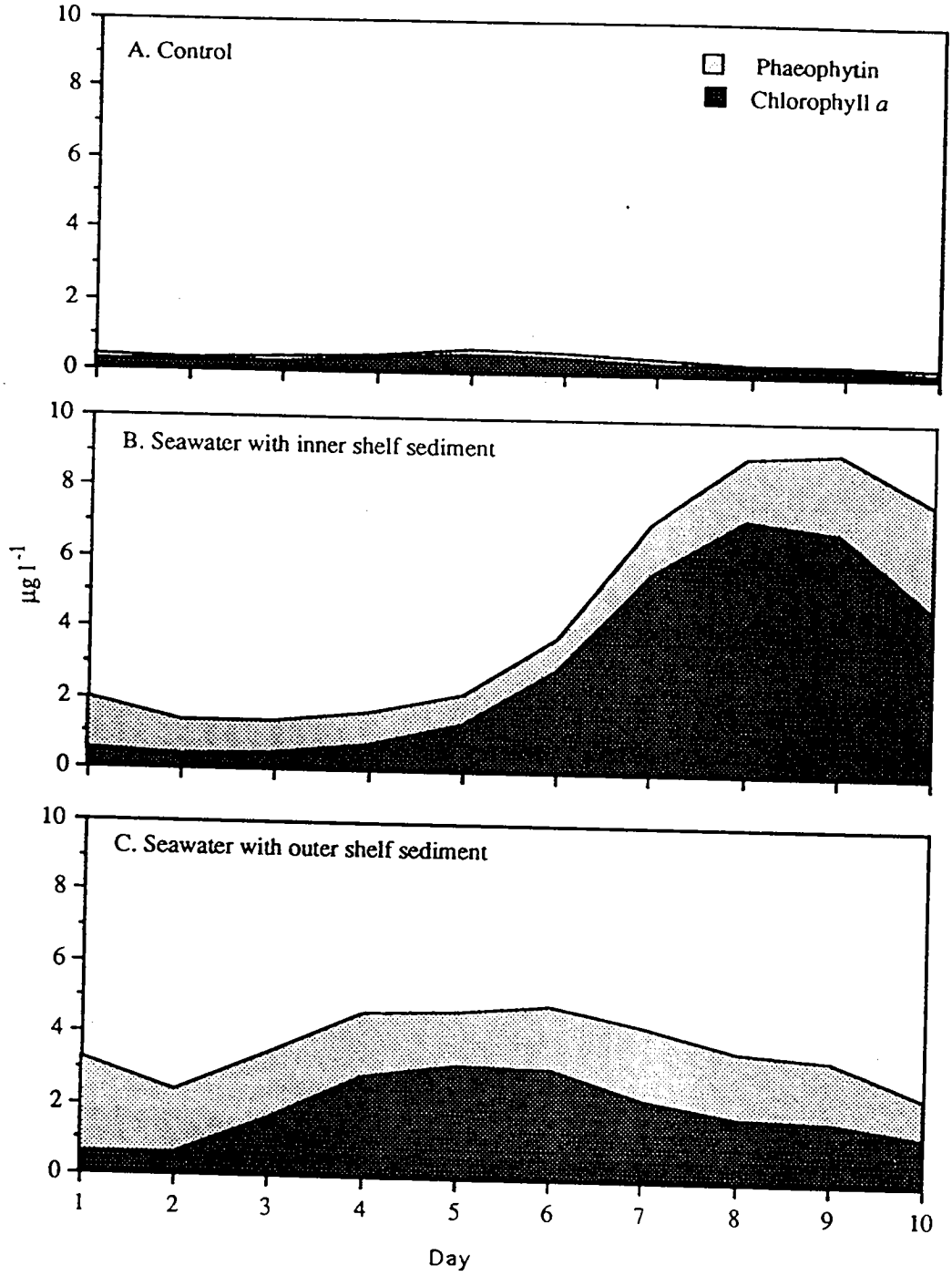


Figure 3.17 Temporal change in chlorophyll *a* and phaeophytin concentrations in the control (A) and experimental carboys with sediment from inner shelf site IS3 (B) and outer shelf site OS3 (C) during trial 1.3. In this trial 24.3 grams wet weight of sediment was added to 20 litres of seawater in each of the experimental carboys.

3.3.2 EXPERIMENT 2: Relationships between wet sediment mass and amounts of nutrients promptly released from resuspended inner and outer shelf sediments.

The objectives of this experiment were to determine the relationships between the amounts of nutrients promptly released during a sediment resuspension event and the mass of sediment resuspended. If there were, were there different sediment mass-prompt nutrient release relationships between inner and outer shelf sediments? The experimental design is shown schematically in Figure 3.18.

a. Experimental design

Sediment samples used in this experiment were collected at inner (IS2, IS3, IS4) and outer shelf (OS2, OS3, OS4) sites (Figure 2.1 & Table 2.1). A cut-off plastic syringe was used as a piston corer to collect replicate sediment subsamples of different volume from Smith-MacIntyre grab samples at each site (approximately : 1, 2, 3, and 4 ml). The sediment subsamples were stored frozen in pre-weighed glass vials. Each wet sediment subsample was re-weighed and then mixed with two litres of screened (20 μm mesh size) mid-shelf seawater in a 2-litre polycarbonate bottle (Nalge, USA). After thorough mixing, two water samples were taken from each bottle for chemical analysis of nutrient concentrations. Subsamples taken for measurement of chl *a* and phaeophytin concentrations were analysed immediately. After initial filtration, the water samples were stored frozen until analysis. Water samples from control bottles (no sediment added) were also collected, processed and analysed in parallel.

b. Data analysis

The relationships between the amounts of nutrients released and sediment mass resuspended were evaluated by regression analysis (Montgomery and Hines, 1990; Analytical software, 1990). The regression procedure was performed for each individual nutrient species. The analysis was used to determine whether the magnitude of prompt nutrient release was related to the weight of either inner or outer shelf sediment, and to assess whether the slopes of any significant relationships differed between sediment types. If there was no significant differences between slopes and/or intercepts ($\underline{P} > 0.05$) for the two sediment types, data from the inner and outer shelf sediment sites were pooled.

Fitted values from regressions were plotted against standardized residuals to check that the

data were normally distributed. From inspection of these plots, the data were found to be normally distributed, obviating the need for transformation.

c. Results

Relationship between suspended solid concentrations and sediment weight.

Concentrations of suspended solids in experimental bottles were directly correlated to the weight of added sediment (Figure 3.19). Suspended solid concentrations created per gram wet weight of outer shelf sediment (158 mg l^{-1} g^{-1}) were significantly greater ($P < 0.05$) than that produced from inner shelf sediment (69 mg l^{-1} g^{-1}).

Relationships between prompt nitrogen release and sediment weight.

There were significant positive relationships between the weight of sediment added and the resulting concentrations of total N, PN, TDN and DON measured in experimental bottles (Figure 3.20 A,B,C and D, respectively). On a weight-specific basis, releases of total N, PN, TDN and DON from inner and outer shelf sediments were not significantly different ($P < 0.05$), therefore, regression equations were calculated from the pooled inner and outer shelf data.

There was no positive correlation between the weight of sediment added and resulting concentrations of total DIN ($r^2 = 0.14$), NH_4^+ ($r^2 = 0.17$), $NO_2^- + NO_3^-$ ($r^2 = 0.17$), NO_3^- ($r^2 = 0.07$) or NO_2^- ($r^2 = 0.01$) (Figure 3.20 E,F,G,H,I). Overall, there was little difference between releases from inner and outer shelf sediments. However, mean NH_4^+ concentrations resulting from resuspension of the inner shelf sediment were greater than those from the outer shelf sediment ($P < 0.05$). DIN concentrations were dominated by NH_4^+ releases. Mean NO_3^- releases per gram of inner shelf sediment were slightly higher but not significantly, than those released from outer shelf sediments. Mean NO_2^- concentrations released from both inner and outer shelf sediments were very low and near the detection limit (< 0.02 μM).

Relationship between prompt phosphorus release and sediment weight.

There was a significant positive correlation between weight of sediment added and the resulting concentrations of total P, PP and PO_4^{3-} ($P < 0.05$; Figure 3.21 A,B,C, and E). Inner and outer shelf sediment yielded similar concentrations of total P and PP ($P > 0.05$)

per unit weight. PO_4^{3-} released per unit weight of outer shelf sediment (0.037 μM, Figure 3.21 E) was significantly greater ($\underline{P} < 0.05$) than that derived from inner shelf sediment (0.025 μM). There was a slight positive relationship between TDP concentrations and the weight of inner shelf sediment added ($r^2 = 0.28$) or outer shelf sediment ($r^2 = 0.14$). DOP releases did not appear to relate to added sediment weight at all ($\underline{P} > 0.05$, Figure 3.21D); however mean DOP concentrations (0.206 μM) in water to which inner shelf sediments were added, were greater (but not significantly) than those to which outer shelf (0.115 μM) sediment was added ($\underline{P} < 0.05$).

Relationships between prompt silicate release and sediment weight.

There was a positive linear relationship between $Si(OH)_4$ concentration and weight of sediment added from outer shelf sites, while only a small positive slope was found arising from inner shelf sediment ($\underline{P} < 0.05$, Figure 3.22). However, overall releases of $Si(OH)_4$ from inner shelf sediment were of greater magnitude than those from outer shelf sediment ($\underline{P} < 0.05$).

Relationship between chlorophyll a, phaeophytin release and sediment weight.

The release of chlorophyll *a* plus phaeophytin (hereafter referred to as total pigments) was correlated with the weight of sediment added for outer shelf sediment but not inner shelf sediment (Figure 3.23 A). There was little relationship between added sediment weight and the concentration of chl *a* ($r^2 = 0.18$, Figure 3.23 B). Phaeophytin, however, was correlated with added sediment weight (Figure 3.23 C). Weight-specific phaeophytin releases for inner shelf sediment were significantly greater than outer shelf sediment ($\underline{P} > 0.05$). The linear relationship found for total pigments resulted therefore, mostly from the phaeophytin released.

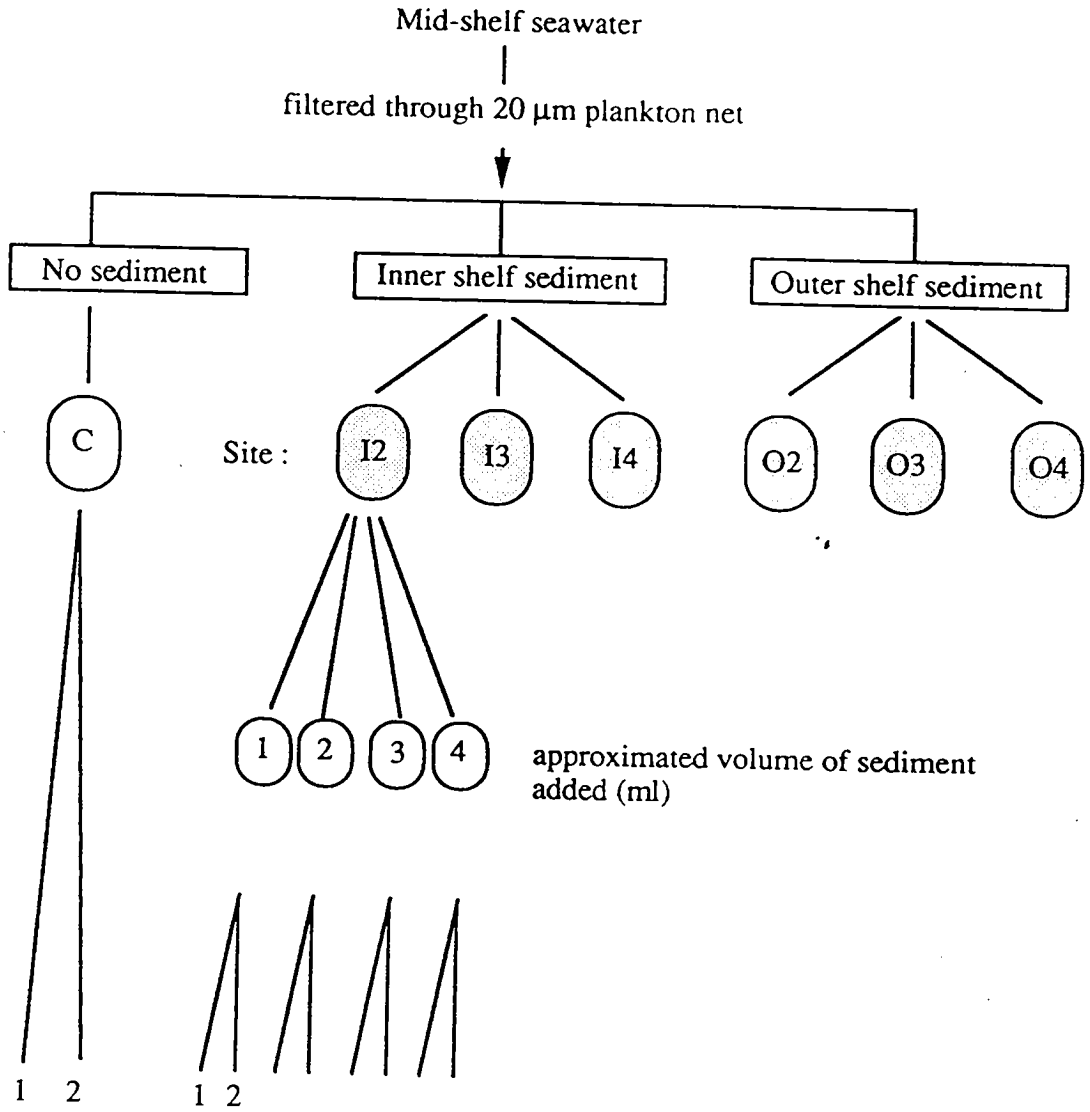


Figure 3.18 Schematic design for experiment 2: relationships between wet sediment mass and amounts of nutrient released from resuspended inner and outer shelf sediment.

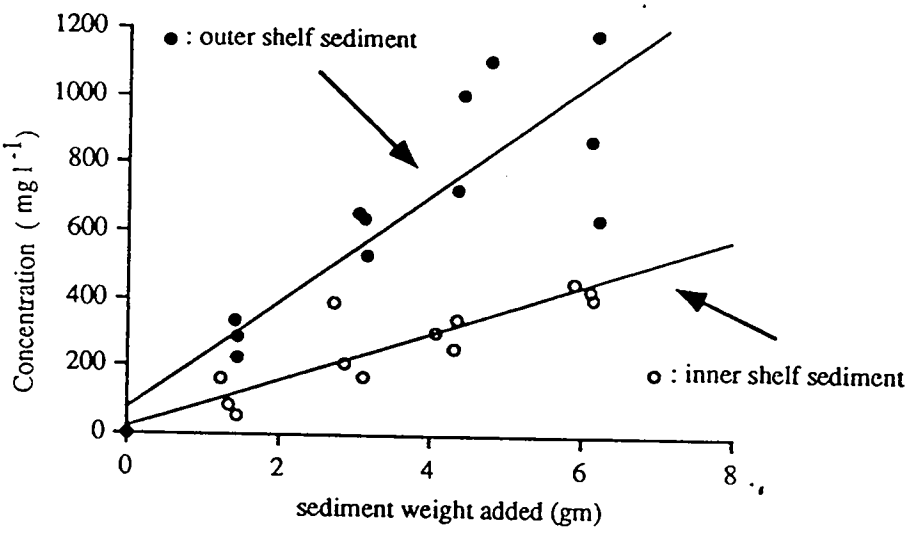


Figure 3.19 Relationships between suspended solid concentrations measured in 2 litres of seawater and the mass of sediment resuspended.

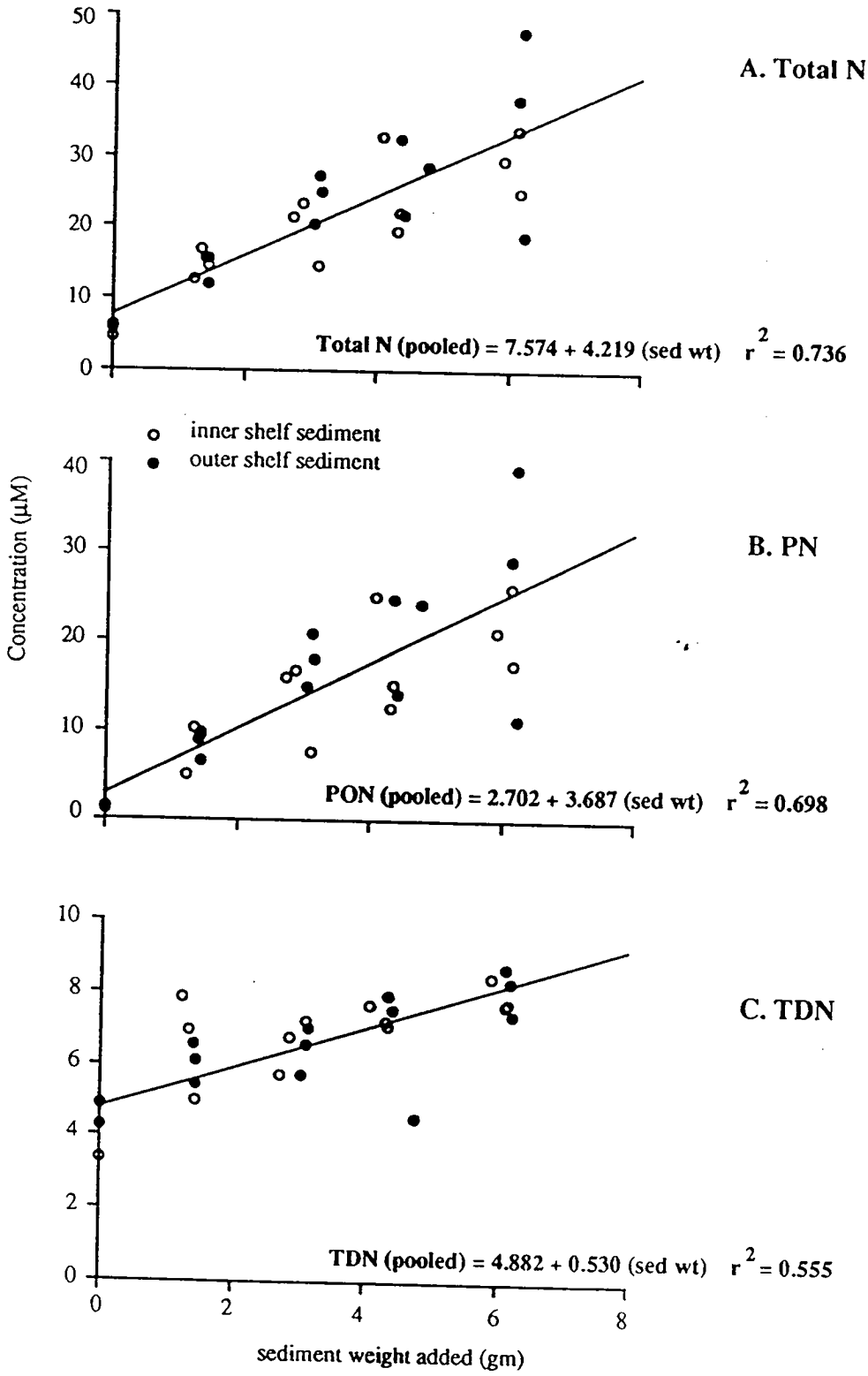


Figure 3.20A, B, C Relationships between concentrations of total N (A), PN (B) and TDN (C) measured in 2 litres of seawater and the mass of sediment resuspended.

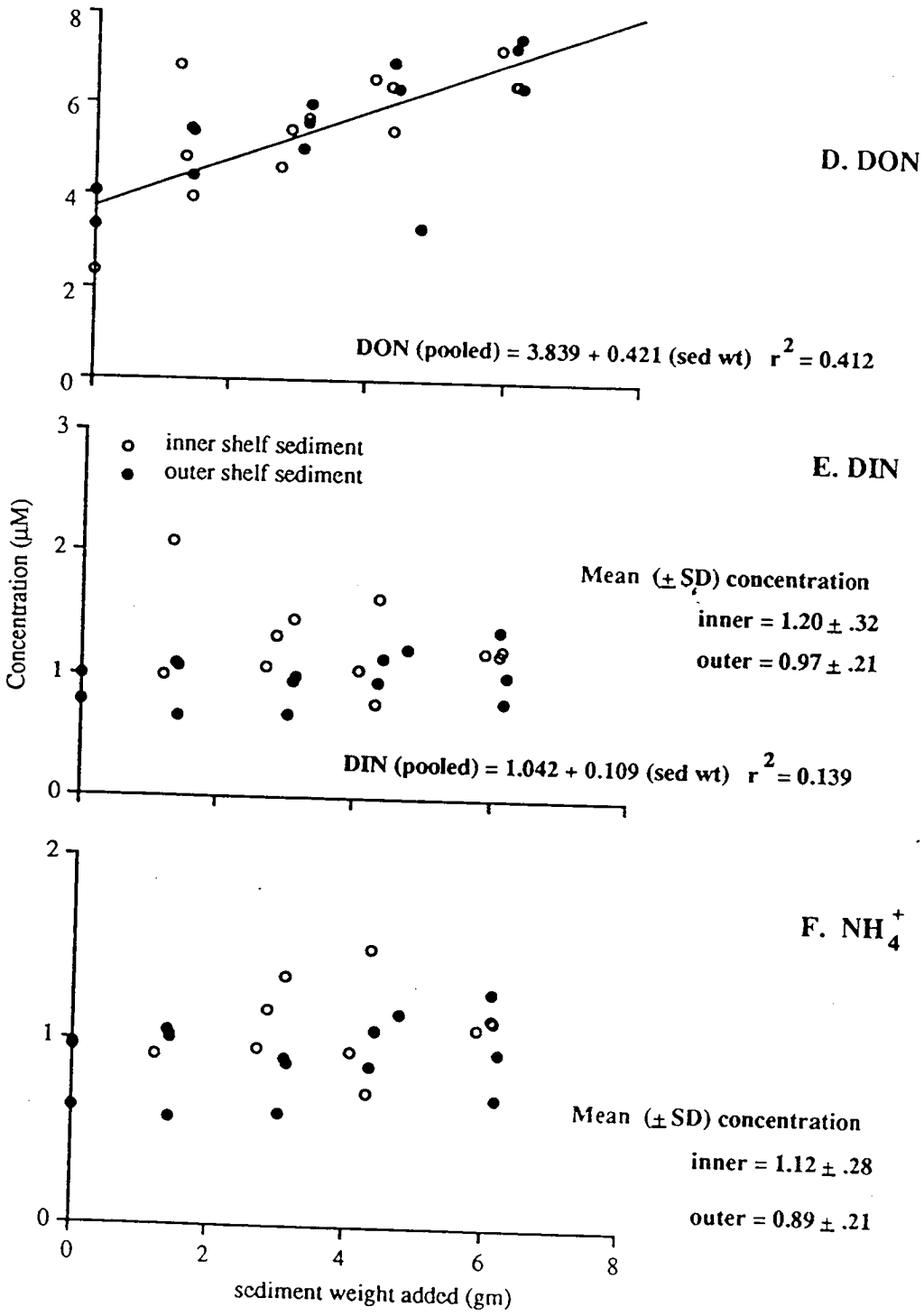


Figure 3.20D, E, F Relationships between concentrations of DON (D), DIN (E) and NH_4^+ (F) measured in 2 litres of seawater and the mass of sediment resuspended.

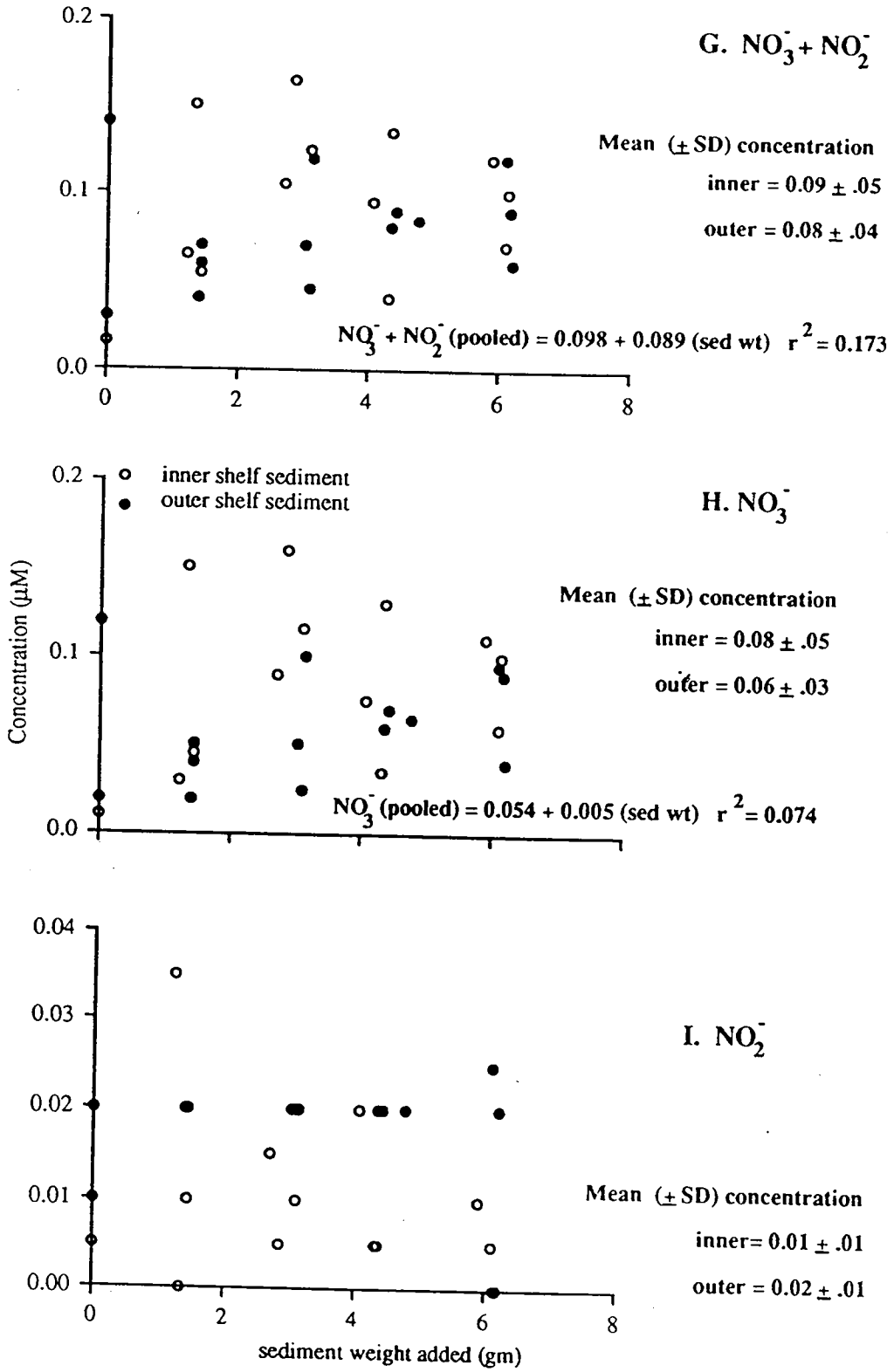


Figure 3.20G, H, I, Relationships between concentrations of $NO_3^- + NO_2^-$ (G), NO_3^- (H) and NO_2^- (I) measured in 2 litres of seawater and the mass of sediment resuspended.

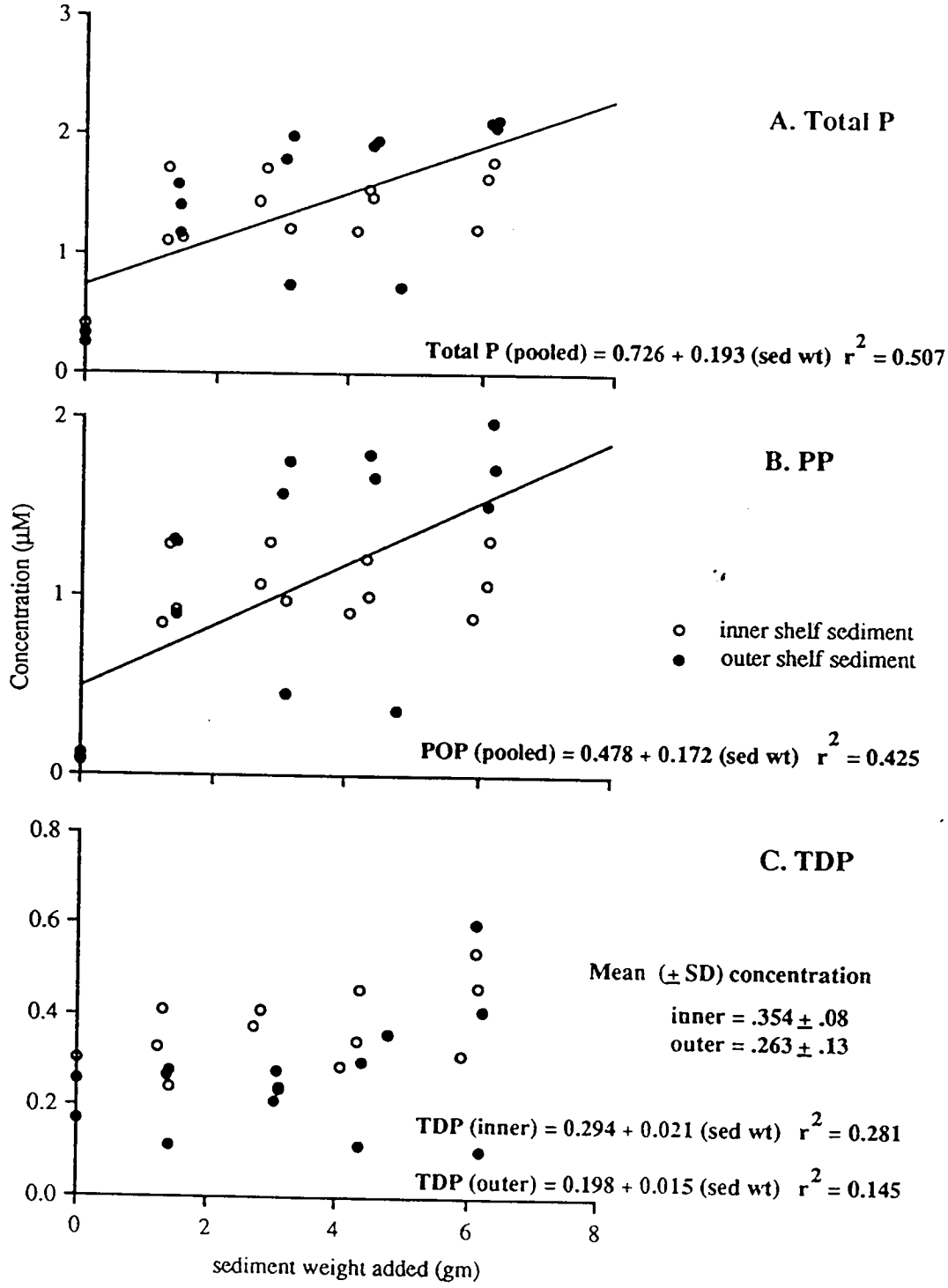


Figure 3.21A, B, C Relationships between concentrations of total P (A), PP (B) and TDP (C) measured in 2 litres of seawater and the mass of sediment resuspended.

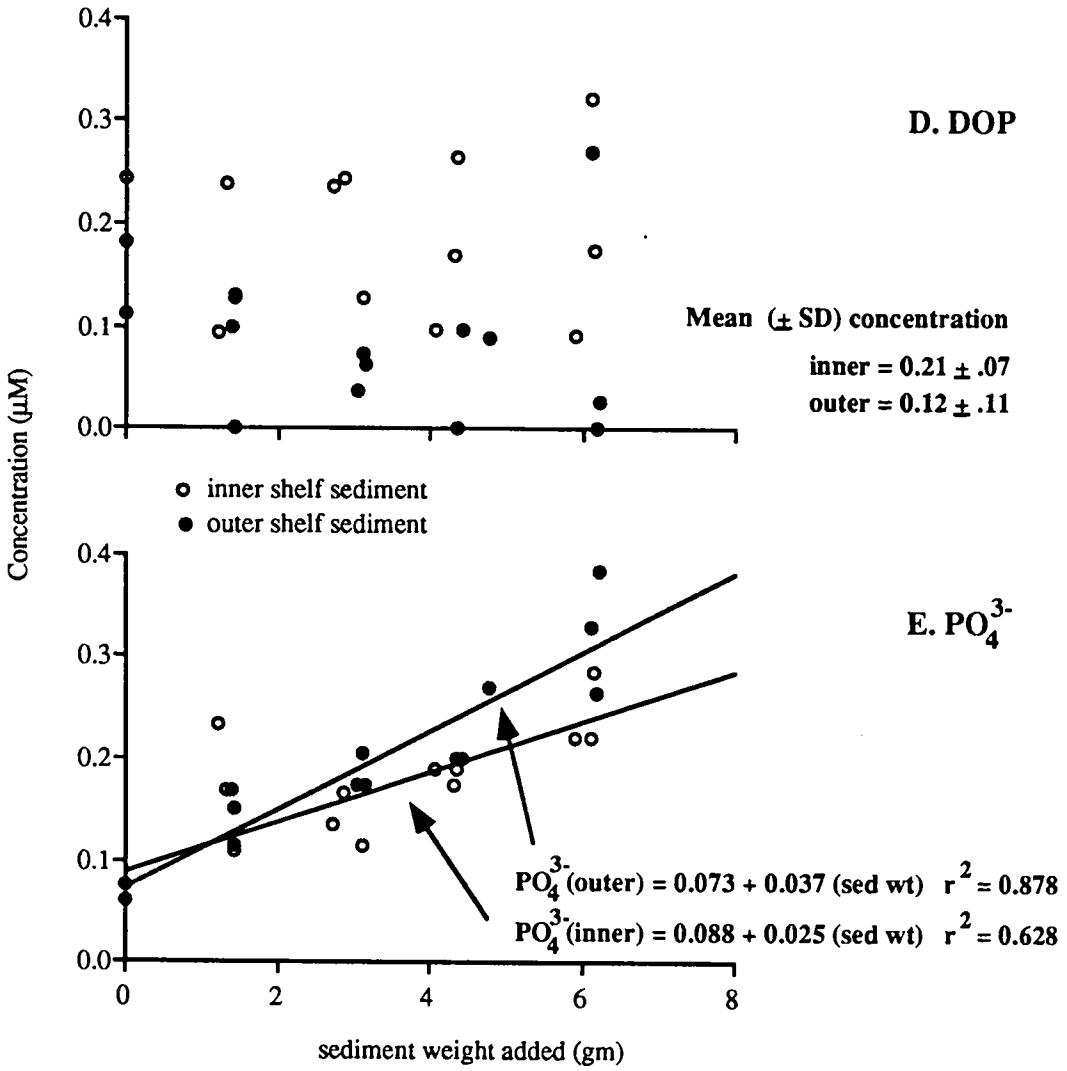


Figure 3.21D,E Relationships between concentrations of DOP (D) and PO_4^{3-} (E) measured in 2 litres of seawater and the mass of sediment resupended.

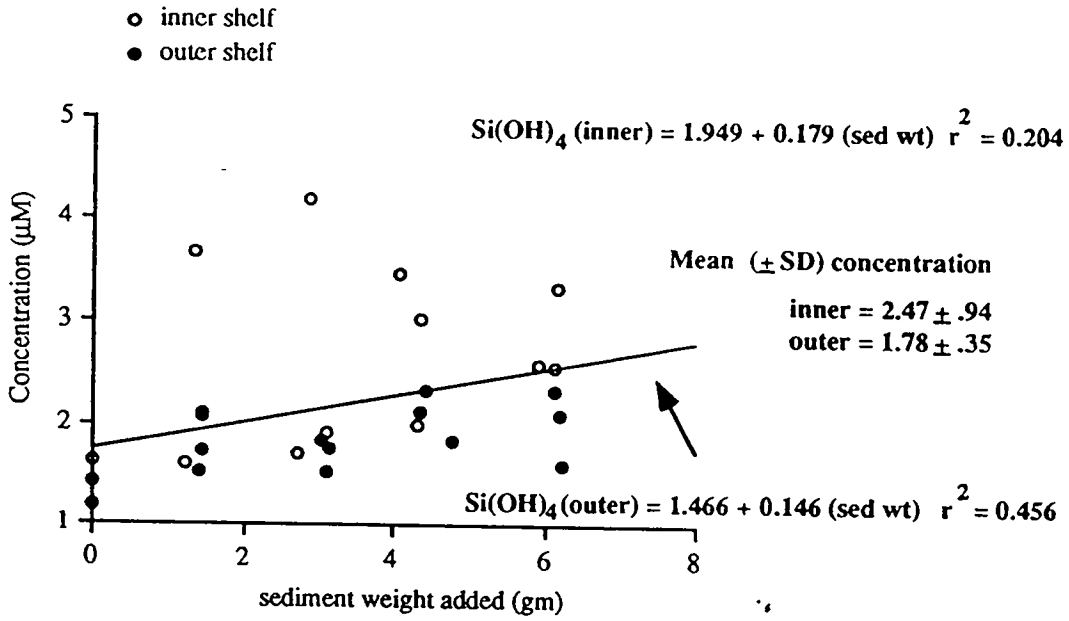


Figure 3.22 Relationship between concentrations of $Si(OH)_4$ measured in 2 litres of seawater and the mass of sediment resuspended. The regression line shown only applies to outer shelf data. No relationship was found for inner shelf data.

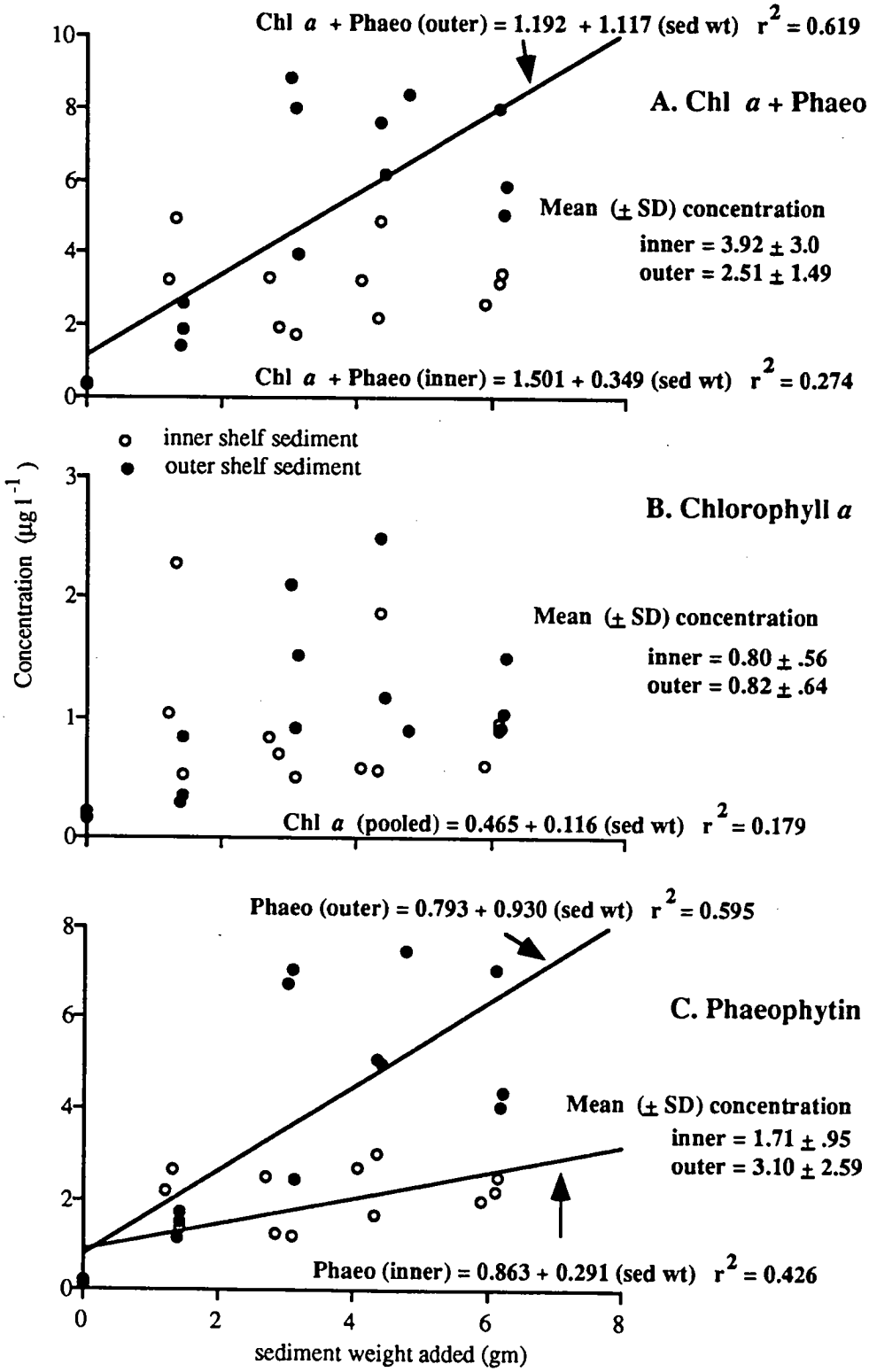


Figure 3.23 Relationships between concentrations of chlorophyll *a* + phaeophytin (A), chlorophyll *a* (B) and phaeophytin (C) measured in 2 litres of seawater and the mass of sediment resuspended.

3.3.3 EXPERIMENT 3: Variability of measured nutrient releases related to sediment and water subsampling.

This experiment was carried out to assess levels of variability associated with sediment and water subsampling. In order to detect whether regional differences in nutrient release attributable to inner (terrigenous) and outer shelf (carbonate) sediment types, levels of local geographical and methodological variability must be resolved. Nutrient concentrations derived from resuspension of sediment were compared between controls and experimental seawater (suspended sediment added) at time intervals of one and nine days after a simulated experimental resuspension event, and between the amount of nutrients released from sediment collected at inner and outer shelf sites.

a. Experimental design

The experimental design used to resolve this variability is shown schematically in Figure 3.24. Sediment was collected from sites on the inner (IS1) and outer shelf (OS1; Table 2.1 & Figure 2.1). On the first day of the experiment (called "Day 1"), 1.5 litres of seawater collected from a mid shelf site (Table 2.1 & Figure 2.1) was added to each of twelve 2-litre polycarbonate bottles (Nalge, USA). This water was pre-filtered through nylon netting (20 μm mesh size). Subsamples of inner shelf (n = 4) and outer shelf (n = 4) sediment were added to individual bottles. No sediment was added to the four bottles (control). The water in all bottles was then mixed by shaking. After mixing, two 700 ml water subsamples were taken from two bottles containing inner shelf sediment, two bottles containing outer shelf sediment and two controls. The remaining six bottles were put onto a shaker in a controlled temperature room (27° C) and kept mixed until the ninth day of the experiment (Figure 3.25). At this time, two 700 ml samples of water were taken from each of the remaining bottles.

b. Data analysis

The significance of differences between the mean amounts of individual nutrient species released from inner and outer shelf sediments was determined by an analysis of variance (4-way nested ANOVA, Analytical software, 1990) (Appendix I-1). Because the results of the previous experiment showed that a variety of relationships can exist between the magnitude of prompt nutrient release and resuspended sediment mass, adjustments were made for the weight of sediment added (range 0.69-0.91 g wet weight) to each bottle. Concentrations of individual nutrient species in individual bottles were normalized by

analysis of covariance relative to the wet weight of sediment added (AOCV, Analytical software, 1990). If the measured nutrient concentrations were significantly related to the differing weights of sediment added ($P < 0.05$), the ANOVA was adjusted for the appropriate covariate(s). If the covariate was not significant ($P > 0.05$), the unadjusted data were used in the ANOVA. The results of the ANOVA and AOCV analyses are given in Appendix I: Tables I-1, I-2, I-3, I-4).

Prior to carrying out the ANOVA procedures, the heteroscedasticity of the data was evaluated using Cochran's C statistic test (Dixon and Massey, 1969, Analytical software, 1990). In some cases, data transformations (square root, logarithm, arcsine) could not make the variance homogenous. In these cases, the residuals were plotted against the fitted values after the ANOVA analysis (Day and Quinn, 1989; G. De'ath; pers. comm.).

Outliers were then removed after careful consideration (Anscombb, 1960) as they probably resulted from errors in the chemical analysis e.g. high concentrations of ammonium (1-3 μM) when most other values were less than 1 μM (Note : ammonium is a likely contaminant).

Sediment source and sampling date were taken as fixed factors while sediment and water subsamples were taken as random factors. The ANOVA analyses compared mean concentrations between treatments (control and seawater with sediment); sampling dates (day 1 and day 9) of the experimental period; sediment subsample within sediment site; and water subsample within the same bottle. Multiple comparison tests (Tukey test, Zar, 1984) were used to carry out *a posteriori* comparisons of mean concentrations across factors found to be significant.

c. Results

Variability of nutrient concentrations due to sediment subsampling and water subsampling

Measured concentrations of TDN, DON, DIN, NH_4^+, PP, TDP, DOP and chl *a* differed significantly between the two water subsamples (Table 3.2), indicating that these nutrient species were not homogenously distributed between the water bottles. Concentrations of NH_4^+, NO_2^-, $Si(OH)_4$ and chl *a* plus phaeophytin (total pigments) were found to be significantly different between two sediment subsamples within individual sediment sites (Table 3.2), suggesting that NH_4^+, NO_2^-, $Si(OH)_4$ and total pigments concentrations are

patchy in sediment samples of such a small size (approximately 2 g).

Comparison of nutrient and chlorophyll concentrations in experimental bottles with concentrations in control bottles.

Nutrient concentrations in control and experimental bottles were compared for the day 1 and day 9 of sampling. On day 1, concentrations of total N, PN, chlorophyll *a*, phaeophytin and total pigments in the experimental bottles as a result of prompt release (with either inner or outer shelf sediment) were significantly higher than those in the control (Figure 3.26; Appendix I: Tables I-2, I-3). After nine days, concentrations of some nutrient species (total N, PN) continued to be higher in the experimental bottles, while chl *a* and phaeophytin did not (Figure 3.27; Appendix I: Table I-3). The lack of a difference for pigments was due to a decline in chl *a* and phaeophytin concentrations in the experimental bottles after 9 days. In a number of cases, concentrations of individual nutrient species were higher in the control than in the experimental bottles on day 1 (NO_3^-, total P, TDP, DOP) or day 9 (DIN, NH_4^+, $NO_3^- + NO_2^-$, NO_2^-), and on both days (TDN, DON). However, only DOP concentrations were found to be significantly higher in the control than that in the experimental bottles (Figure 3.26; Appendix I: Table I-3). The concentrations of NO_2^-, $NO_2^- + NO_3^-$, NH_4^+, DIN, DON, TDN, PP, TDP, PO_4^{3-}, $Si(OH)_4$ in the experimental bottles were not significantly different from those in the control bottles ($\underline{P} > 0.05$, Appendix I: Table I-3).

Nutrient and chlorophyll releases from resuspended inner and outer shelf sediments.

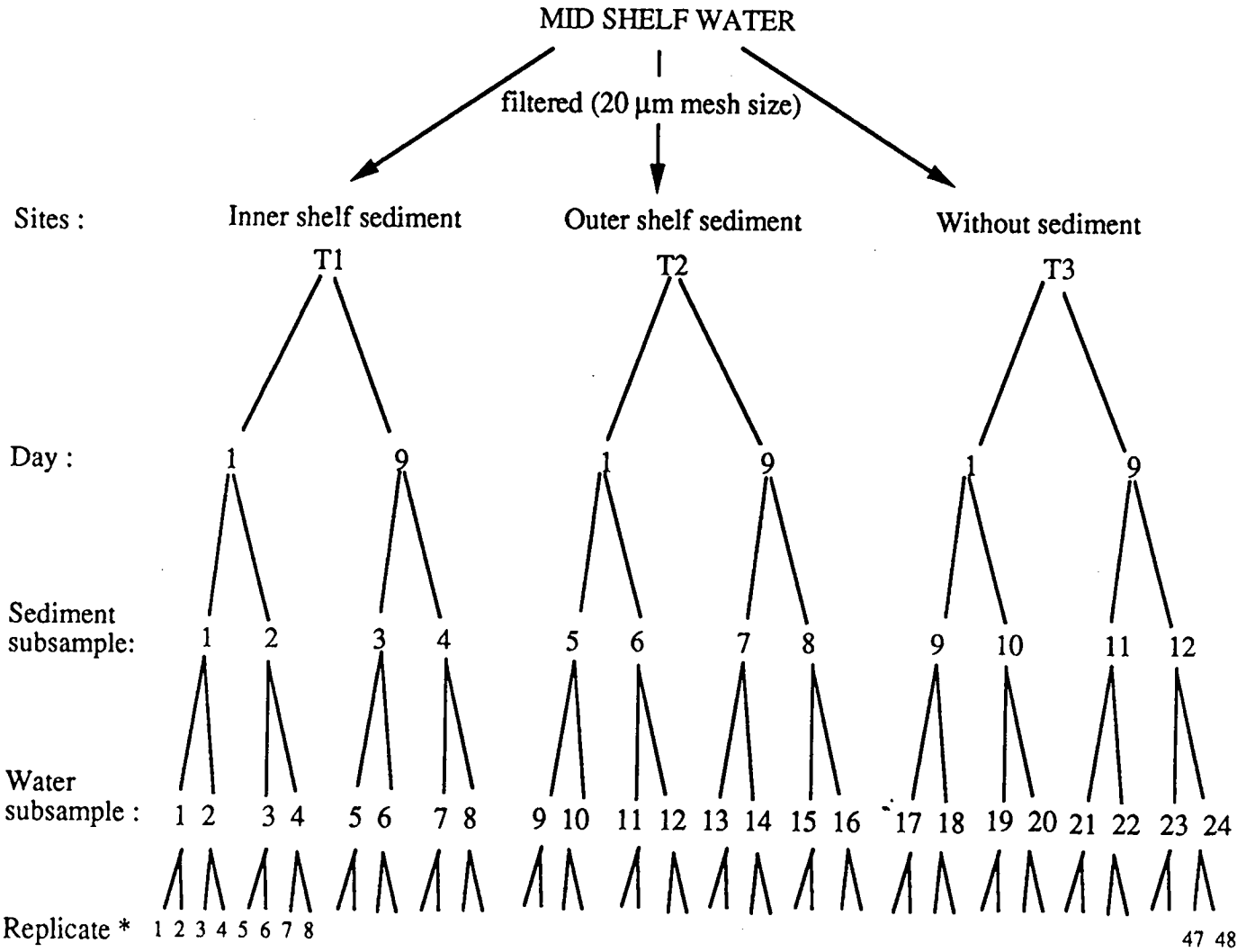
Nutrient concentrations in seawater with resuspended inner and outer shelf sediment were determined at the start of the experiment (day 1) and eight days later (day 9). On day 1, differences in nutrient concentration between the experimental and control bottles were caused by nutrients promptly released from the stirred sediments. Concentrations measured on day 9 included changes due to transformations by microorganisms in the water-sediment mixture. On day 1 (Figure 3.28; Appendix I: Table I-3) only chl *a* and total pigments showed significantly greater releases from inner shelf sediment as compared to outer shelf sediment ($\underline{P} < 0.05$). The concentration of other nutrient species promptly released from inner and outer shelf sediments were not different ($\underline{P} > 0.05$, Figure 3.28). After sediments were shaken in the bottles for 9 days, changes in the concentration of nutrients and chlorophyll were observed. Concentrations of total P, PN and PO_4^{3-} in the bottles with inner shelf sediment were significantly higher than those with outer shelf

sediment ($P < 0.05$; Figure 3.29; Appendix I: Table I-3). Release of the other nutrient species measured did not differ between the inner and outer shelf on either day 1 and day 9.

Changes in nutrient concentrations over the nine day experimental period

Nutrient concentrations in the experimental bottles on day 1 and day 9 were compared. Table 3.3 summarizes net changes in concentration from day 1 to day 9 (increasing or decreasing). Concentrations of NO_2^- and $NO_2^- + NO_3^-$ increased from day 1 to day 9 in the control ($P < 0.05$), but not in the experimental bottles ($P > 0.05$). Silicate ($Si(OH)_4$) concentrations increased significantly in the experimental bottles (both inner and outer shelf sediment) from day 1 to day 9, but not in the control. Chl *a*, phaeophytin and total pigments concentrations decreased from day 1 to day 9 in both the control and experimental bottles. The concentration of individual nutrient species not specifically mentioned above (see Table 3.3) did not significantly change over time ($P > 0.05$).

The results of this experiment indicate that significant levels of variability in nutrient concentrations can occur between water subsamples and sediment subsamples from a single site. The variability at this very local scale necessarily affects detection of differences at higher levels i.e. treatment, site, day. It should be noted that differences between factors (treatment, day and shelf type) can be most easily detected when concentrations of these nutrient species are high above the noise level. Conversely, detection of changes when concentrations are low (as in these experiments) may be difficult.



* Replicates were 2 filters or aliquots of solution for chemical assay of PN, PP, Chlorophyll *a* and phaeopigment

Figure 3.24 Design for experiment 3 : Variability related to sediment subsamples and water subsamples.

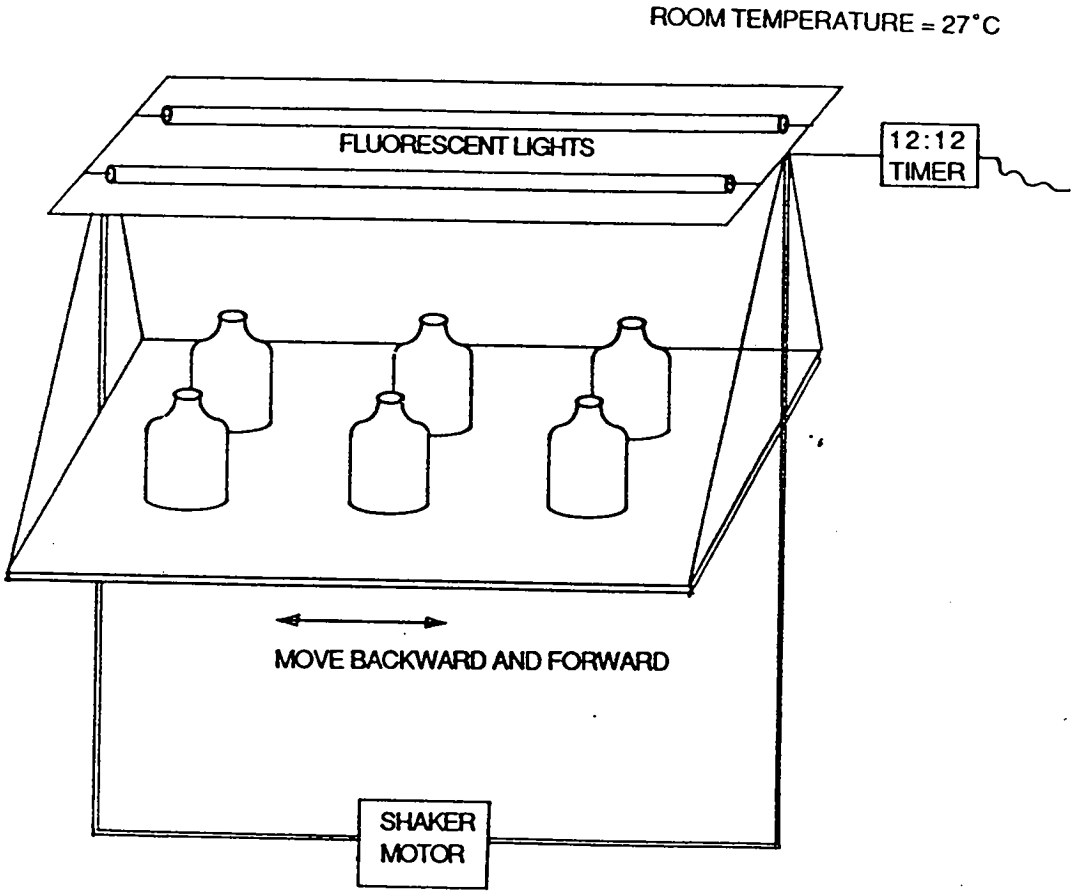


Figure 3.25 Experimental apparatus.

Table 3.2

Summary of ANOVA results for comparisons of variability in sediment and water subsample from experiment 3. Differences significant at the $\underline{P} < 0.05$ level are shown as bold probability values.

Variables	Sediment subsample		Water subsample	
	D.F.	Probablility	D.F.	Probablility
Total N	6,12	0.498	12,24	0.117
PN	6,12	0.171	12,24	0.132
TDN	6,12	0.066	12,48	**0.004**
DON	6,12	0.322	12,48	**0.001**
DIN	6,12	0.879	12,41	**0.001**
NH_4^+	6,12	**0.048**	12,39	**<0.001**
$NO_3^- + NO_2^-$	6,12	0.240	12,48	0.285
NO_3^-	6,12	0.198	12,48	0.205
NO_2^-	6,12	**0.050**	12,48	0.148
Total P	6,12	0.118	12,18	0.245
PP	6,12	0.503	12,18	**0.038**
TDP	6,12	0.736	12,48	**<0.001**
DOP	6,12	0.592	12,48	**0.015**
PO_4^{3-}	6,12	0.181	12,48	0.742
$Si(OH)_4$	6,12	**<0.001**	12,48	0.463
Chl *a*	6,12	0.655	12,24	**<0.001**
Phaeophytin	6,12	0.797	12,24	0.477
Chl *a* +Phaeo	6,12	**0.042**	12,24	0.059

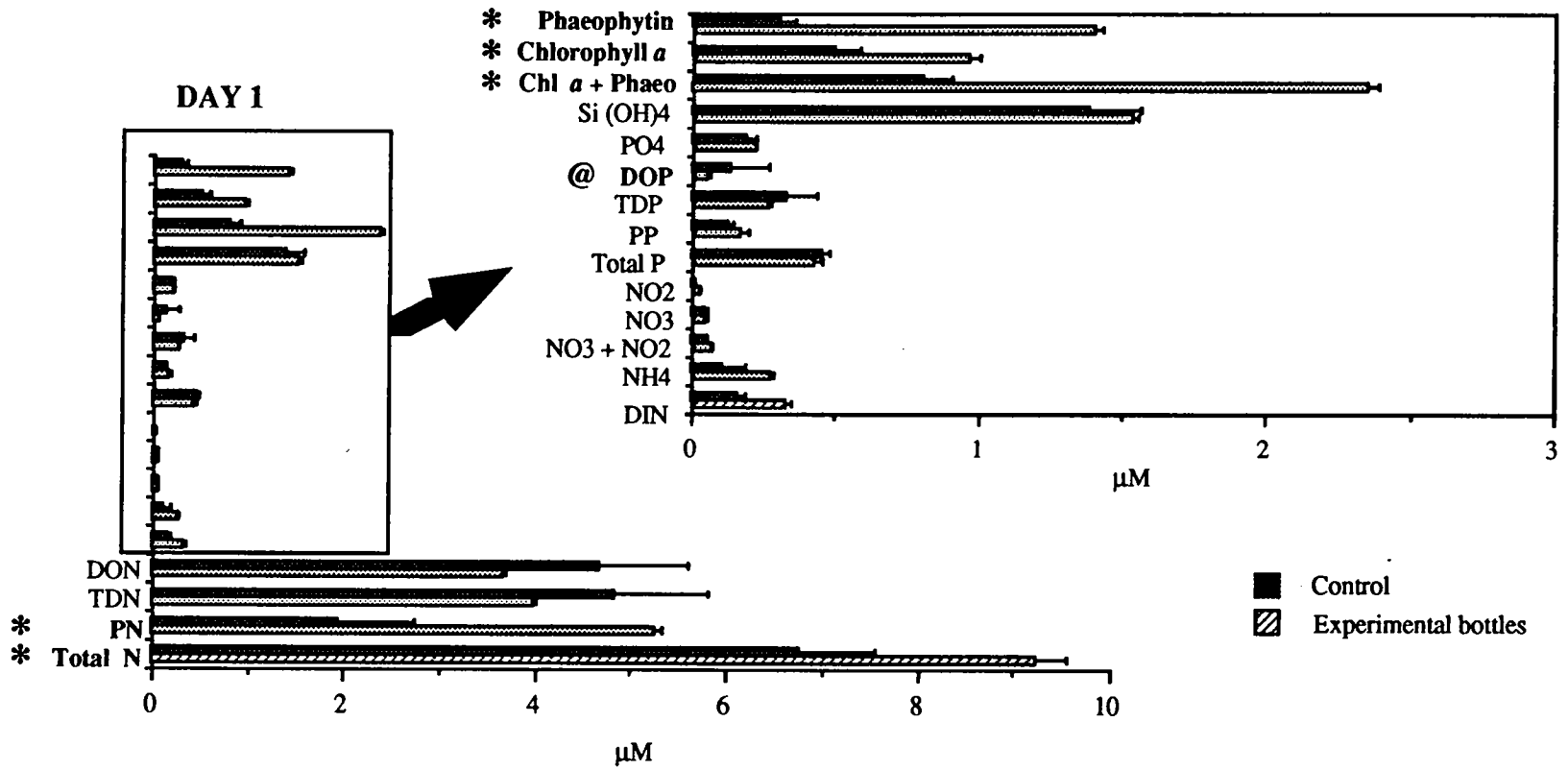


Figure 3.26 : Nutrient and chlorophyll concentrations in the control and experimental bottles (sediment added) (inner and outer shelf pooled) on day 1 of experiment 3. Error bars shown are one standard error (n = 12 or 8 in control and 24 or 16 in experimental bottles; see Appendix I). * indicates that the concentrations in the experimental bottles are significantly higher than in the control ($P < 0.05$) ; @ indicates the reverse . Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

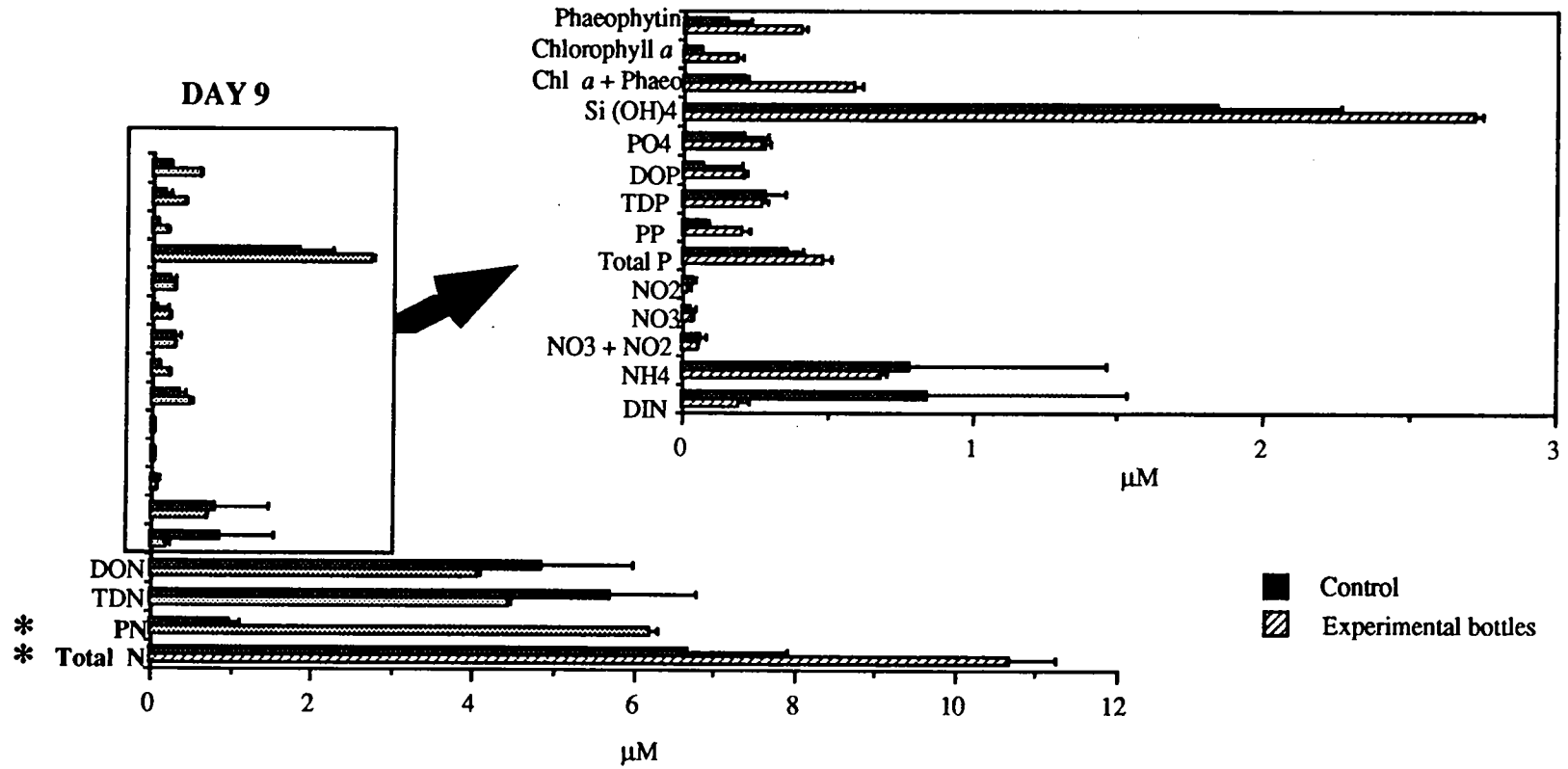


Figure 3.27 : Nutrient and chlorophyll concentrations in the control and experimental bottles (sediment added) (inner and outer shelf pooled) on day 9 of experiment 3. Error bars shown are one standard error (n = 12 or 8 in control and 24 or16 in experimental bottles; see Appendix I). * indicates that the concentrations in the experimental bottles are significantly higher than in the control ($P < 0.05$). Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

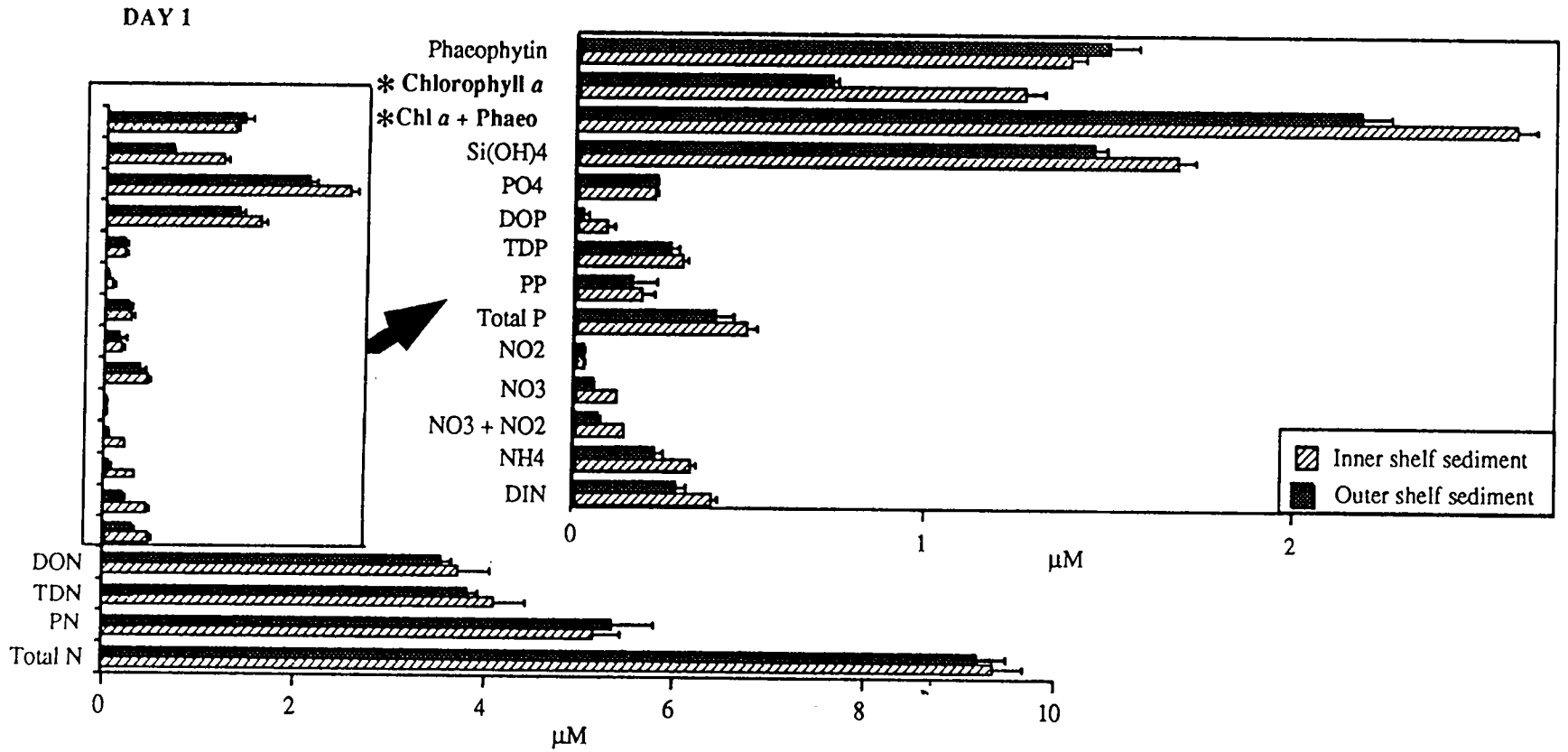


Figure 3.28 : Comparison of nutrients and chlorophyll concentrations released from the inner and outer shelf sediment on day 1 of experiment 3. Error bars are one standard error (n = 12 in control and experimental bottles).

* indicates that the nutrients released from inner shelf sediment were significantly ($P < 0.05$) greater than outer shelf sediment (see Appendix I). Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

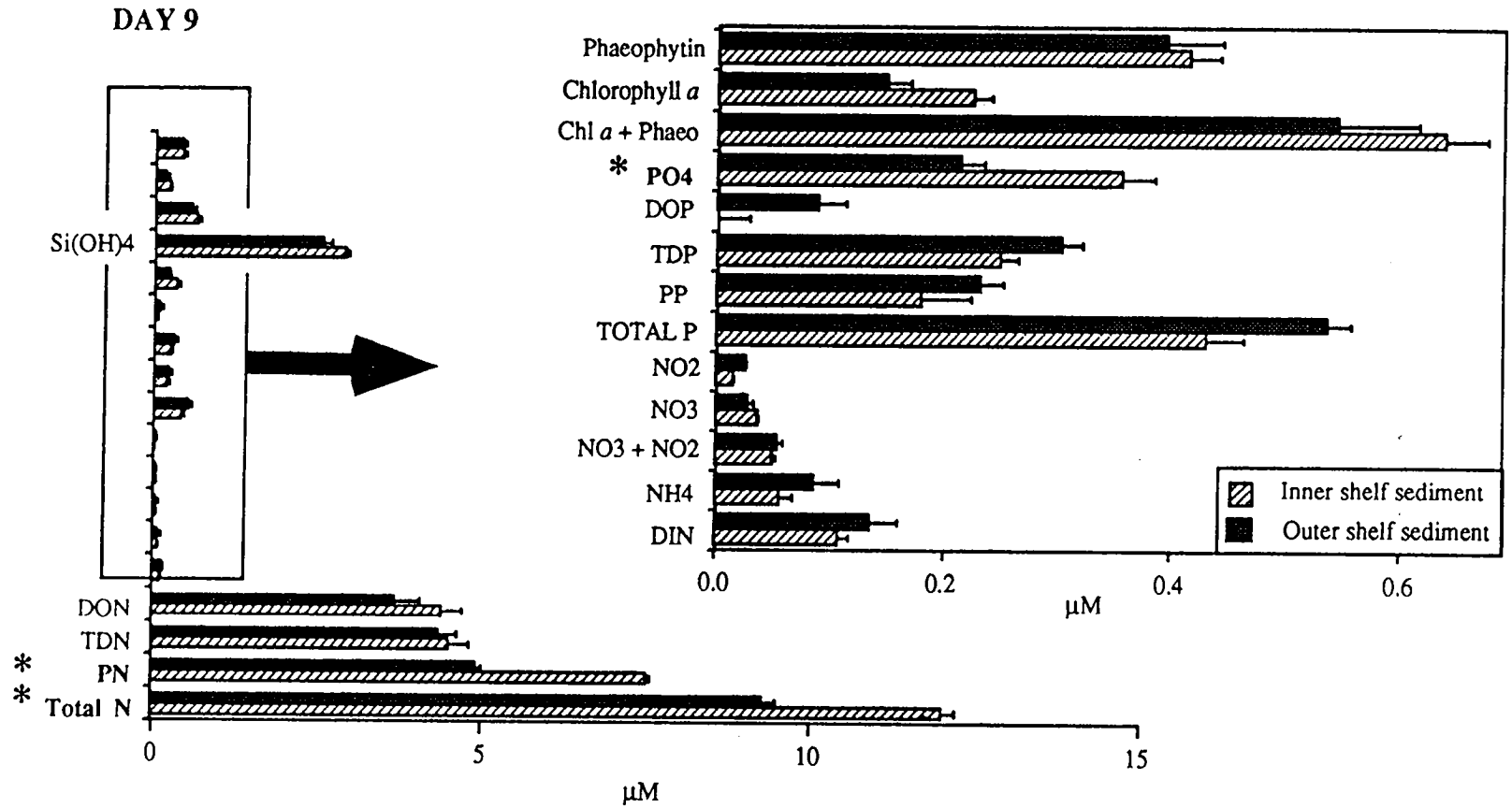


Figure 3.29 : Comparison of nutrient and chlorophyll concentrations released from the inner and outer shelf sediments by day 9 of experiment 3. Error bars are one standard error (n = 12 in control and experimental bottles). * indicates that the nutrients released from inner shelf sediment were significantly ($\underline{P} < 0.05$) greater than those from outer shelf sediment (see Appendix I). Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

Table 3.3

Summary of changes in nutrient concentrations between day 1 and day 9 of experiment 3 using seawater mixed with inner or outer shelf sediments, and without sediment (control). Actual values are shown in Appendix I, Table I-2, I-3.
(Concentration differences given between the two dates are significant at a level of $\underline{P} < 0.05$; - : concentration decrease from day 1 to day 9; +: concentration increase from day 1 to day 9; = : no difference in concentration).

Variables	Experiment 3		
	Seawater with Inner shelf sediment	Seawater with Outer shelf sediment	Control
Total N	=	=	=
PN	=	=	=
TDN	=	=	=
DON	=	=	=
DIN	=	=	=
NH_4^+	=	=	=
$NO_3^- + NO_2^-$	=	=	+.01
NO_3^-	=	=	-.02
NO_2^-	=	=	+.03
Total P	=	=	=
PP	=	=	=
TDP	=	=	=
DOP	=	=	=
PO_4^{3-}	=	=	=
$Si(OH)_4$	+1.25	+1.13	=
Chl *a*	-1.00	-1.60	-0.43
Phaeophytin	-0.93	-0.54	-0.15
Chl *a* + Phaeo	-0.93	-1.05	-0.59

3.3.4 EXPERIMENT 4: A comparison of the amount of nutrients released from inner and outer shelf sediment.

This experiment was conducted to compare the amount of nutrients which may be released from resuspended inner and outer shelf sediments. The comparison was made with regard to the nutrients released promptly into the water column upon stirring from these two types of sediment, and for nutrient concentrations found in the water column at some time following the sediment resuspension event (9 days).

a. Experimental design

The experimental design is shown schematically in Figure 3.30. Sediment from three sites on the inner (IS2, IS3, IS4) and outer (OS2, OS3, OS4) shelf regions were used to assess regional variability of nutrient release. As a result of variability associated with sediment and water subsampling (Experiment 3), the design of this experiment was modified from that used in the previous experiment (3) in that sediment was collected from three sites. Water subsamples were not taken for bottles from each sediment site in this experiment because of the larger number of sediment samples used. To assess the potential magnitude of water subsample variability, four replicates were collected from one bottle.

At the start of the experiment ("day 1"), 2 litres of seawater which had been collected from a mid-shelf site and had been filtered through a plankton net (20 μm mesh size), were added to each of thirty 2 litre polycarbonate bottles (Nalge, USA). The number of bottles available and time constraints on filtration necessitated a smaller subsample size than used previously. Pre-weighed subsamples of sediment (approximately 2.5 ml sediment volume) were added to individual bottles. Four replicate experimental bottles were prepared using sediment from each inner shelf (IS2, IS3, IS4) and each outer shelf (OS2, OS3, OS4) sites. No sediment was added to the six control bottles. All bottles were then manually shaken until the sediment was dispersed. After mixing, water subsamples were taken from two of the four experimental bottles from each site and from three of the controls. The remaining fifteen bottles were incubated for 9 days on a motorized shaker in a control temperature room (27 °C). The bottles were left uncapped to oxygenate the water. Water subsamples were collected from the remaining bottles on day 9 of the experimental period ("day 9").

b. Data analysis

An analysis of variance and covariance (A General statistical {Genstat} program, Rothamsted Experimental Station, 1980) was performed on the concentrations of nutrient species measured in this experiment (Appendix II). The Genstat program was used because it is capable of executing a three-way nested analysis of variance or covariance involving five factors. Data for sediment subsample and site were pooled to reduce the number of factors involved to a manageable level for an unbalanced design. A three-way nested analysis of variance was conducted to compare nutrient concentrations between different treatments (with and without sediment), sampling dates (day 1 and day 9) and sediment types (inner and outer shelf sediments). The analysis of covariance was used to adjust the amounts of nutrients measured for different weights of sediment added to individual bottles. The results of the analysis of covariance indicated that except for total N, PN, TDP, $Si(OH)_4$ and chl *a* concentrations (Appendix II: Table II-1), sediment weight did not have a significant effect on the concentration of nutrient species. The data was tested for heteroscedasticity using Cochran's C test (Dixon and Massey, 1969) prior to carrying out the ANOVA or AOCV procedure. A multiple comparison test (Tukey Test; Zar, 1984) was used to carry out *a posteriori* comparisons of means across factors found to be significant.

c. Results

Nutrient releases related to sediment resuspension

Nutrient concentrations sampled in control and experimental bottles on day 1 and day 9 were compared. On day 1 concentrations of total N, PN, DIN, NH_4^+, $NO_3^- + NO_2^-$, total P, PP, $Si(OH)_4$, Chl *a*, phaeophytin and total pigments in the experimental bottles (with either inner or outer shelf sediment) were significantly higher than those in the control (Figure 3.31; Appendix II: Table II-3). These higher concentrations reflect prompt nutrient release during sediment resuspension. After nine days, concentrations of several nutrient species (total N, PN, total P, PP, $Si(OH)_4$, Chl *a*, phaeophytin, total pigments) remained higher in the experimental bottles while differences for some nutrient species such as DIN and NH_4^+ declined (Figure 3.32; Appendix II: Table II-3). Since the concentrations of NH_4^+ in the controls did not significantly change over the 9 days periods, the resulting decline in NH_4^+ concentration in the experimental bottles can be best explained by the uptake of NH_4^+ by phytoplankton, as shown by the increase in Chl *a*. Concentrations of $NO_3^- + NO_2^-$ concentrations were higher in the control than in the experimental bottles on day 9.

Comparison of nutrients and chlorophyll released from inner and outer shelf sediments

The comparison of nutrient concentrations in bottles with either inner or outer shelf sediment was made separately for days 1 and 9 results. More total P released from the outer shelf sediment as compared to the inner shelf sediment was found on both days 1 (Figure 3.33) and 9 (Figure 3.34). On day 1, $Si(OH)_4$ release from inner shelf sediment were greater but not significantly than that from the outer shelf sediments ($\underline{P} > 0.05$). After 9 days however, $Si(OH)_4$ concentrations in the experimental bottles with inner shelf sediment added had significantly increased beyond that in outer shelf bottles ($\underline{P} < 0.05$, Figure 3.34). Similar amounts of PP were promptly released from inner and outer shelf sediments as measured on day 1 ($\underline{P} > 0.05$, Figure 3.32). By day 9, the concentration of PP in the experimental bottles had also increased. This increase resulted in significantly greater PP concentration in the outer-shelf sediment bottles than inner-shelf sediment bottles ($\underline{P} < 0.05$, Figure 3.34). With the exception of total P, PP and $Si(OH)_4$, the concentrations of total N, PN, TDN, DON, NH_4^+, NO_3^-, NO_2^-, PP, TDP, PO_4^{3-}, Chl *a* and phaeophytin released from either inner or outer shelf sediment on both day 1 and day 9 were not significantly different (Figure 3.33; 3.34; Appendix II: Table II-3). The lack of detectable difference was due to the low degree of freedom in the statistical analyses.

Changes in nutrient concentrations over the 9 day experimental period

Table 3.4 summarizes net changes in the concentration of individual nutrient species from day 1 to day 9. The concentrations of TDN, DON, DIN, NH_4^+ decreased from day 1 to day 9 in both the control and experimental bottles. However, concentrations of $NO_3^- + NO_2^-$ in the control increased from day 1 to day 9 while NO_3^- alone did not change. In both the control and experimental bottles, concentrations of NO_2^-, total P, PP and PO_4^{3-} increased from day 1 to day 9. TDP concentrations in the experimental bottles increased over time while in the controls they remained the same. Concentrations of total N, PN, DOP, $Si(OH)_4$, Chl *a*, phaeophytin and total pigments measured in the control and experimental bottles on both day 1 and day 9 were not significantly different.

It shold be noted that after nine days of sediment resuspension, DIN concentrations decreased while concentrations of Chl *a* increased in both experimental carboys with inner and outer shelf sediment. The increase in Chl *a* reflected the changes in DIN concentrations. This was due to dissolved inorganic nitrogen being taken by phytoplankton.

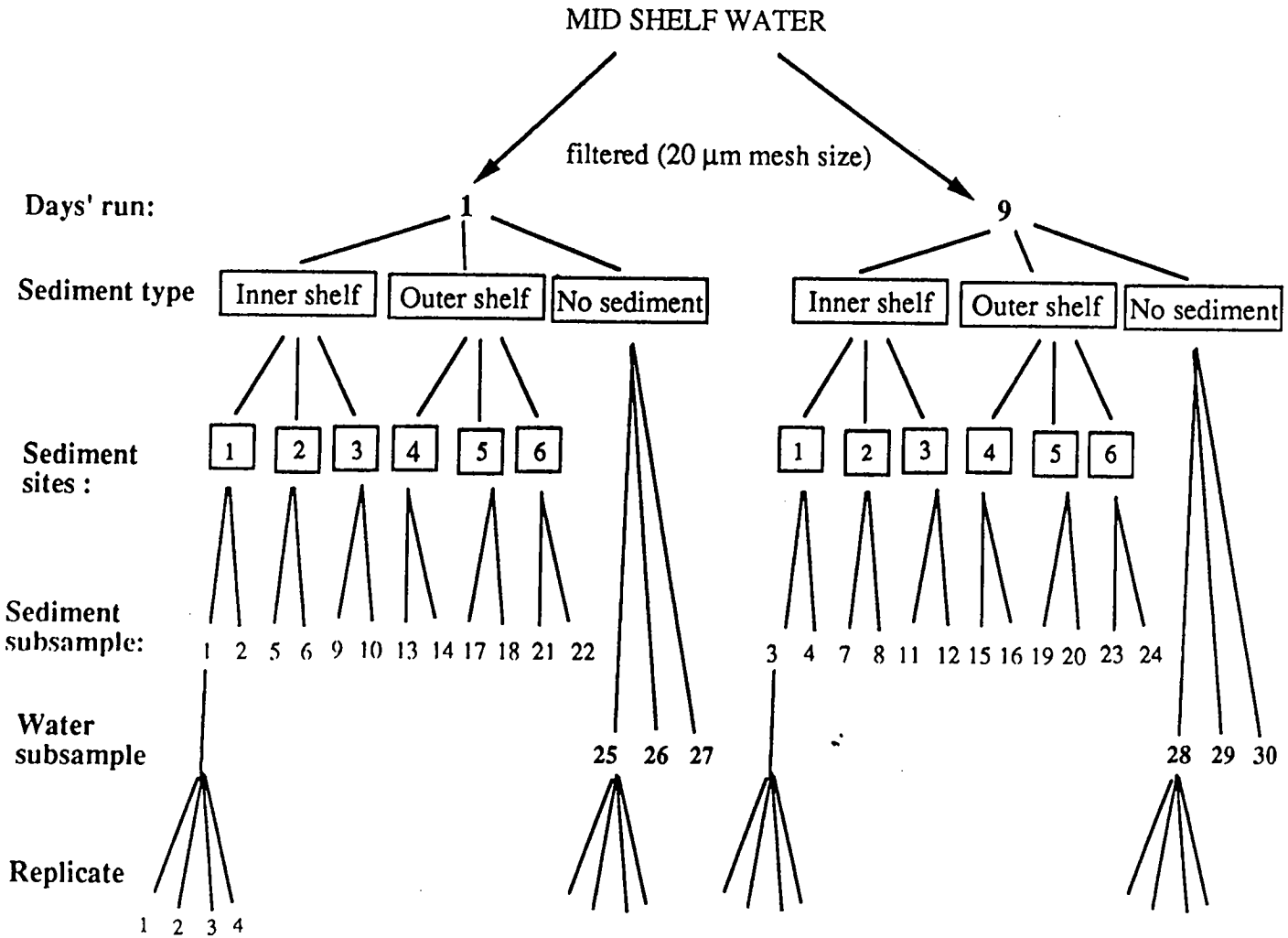


Figure 3.30 Design for experiment 4 : Comparison of the amount of nutrient released from inner and outer shelf sediments.

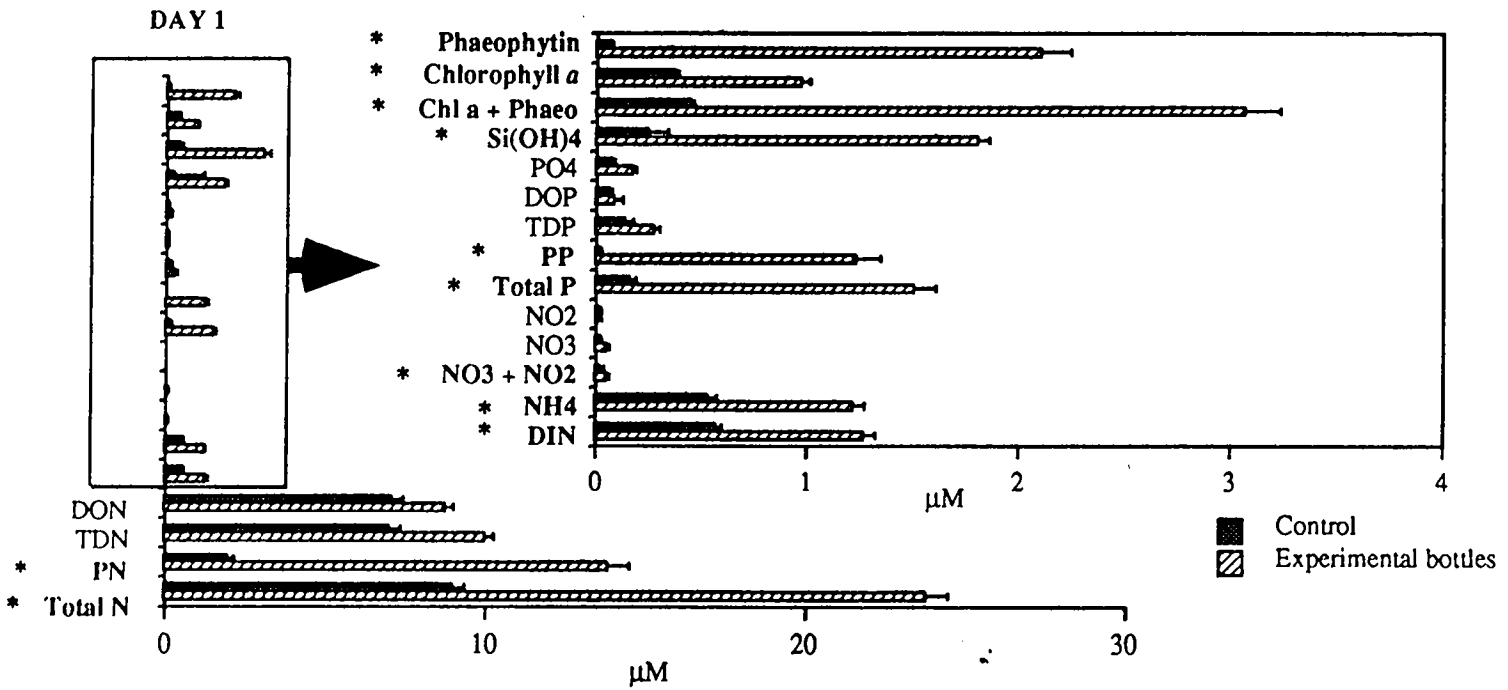


Figure 3.31 Nutrient and chlorophyll concentrations in the control and experimental bottles with sediment added (inner and outer shelf pooled) on day 1 of experiment 4. Error bars are one standard error (n = 12 in control and 48 in experimental bottles). * Indicates that the concentrations in the experimental bottles are greater than control ($P < 0.05$; see Appendix II). Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

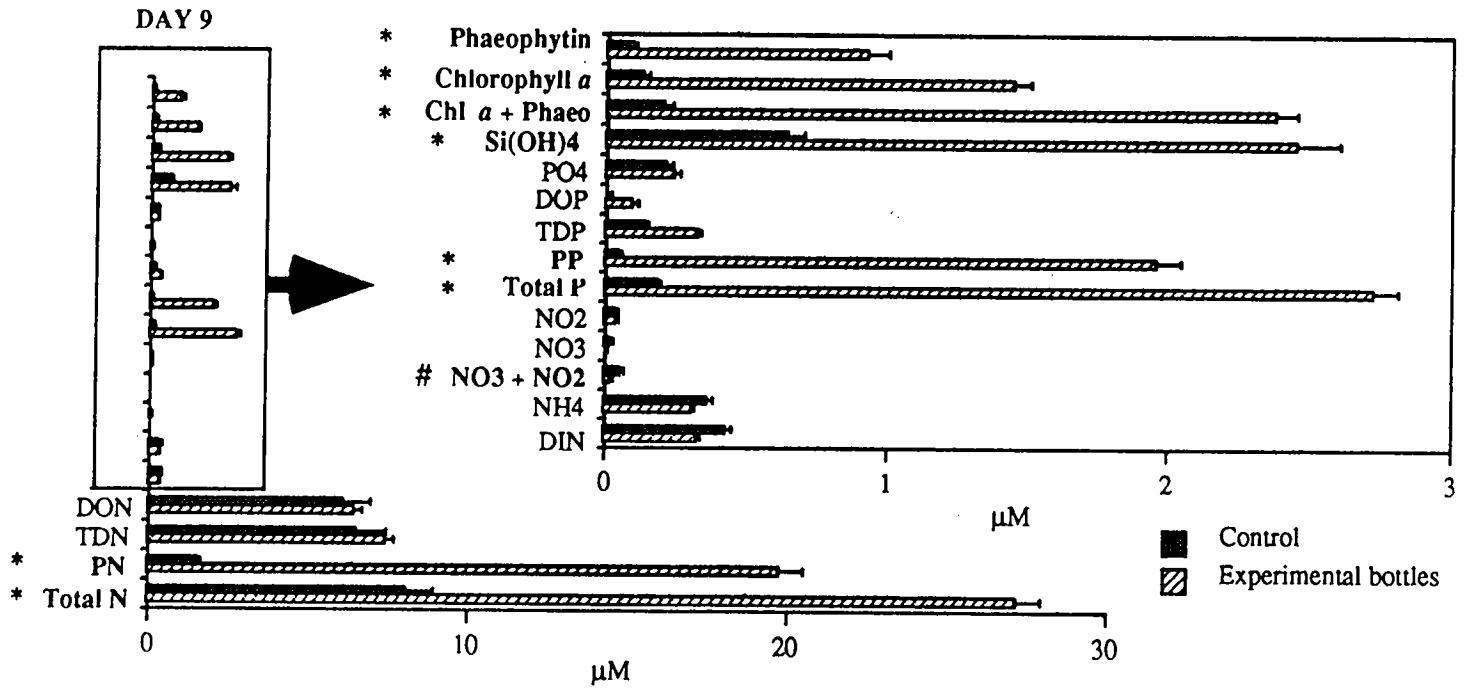


Figure 3.32 Nutrient and chlorophyll concentrations in the control and experimental bottles with sediment added (inner and outer shelf pooled) on day 9 of experiment 4. Error bars are one standard error (n = 24 in control and experimental bottles). * indicates the concentrations in the experimental bottles are greater than the control ($P < 0.05$; see Appendix II). # indicates the reverse. Units are in µM except chlorophyll and phaeophytin which are in µg/l.

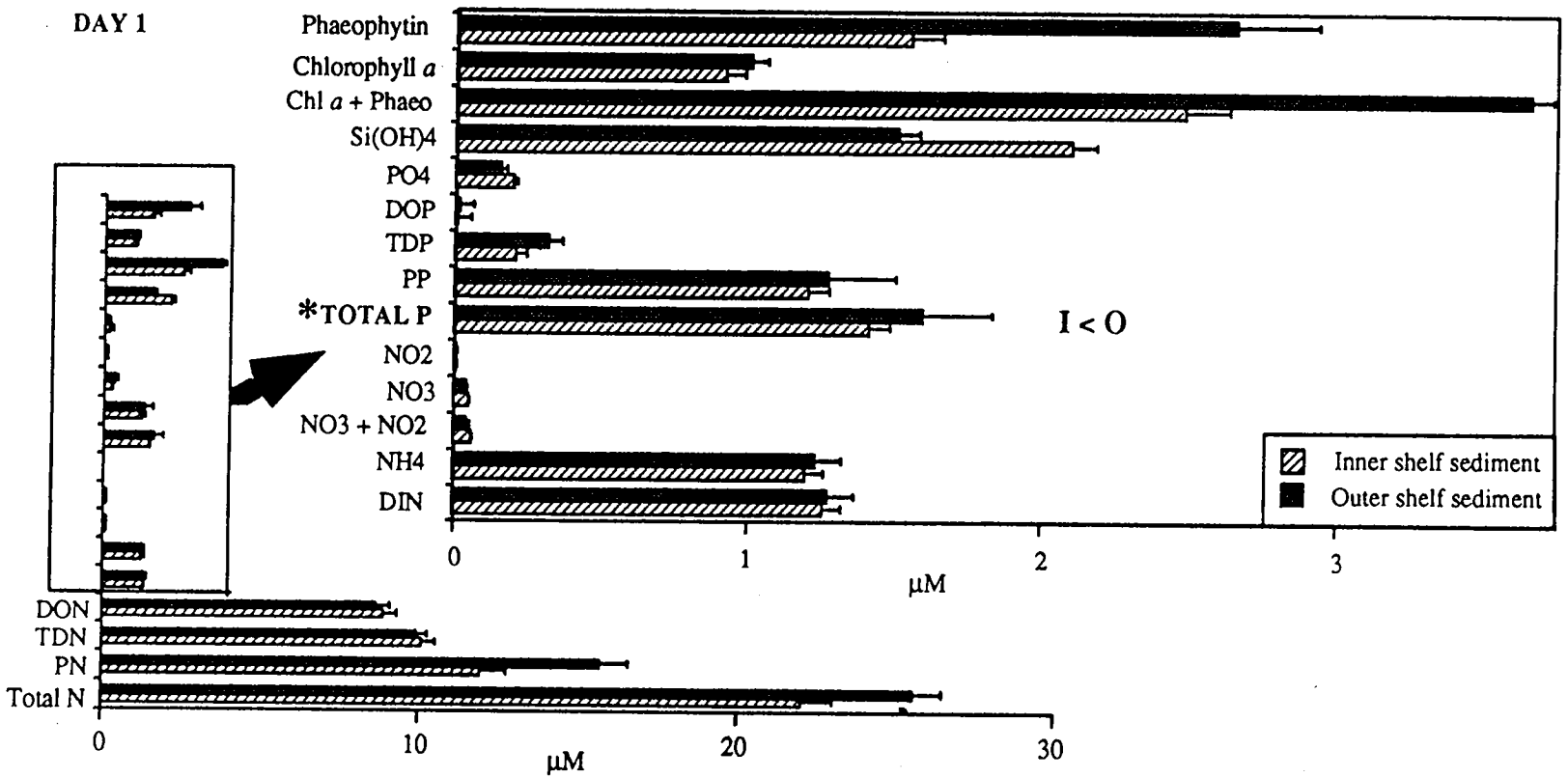


Figure 3.33 : Comparison of nutrient and chlorophyll concentrations measured on day 1 of experiment 4 after resuspension of inner and outer shelf sediments. Error bars are one standard error (n = 24 in control and experimental bottles). * indicates significant differences in concentrations between inner and outer shelf sediment ($P < 0.05$; see Appendix II). Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

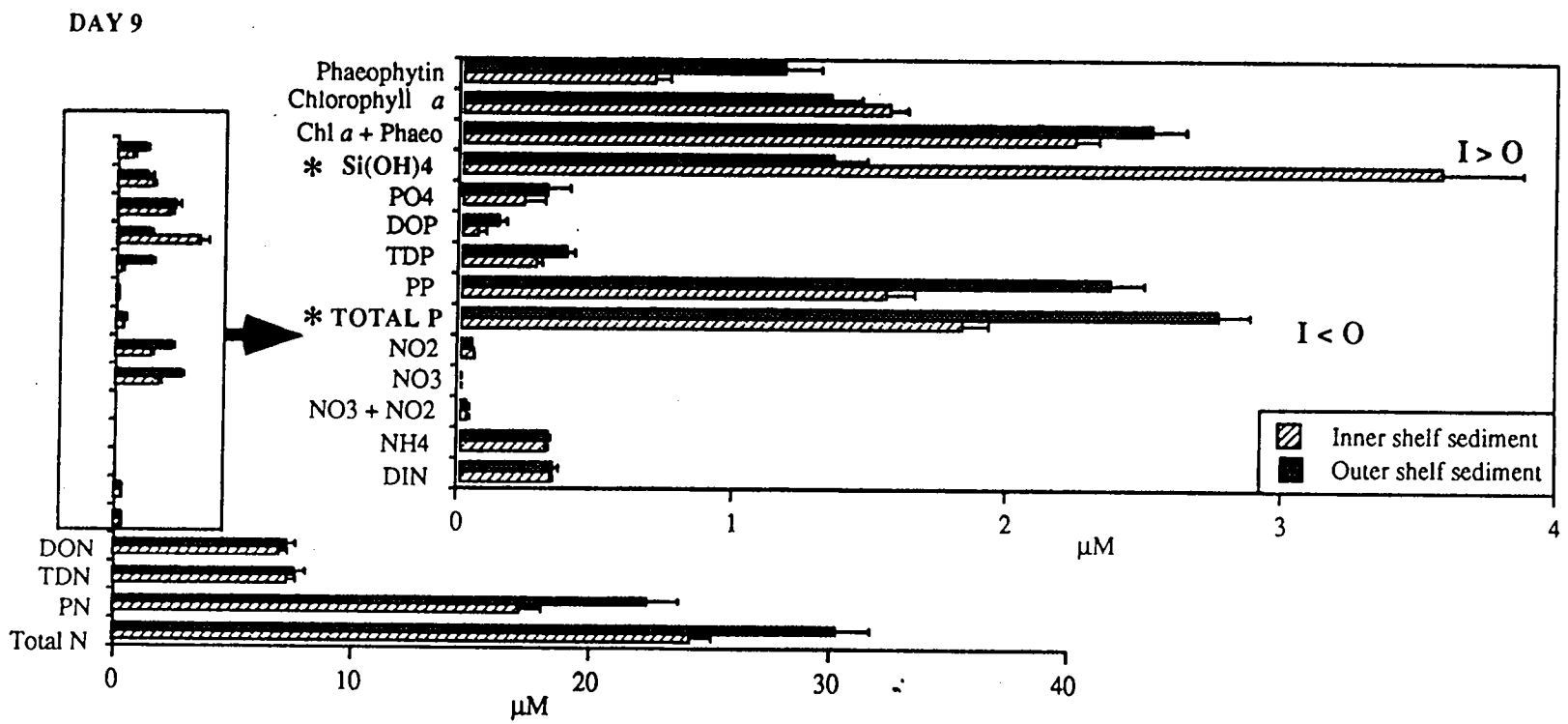


Figure 3.34 : Comparison of nutrient and chlorophyll concentrations measured on day 9 of experiment 4 after resuspension of inner and outer shelf sediment. Error bars are one standard error (n = 24 in control and experimental bottles) . * indicates significant differences in concentrations between inner and outer shelf sediment ($P < 0.05$; see Appendix II).
Units are in µM except chlorophyll *a* and phaeophytin which are in µg/l.

Table 3.4

Summary of changes in nutrient concentrations between day 1 and day 9 of experiment 4 using seawater mixed with inner- or outer shelf sediments and without sediment (control). Actual values are shown in Appendix II, Tables II-3 and II-4.
(Concentration differences given between the two dates are significant at a level of $\underline{P} < 0.05$; - : concentration decrease from day 1 to day 9; + : concentration increase from day 1 to day 9; = : no difference in concentration).

Variables	Experiment 4		
	Seawater with Inner shelf sediment	Seawater with Outer shelf sediment	Control
Total N	=	=	=
PN	=	=	=
TDN	-2.80	-2.25	-0.44
DON	-1.92	-1.31	-0.30
DIN	-0.93	-0.94	-0.14
NH_4^+	-0.89	-0.92	-0.18
$NO_3^- + NO_2^-$	-0.04	-0.02	+0.03
NO_3^-	-0.03	-0.02	=
NO_2^-	+0.03	+0.03	+.03
Total P	+0.40	+1.15	+0.02
PP	+0.34	+1.09	+0.03
TDP	+0.06	+0.06	=
DOP	=	=	=
PO_4^{3-}	+0.02	+1.36	+0.14
$Si(OH)_4$	=	=	=
Chl *a*	=	=	=
Phaeophytin	=	=	=
Chl *a* +Phaeo	=	=	=

3.3.5 Amounts of nutrient promptly released from inner and outer shelf sediment.

Sediments from different sites or shelf areas contain different concentrations of porewater and solid phase components (Alongi, 1989c; Table 2.3 in this study). Different nutrient species were preferentialy associated with different components of the sediment. For example, PN and PP are largely associated with the particulate fraction while DIN, DON, DIP and DOP are dissolved in the sediment porewater. In order to directly compare the different amounts of nutrients released from each sediment site, it was necessary to standardize the concentrations of nutrients released to unit volumes and masses of sediment.

Descriptive comparisons were made of the amounts of nutrients promptly released by the resuspension of sediment from each collection site within inner, mid- and outer shelf areas. The estimates of nutrient release are normalized to volume of wet sediment, water-free sediment and estimated porosity of the sediment as appropriate. Data normalized to volume of wet sediment is used to assess the total amount of nutrients which would be released when bulk sediments are naturally resuspended into the water column. As each sediment sample contains a different proportion of porewater and solid-phase material, adjusted amounts of sediment normalized to volume of water-free sediment or sediment porewater volume are needed for proper comparisons of the amounts of nutrient promptly release.

The amounts of nutrients promptly released by resuspension from mid-shelf, inner shelf and outer shelf sediments were calculated by subtracting concentrations of each nutrient species in the control container from those in the experimental containers (to which sediment was added) and then dividing by the volume (cm^3) of wet sediment, porewater or water-free sediment added to the container. A rigorous statistical comparison between sets of the nutrients released from all sites could not be made because experiments were carried out at different times with different batches of seawater. The descriptive comparison made here is based on the assumption that there is a linear relationship between the changes of concentrations for individual nutrient species and the amounts of sediment added. The values were expressed as concentration (μM or $\mu g\ l^{-1}$) per cm^3 of wet sediment (Figure 3.35), per cm^3 of porewater (Figure 3.36) and per cm^3 of water-free sediment (Figure 3.37) of sediment.

Amounts of nutrients released per unit volume of sediment varied between sediment

collection sites. When nutrient releases were normalized to estimated porosity of sediment, in some cases the highest amounts of dissolved nutrient release were from the single mid-shelf sediment site (MS1, Figure 3.36). This finding cannot be generalized as mid-shelf sediment was collected from only one mid-shelf site. To compare nutrient releases at sediment from different sites, the volume of water into which the sediment was mixed needed to be adjusted. For sediment sites MS1 and OS5, 20 litres of seawater were used whereas 2 litres of seawater were mixed with sediments from the other sites. The measurement errors for each nutrient species substantially affects the calculated amount of nutrients released, which is in turn multiplied by 20 (litres of seawater used), while release estimates from other sites are multiplied by only 2 (amount of seawater used). The same problem affects very low nutrient release found using sediment from site OS5. The error is also due to the collection procedure of sediment from site MS1 and OS5. These two sediment sites were stored in bulk in which the water content may be disturbed and consequently affect the amounts of nutrient in porewater of these sediments. The magnitude of most nutrient species were greater released from sediment site MS1.

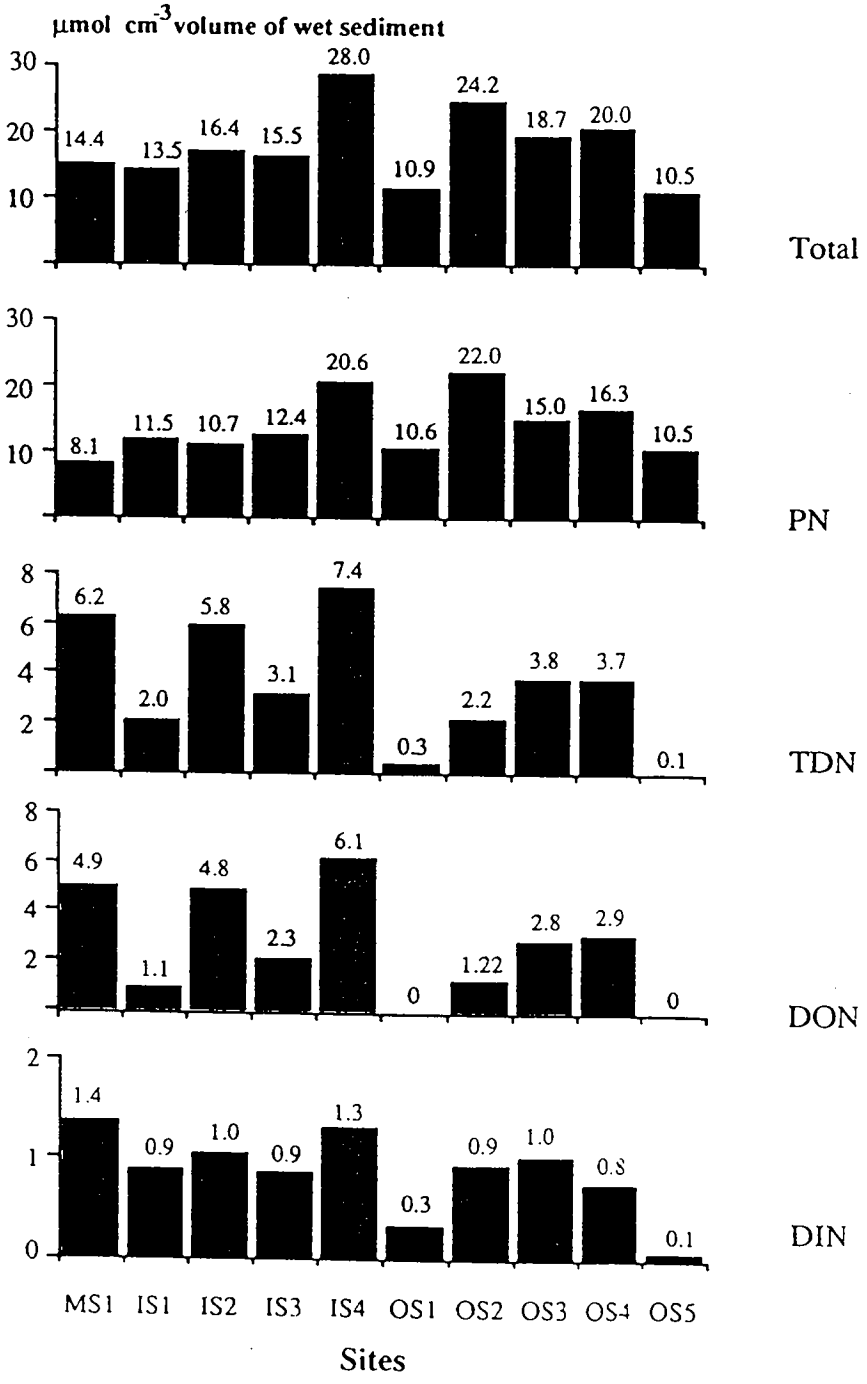


Figure 3.35 Amounts of individual nutrient species promptly released per cubic cm of wet sediment.

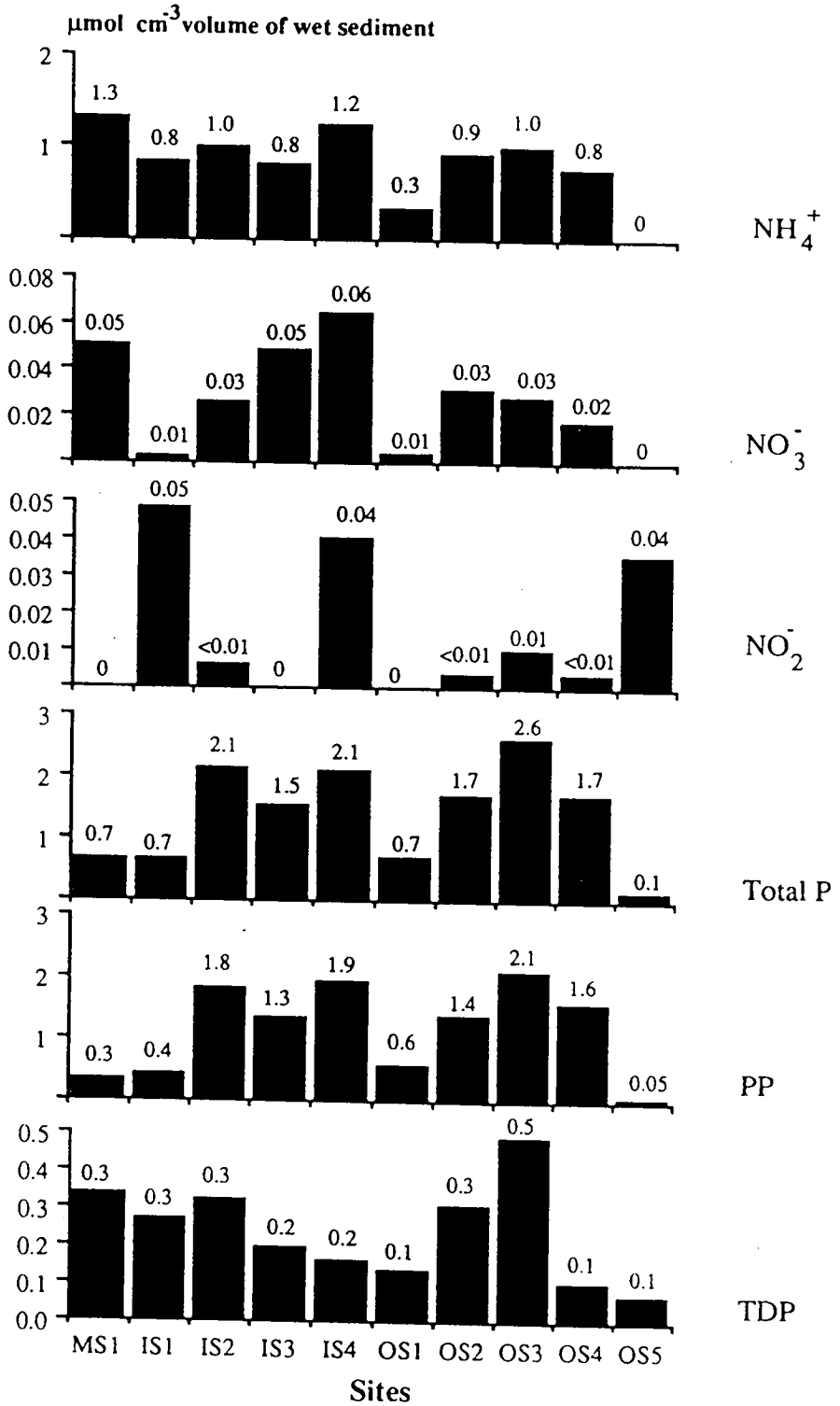


Figure 3.35 cont.

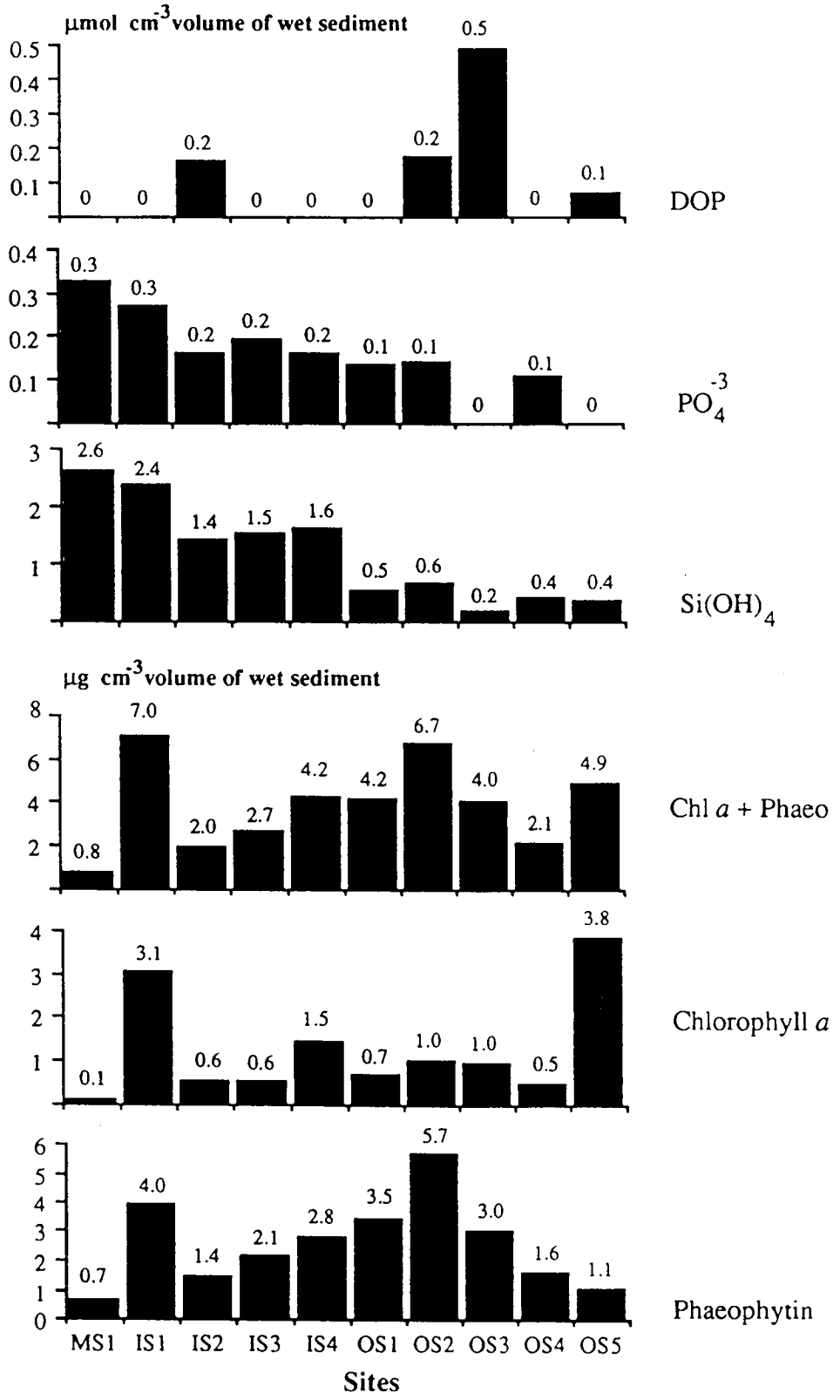


Figure 3.35 cont.

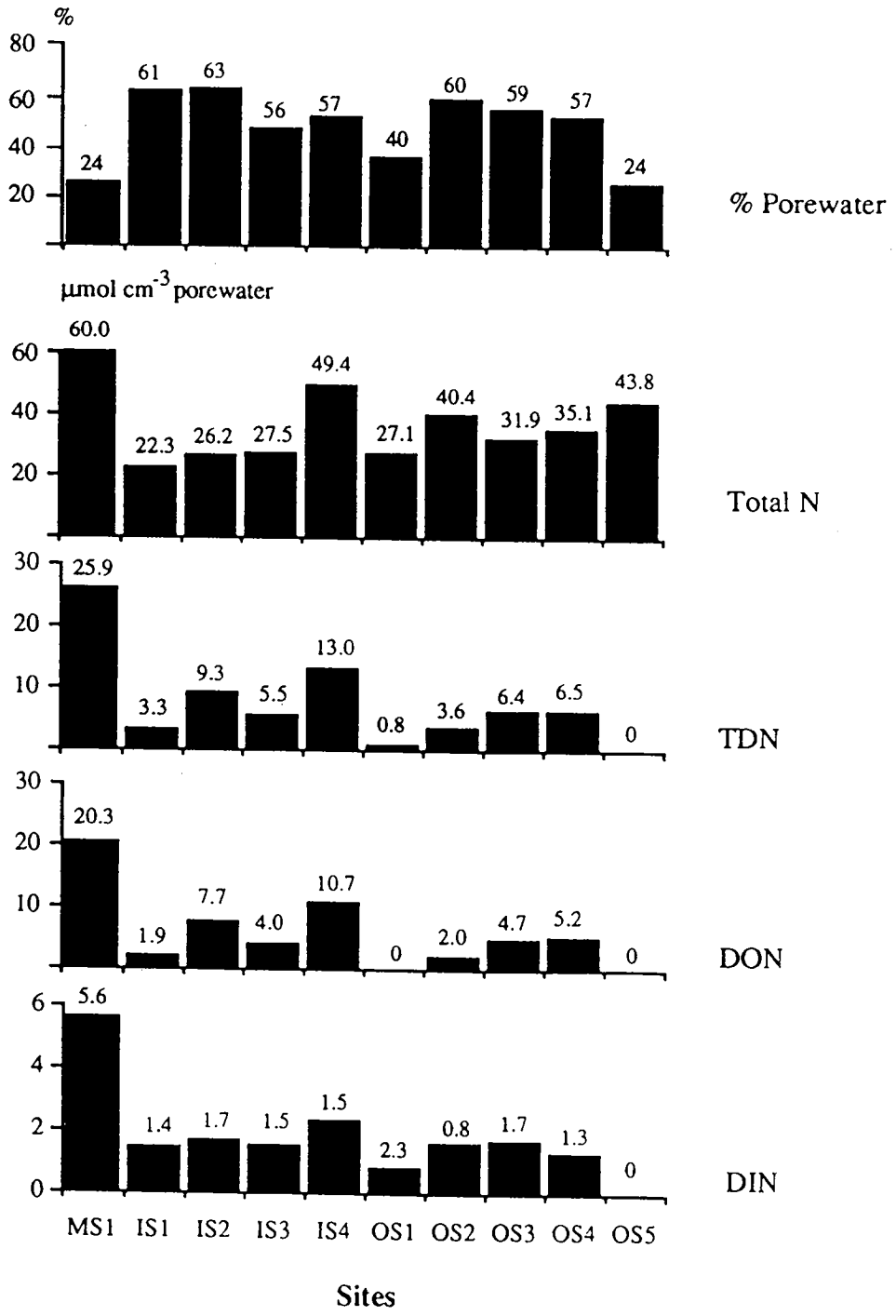


Figure 3.36 Amounts of individual nutrient species promptly released per cubic cm of porewater in sediment.

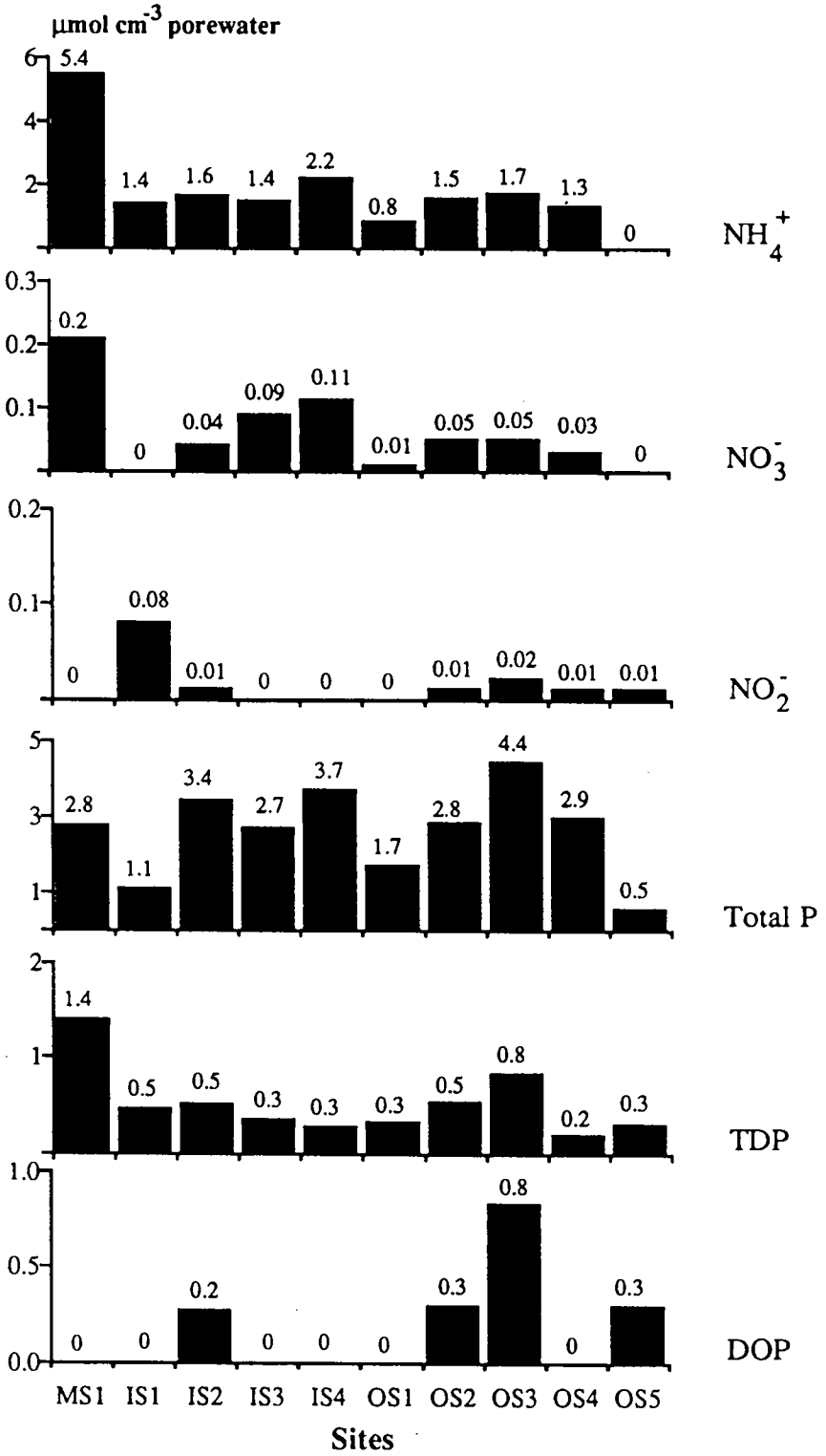


Figure 3.36 cont.

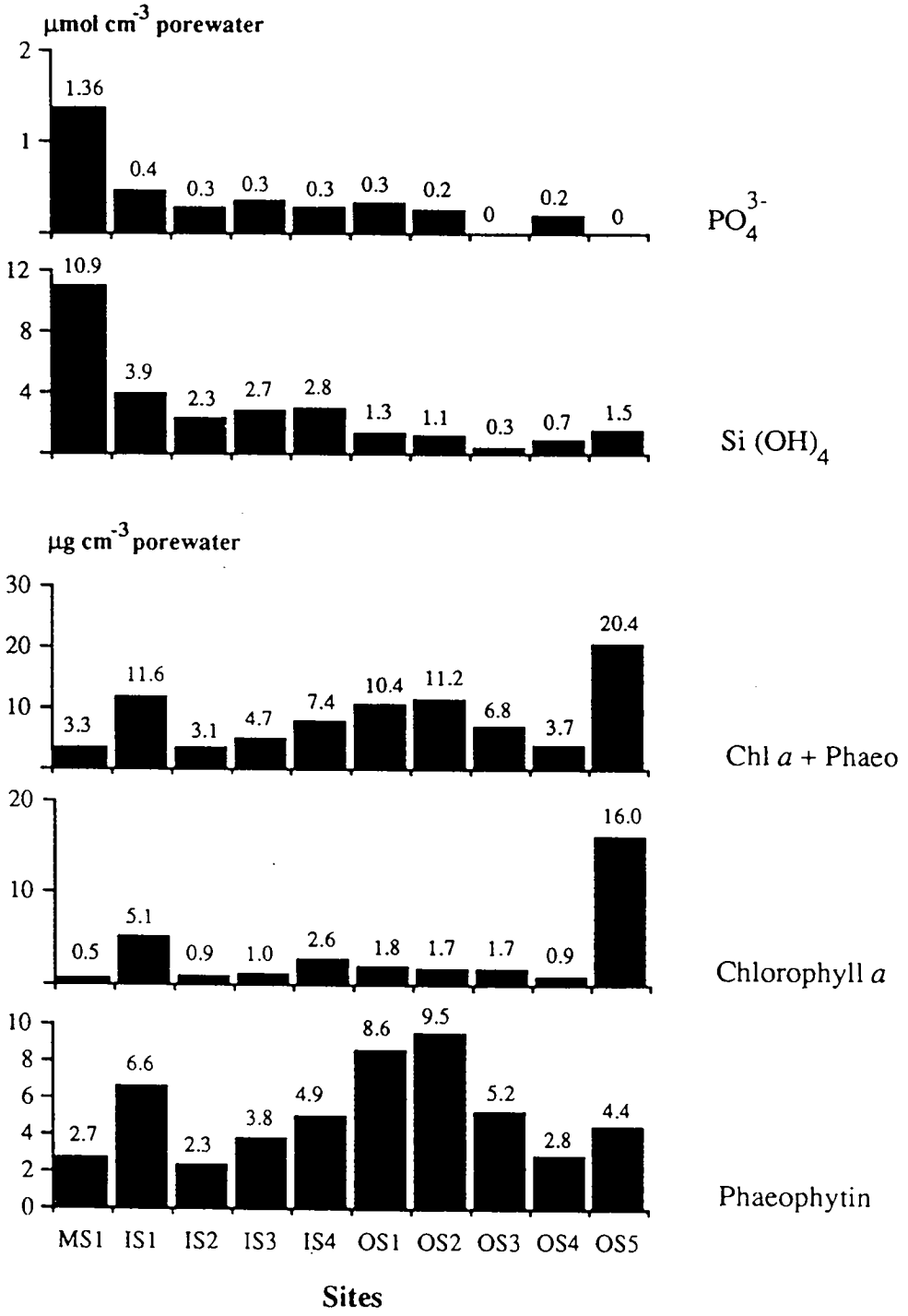


Figure 3.36 cont.

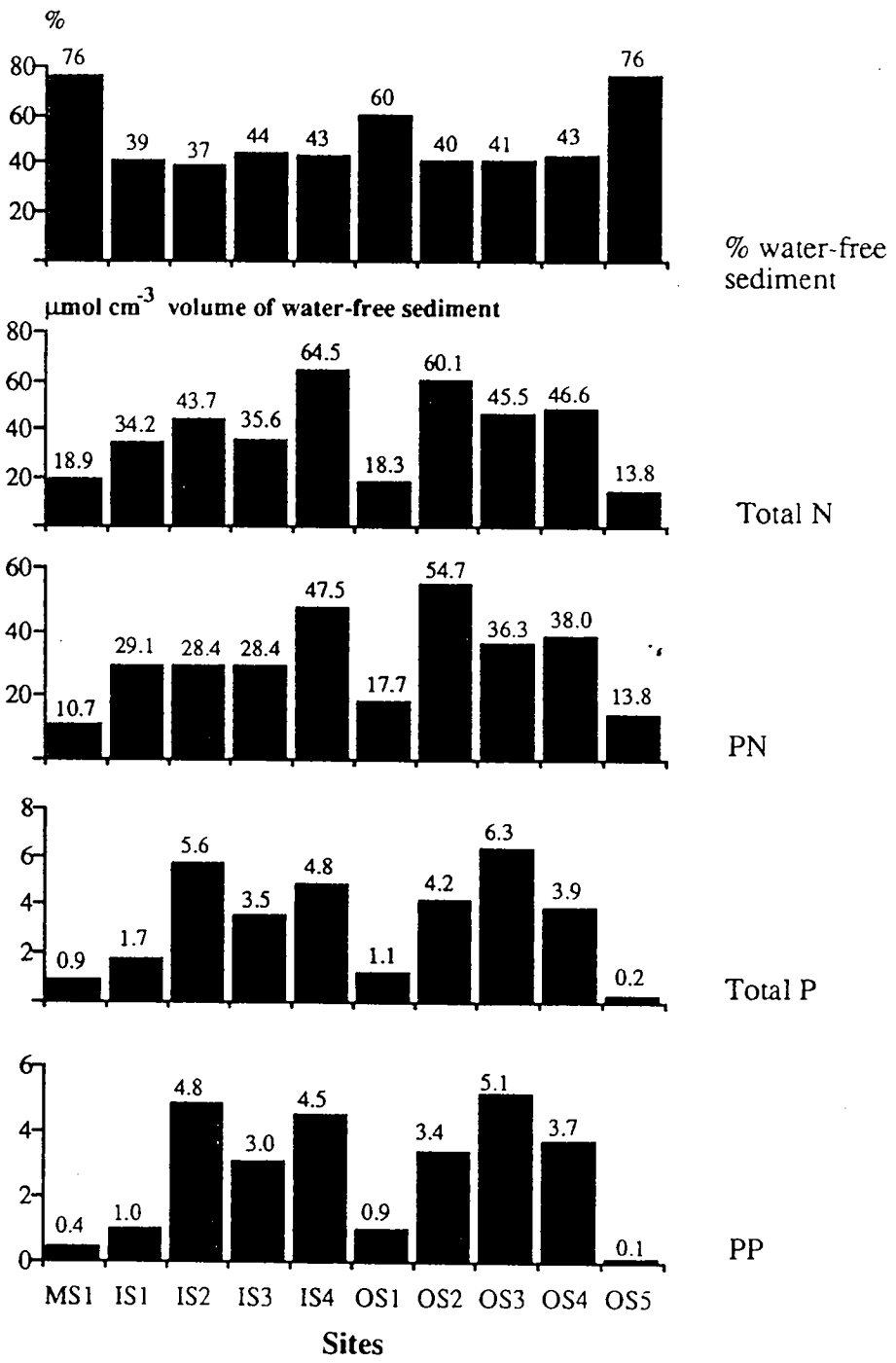


Figure 3.37 Amounts of individual nutrient species promptly released per volume (cubic cm) of water-free sediment.

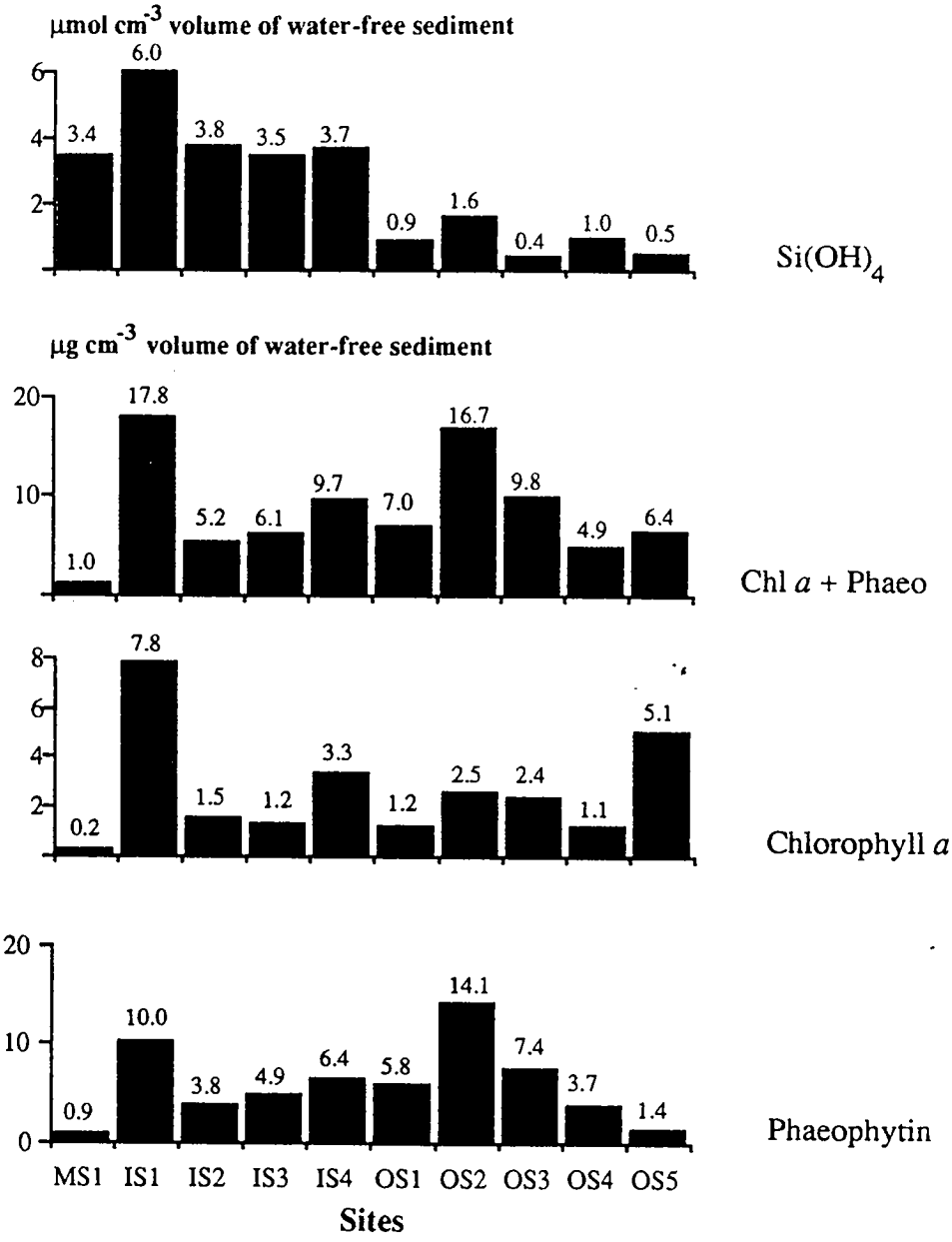


Figure 3.37 cont.

3.4 DISCUSSION

3.4.1 Nutrient releases as a result of shelf scale sediment resuspension

Simulated resuspension of GBR shelf sediments significantly increased concentrations of PN, NH_4^+, $NO_3^- + NO_2^-$, PP, PO_4^{3-}, $Si(OH)_4$, chlorophyll and phaeophytin in water samples. However, releases of several individual nutrient species (e.g. NO_2^-, NO_3^-, DON, DOP) from resuspended shelf sediments were not significant. The very small amounts of NO_2^- and NO_3^- in sediment made it difficult to detect when they were released and diluted into the water column. This may in part, reflect problems with chemical analyses or the variability of these nutrient species at the level of the sediment site, sediment subsample and/or water subsampling. As NO_2^- and NO_3^- concentrations in tropical marine waters tend to be very low and close to analytical detection limits, the chances of detecting such small changes is difficult. In the case of DON and DOP, the analytical methodology involves measurement of TDN and TDP, requiring the subtraction of separately determined concentrations of $NO_3^- + NO_2^-$ and PO_4^{3-} as required. The UV photo-oxidation method yields an average recovery of > 90% for the common DON reference materials (Walsh, 1989). However, there are deficiencies in the UV photo-oxidation method. Ammonium adsorbed on unfilterable small particles or colloids, would be included in the TDN analyses and thus be incorrectly interpreted is DON (Walsh, 1989). The UV photo-oxidation method also failed to measure certain organic N-compounds, such as urea and EDTA (D'Elia, 1983; Jackson and Williams, 1985; Antia *et al.*, 1991). Recalcitrant DON (containing N-N and N=N bonds compounds) which are known to exist in seawater, may also resist UV photo-oxidation (Walsh, 1989). The most likely problem with regard to detecting DON and DOP release from sediments relates to the existing natural high background DON and DOP concentrations. Those high levels make it difficult to detect comparatively small changes in DON or DOP concentration caused by sediment resuspension due to variability associated with their concentrations in the seawater, the sediment subsampling and the site levels.

It should be noted that the use of frozen sediment may inflate the apparent amount of nutrient release. Yamada *et al.* (1990) found that dissolved organic carbon and ammonia nitrogen in the interstitial water of frozen and thawed sediment from the upper layer of the sediment column (5 cm)was higher than that of the freshly collected sediment. Particulate NH_4^+ and NO_3^- pools can be extracted by freezing in liquid N_2 (Lomstein *et al.*, 1990). In addition, freezing may cause death of some proportion of sediment bacteria (Ingraham, 1962; Rheinhermer, 1991) and ruptures algal cells (Thoresen *et al.*, 1982).

Unfortunately, no experiments were conducted to directly check the effect of freezing of sediment on nutrient release. Intrepretation of amounts of nutrient released from sediment is therefore limited.

The absolute amounts of nutrients released from resuspended sediments and their relative balance differed between experiments 3 and 4 (Figures 3.26, 3.27, 3.31 & 3.32). Significant releases of total N, PN, chl *a* and total pigments were found from both experiments 3 and 4. PO_4^{3-} and total pigments were only found to be significantly released from experiment 3 (using sediment from sites IS1 and OS1) while DIN, NH_4^+, $NO_3^- + NO_2^-$, total P, PP, $Si(OH)_4$ were only found to be significantly released from experiment 4 (using sediment from sites IS2, IS3, IS4, OS2, OS3, OS4). This difference most likely occurred because the sediment sites used in these two experiments were different (see Table 2.1) and nutrient release is directly affected by the amount of nutrients in both the porewater and the solid-phase of the sediment. Amounts of nutrients associated with porewater and solid-phase sediment depend, in turn, on the type and grain size of the sediments (Aller and Benniger, 1981; Fisher *et al.*, 1982a). The differing results of the two experiments may therefore be explained by site differences in the amount of particular nutrient species suspended in porewater and bound to the solid-phase of the sediment .

It should be noted that the sediments used in experiments 3 and 4 were collected in different months (May and November, respectively, see Table 2.1). Both solid-phase and porewater nutrients in central GBR sediments are known to vary seasonally (Alongi, 1989c). Alongi (1989c) found that porewater PO_4^{3-} levels were higher in spring (October) than in summer (January) whereas concentrations of the other porewater constituents measured were either greatest in summer (NH_4^+, $Si(OH)_4$) or showed no significant difference between seasons (NO_3^-, NO_2^-). Finally, differences in the amounts of individual nutrient released in particular experiments are related to differing amounts of mass sediment added to the experimental bottles. Even though analysis of covariance were used to adjust for this effect, the masses of sediment in experiment 3 (approximately 0.7-0.9 g wet weight) and experiment 4 (approximately 2-3 g wet weight of sediments) differed by approximately 1-2 grams. As it was shown that the release of individual nutrient species did correlate to sediment weight resuspended in the water column (experiment 2), the higher amount of sediment resulted in a higher amount of nutrient release.

The resuspension of sediments has been shown to be an important mechanism to increased

suspended sediment, organic matter, nutrients and chlorophyll concentrations in the shallow water columns (e.g. Walker, 1981; Ullman and Sandstrom, 1987; Walker and O'Donnell, 1981; Fanning *et al.*, 1982; Hopkinson, 1987; Wainright, 1987, 1990). The experimental results presented herein clearly show that the resuspension of shelf sediments significantly contributes to nutrient stock in the water column.

3.4.2 Cross-shelf differences in nutrient release

The amounts of nutrients released did not strongly depend on sediment type. A pilot experiment (Experiment 3) comparing inner and outer shelf sediments indicated that chlorophyll *a* and total pigments were greater in surficial sediments on the inner shelf while significantly greater amounts of total P were released from outer shelf sediments.

The greater release of total P from the outer shelf sediment largely results from DOP release directly from the porewater. There is at present no data on DOP concentrations in GBR shelf sediment porewaters. Carbonate sediments are known to adsorb phosphate strongly (de Kanel and Morse, 1978). Preferential retention of P by binding to $CaCO_3$ is suggested as the reason for the higher solid phase P content of outer shelf sediments (Alongi, 1989c). Desorption of P from sediments in lakes (Froelich, 1988) and rivers (Chase and Sayles, 1980) is rapid. However, desorption processes in marine carbonate sediments are not well known.

After nine days of incubation, total P concentrations in the bottles with outer shelf sediment increased further over bottles with inner shelf sediment added. The increase was mainly due to increases in the PP fraction (from 1.3 μM on day 1 to 2.4 μM on day 9). However, the sources of P leading to the observed increases were not resolved.

Concentrations of $Si(OH)_4$ measured on day 9 were higher in seawater containing inner shelf sediment. Silicate concentrations are characteristically high in nearshore areas affected by river runoff since this nutrient is derived directly from weathered silicate minerals (Brodie and Mitchell, 1992) while higher $Si(OH)_4$ release fluxes from inner shelf sediment are derived from the $Si(OH)_4$ in porewater (Fanning and Schink, 1969; Fanning and Pilson, 1971). GBR shelf porewaters contain much higher concentrations of $Si(OH)_4$ than overlying water (Ullman and Sandstrom, 1987; Alongi, 1989c). Apart from porewater as a source, $Si(OH)_4$ can also be produced by the solution of biogenic silicate particles following resuspension, though this process is known to be slow.

3.4.3 Relationships between the magnitude of nutrient release and the mass of sediment

As might be expected, there was a linear relationship between the prompt release of most nutrient species measured in this study and the amount of sediment resuspended. The strength of these relationships varied among individual nutrient species. For most nutrients, both inner and outer shelf sediment produced similar magnitudes of nutrient release per unit weight of sediment. Exceptions occurred for suspended solids, PO_4^{3-}, phaeophytin and total pigments, for which the magnitude of nutrient released from outer shelf sediments was higher for a given weight of sediment added. In the case of suspended solids, this may be a direct result of the greater clay content of the outer shelf sediments (see Table 2.3). The total suspended solid concentrations produced were only 200- 500 mg l^{-1} while 4 gm of sediment was added to 2 litres of seawater. The heavier particles sank to the bottom of the containers resulting in a variety of relationships between sediment weight and suspended solid concentration in the jars. Phaeophytin and PO_4^{3-} are known to exist in higher quantities in outer shelf sediment (e.g. Alongi, 1989c).

Where the release of an individual nutrient species (DIN, NH_4^+, NO_3^- + NO_2^-, TDP, DOP, Chl *a*) did not correlate to sediment weight, the discrepancy was most likely the result of high variability in nutrient concentration within the sediment. Nutrients adsorbed to the solid-phase of sediments or dissolved in sediment porewater are not distributed homogenously but change with depth in the sediment (Ullman and Sandstorm, 1987; Alongi, 1989c). Vertical concentration profiles differ between individual nutrient species (Ullman and Sandstorm, 1987). Thus, mixing sediments from different depths will tend to obscure any simple linear relationship that may exist between sediment mass and nutrient concentrations. In addition, detection of funtional relationships between sediment resuspended and the amount of nutrients released is constrained when dealing with nutrient present at very low concentrations such as NO_3^- and NO_2^- and small scale variations in concentration between sediment sites. Analysis of linear correlation calculated from each sediment collection site (Appendix III) showed a wide range of correlation coefficient values (r^2).

3.4.4 Temporal changes in nutrient concentration following sediment resuspension events

Two approaches were used to assess the temporal changes in nutrient concentrations and speciation: point measurements made at the beginning (day 1) and end (day 9) of an

experiment (Experiments 3 & 4) and time-series measurements made at daily intervals over a period of a number of days (Experiment 1). Time-series measurements of temporal changes in nutrient concentrations showed that the pattern of daily changes in individual nutrient species and pigment concentrations, are not consistent differing both between the control and experimental bottles and between individual trials. Concentrations of particulate (PN and PP) and organic nutrients (DON, DOP) were in most cases, relatively stable. Dissolved inorganic nutrients (NH_4^+, NO_3^-, NO_2^-) concentrations fluctuated erratically. Concentrations of PO_4^{3-} tended to decrease through time. The results of most time series incubations indicated that after an initial increases in nutrient concentrations caused by the resuspension of sediment, nutrient concentrations varied little over the following few days (1-4 days) when compared to the concentration measured immediately after the sediment resuspension. Measurements of nutrient concentrations immediately after the passage of a cyclone are logistically difficult to make. The results obtained in experiment 1 indicate that water sampling up to a few days after a massive sediment resuspension event may yield nutrient concentrations that are representative of that event.

As pattern of temporal changes in nutrient concentration and speciation immediately following cyclonic events in the GBR are not known, experimental investigation of temporal changes of nutrient concentrations and speciations under sediment resuspension provided a view of nutrient concentrations and speciation in water column and of how long pronounced cyclonic effects might persist. In the experiments where nutrient concentrations were measured on day 1 vs day 9, nutrient concentration and speciation of some species, changed significantly. The degree of temporal change was greatest in the bottles with added sediment. The pattern of changes in nutrient concentrations also varied between inner and outer shelf sediments. Even though significant changes in concentration of nutrients may be detected for 9 days, point measurements on day 9 could not provide the whole complex changes following resuspension events and detailed of temporal dynamics remain unresolved.

3.4.5 Nutrient release and cyclone disturbance

It is known that cyclones and other large storms can affect oceanographic processes, sediments and water column nutrient levels over wide areas (Furnas, 1989). As GBR waters have not been sampled immediately after the passage of a cyclone, concentrations of nutrients and chlorophyll promptly released from the sediment are still unconfirmed. In order to estimate the quantity of nutrients which might be released as a result of resuspension during a cyclone, the experimental measurements of nutrient release from

stirred inner, mid and outer shelf sediments in this study can be applied. Cyclone "Winifred" has been chosen as an example because of the body of pre- and post cyclone nutrient data.

Cyclone "Winifred" crossed the North Queensland shelf on 1 February 1986, resulting in abrupt, short-lived changes in the nutrient status of the water column (Furnas, 1989). Salinities, sub-surface light intensities, dissolved nutrient concentrations and chlorophyll concentrations in the water column were measured at stations across the shelf a few days after and one year after cyclone "Winifred". Two sets of stations in the area which was directly affected by the cyclone are shown in Figure 3.38. Representative hydrographic, chlorophyll and dissolved nutrient profiles from the cross-shelf transect in the cyclone affected area are compared to profiles which would normally be observed in the central GBR during summer (Figure 3.39).

Sub-surface light penetration after the cyclone was sharply reduced due to the suspension of fine sediment particles. Near-surface salinities measured at nearshore stations decrease due to dilution with fresh water. Concentrations of ammonium, nitrate and nitrite increased when compared to their concentrations measured under normal conditions. The observed increases in dissolved nutrients were hypothesized to result from enhanced river runoff, rainfall, porewater from resuspended sediment (Furnas, 1989) and Coral Sea intrusion (Furnas *et al.*, 1993).

The magnitude of nutrient release from sediment is related to the concentration of nutrients in porewater which usually varies with the depth in the sediment (e.g. Ullman and Sandstrom, 1987; Alongi, 1989c). For most nutrient species, greater amounts of sediment resuspension were coupled to greater amounts of nutrients being released into the water column. Before estimates of total nutrient release can be calculated, it is necessary to estimate the amount of sediment that is resuspended after a cyclone. The available data on sediment volumes reworked during cyclone "Winifred" were presented by Gagan *et al.* (1990). Gagan *et al.* (1990) estimated the thickness of the cyclone-disturbed layer in the mid-shelf (between 17° 15' - 17° 40' latitude) using the depth of erosion, while in inner shelf areas the change in the activity of ^{210}Pb sediment profiles were used. There is considerable spatial variation in erosion depth between adjacent sites which is likely to be due to local redistribution of the coarse sand fraction. The erosion depth in the mid lagoon ranged from 0.6-14.4 cm (n = 8 sites) while on the inner shelf, the range was 0 cm to 14 cm (n = 7 sites). As there was sediment sampling on outer shelf, I therefore used two sites which outside the 40 m isobath in Gagan *et al.*'s (1990)

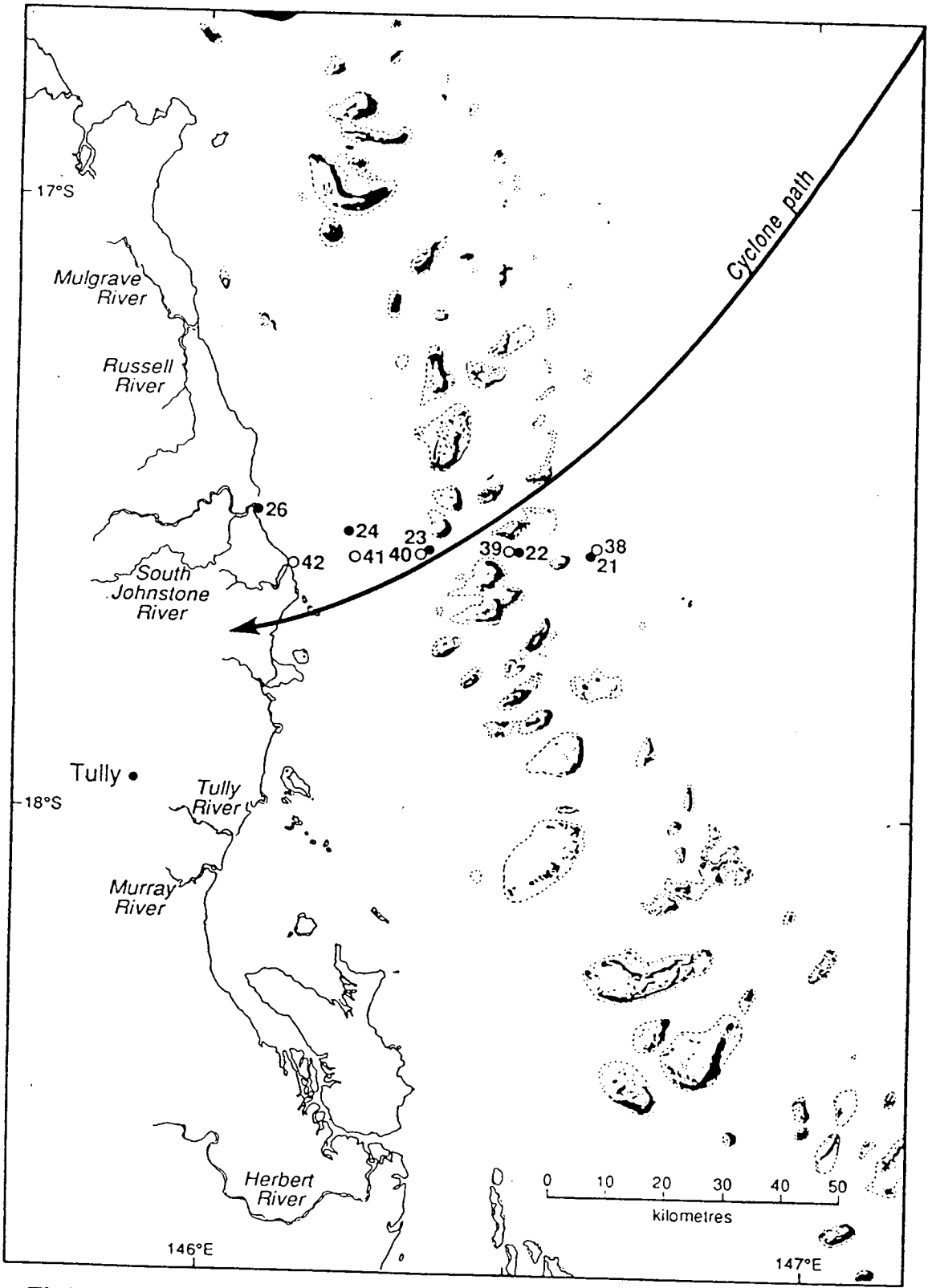


Figure 3.38 The path of Cyclone "Winifred" showing water stations closed to its path and sampled a few days following cyclone RWinifredS (●) and during normal summer time (O).

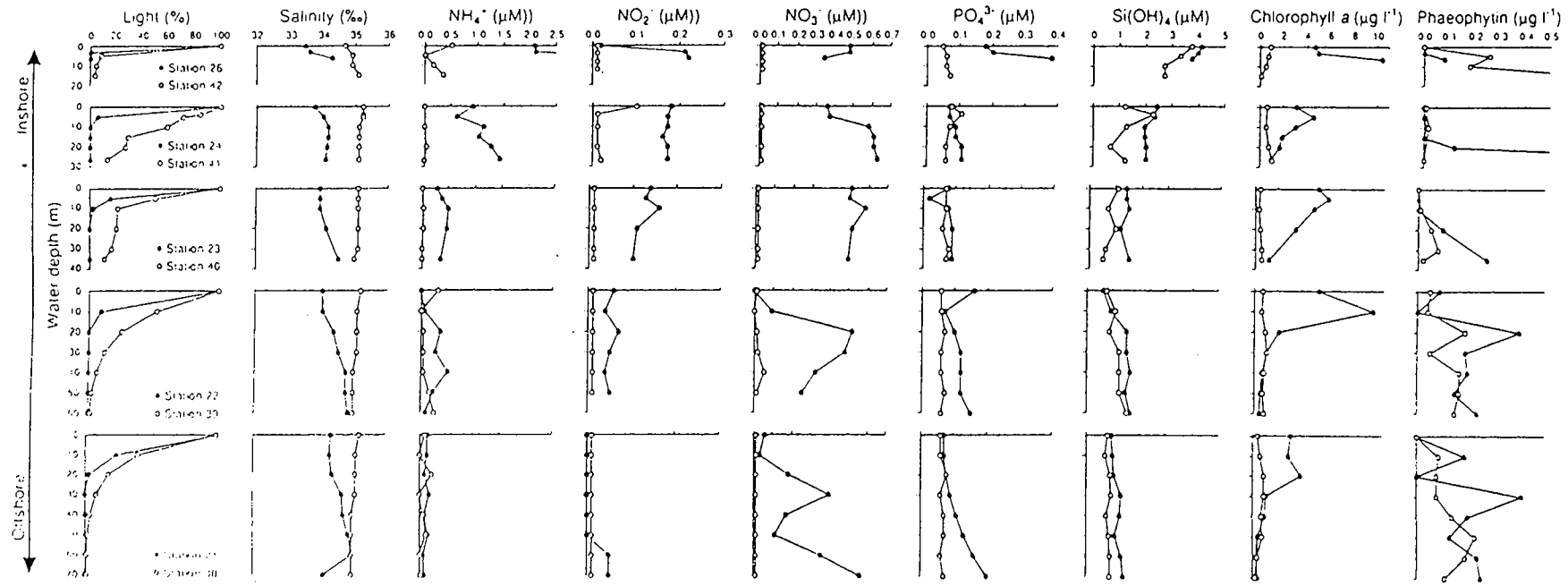


Figure 3.39 Vertical profiles of percent surface light, salinity, nutrients and chlorophyll in the water column at stations across the shelf (see Figure 3.38), measured 4 days after cyclone "Winifred" (●) and one year later (O), under summer conditions (data from M. Furnas and A. Mitchell, unpub. data)

study to provide a first-order estimate of a storm related erosion depth for outer shelf area (0.6 - 11 cm, n =2 sites).

According to Gagan *et al.*'s (1990) analysis, the sediment with the inner, mid and outer shelf areas was, on average, eroded to mean depth of 5.1 (n = 7 sites), 6.9 (n = 8 sites) and 5.8 (n = 2 sites) cm, respectively. Table 3.5 presents an estimate of the amounts of nutrient species which would be released from a cross-shelf strip of sediment based on resuspension to these depth, 1 metre wide. The estimated volume-averaged concentrations of nutrients released promptly into the water column (volume 2258.4 Ml for the cross shelf strip) due to sediment resuspension are based on the total amount of nutrient released from the cross shelf strip. The calculations show that benthic nutrients are mainly released in particulate form: PN and PP. In particular, the initial PN concentration for shelf waters estimated is very high (17 μM). Unfortunately, PN and PP concentrations were not measured in the water column after cyclone "Winifred" to confirm this estimate. Ammonium was the main source of dissolved inorganic nitrogen released from the resuspended sediment. Most of the pigments are in the degraded forms of phaeophytin, which would be typical of detritus.

These estimated post-cyclone nutrient concentrations produced as a result of prompt release during resuspension are considerably higher than the depth-weighted mean water column concentrations of nutrients measured on the same cross-shelf transect (Stations 38-42: Figure 3.38) under normal summer conditions (Table 3.6). For comparative purposes, non-cyclone PN and PP concentrations were averaged from other stations measured elsewhere in the central GBR. Estimates of nutrients released from the sediment showed that PN, PP, NH_4^+, NO_3^- and PO_4^{3-} were 9, 11, 13, 4 and 4 times greater than mean concentrations occurring during normal summer conditions. In particular, the very large amounts of PN and PP injected into the water column would be important sources of N and P for remineralization processes resulting in further production of NH_4^+ and PO_4^{3-}. Sediment resuspension did not lead to increased concentrations of DON, DOP, NO_2^- and chl *a*. Only slight increases in $Si(OH)_4$ (1.7-fold) and phaeophytin (1.5-fold) as a result of the resuspension event are indicated.

Some of the increase in nitrate in outer shelf waters may be a result of intruded Coral Sea water which coincided with occurrence of a cyclone (Furnas *et al.*, 1993). Most of the N inputs from intrusions are in the form of nitrate (50 percent). Using the data of N inputs to outer shelf water in central GBR region from intrusion during the summer of 1990-91, Furnas *et al.* (1993) calculated that about 20.15 Mmoles of NO_3^- were intruded in the

Table 3.5

Estimated amounts of nutrients released as a result of resuspension of inner-, mid- and outer shelf sediments by cyclone Winifred (1986) in the central GBR, for a 1 metre wide transect across the shelf at approximately 17° 30' latitude.

	Inner shelf sediment	Mid-shelf sediment	Outer shelf sediment	Total
Average depth of sediment resuspended	5.1 cm	6.9 cm	5.8 cm	
Cross-shelf distance	9 km	26 km	22.64 km	57.64 km
Integrated water volume of transect				2258.4 Ml
Nutrient species	kmole	kmole	kmole	µmol l^{-1}
Total N	8.92	26.44	19.90	24.47
PN	6.77	14.59	17.89	17.38
TDN	2.16	11.85	2.01	7.10
DON	1.68	8.76	1.11	5.11
DIN	0.50	3.09	0.90	1.99
NH_4^+	0.47	2.91	0.84	1.87
NO_3^-	0.02	0.18	0.05	0.11
NO_2^-	0.01	0.00	0.01	0.01
Total P	0.71	1.16	1.65	1.56
PP	0.64	0.58	1.52	1.22
TDP	0.07	0.58	0.13	0.35
DOP	0.00	0.00	0.01	0.00
PO_4^{3-}	0.10	0.58	0.12	0.36
$Si(OH)_4$	0.88	4.67	0.58	2.71
	kg	kg	kg	µg l^{-1}
Total pigments (Chl. *a* + Phaeo.)	2.09	1.40	4.84	3.69
Chlorophyll *a*	0.76	0.23	0.90	0.84
Phaeophytin	1.33	1.17	3.94	2.85

Table 3.6

A comparison of estimated concentrations of nutrient released as a result of resuspension of shelf sediments, with depth-weighted water column concentrations of nutrients averaged in a cross-shelf transect (Stations 38-42: Figure 3.38) during normal summer conditions. Normal PN and PP concentrations were calculated from values averaged from other stations in the central GBR as PN and PP data from the transect stations were not available.

	Estimated amounts of nutrient concentration after prompt release	Mean concentrations of nutrients measured under normal summer conditions	Ratio
Nutrient species	µmol l^{-1}	µmol l^{-1}	
Total N	24.47	6.71	3.6
PN	17.38	1.98	8.8
TDN	7.10	4.73	1.5
DON	5.11	4.55	1.1
DIN	1.99	0.18	11.1
NH_4^+	1.87	0.14	13.4
NO_3^-	0.11	0.03	3.7
NO_2^-	0.01	0.01	1.0
Total P	1.56	0.61	2.6
PP	1.22	0.11	11.1
TDP	0.35	0.50	0.7
DOP	0.00	0.40	-
PO_4^{3-}	0.36	0.09	4.0
$Si(OH)_4$	2.71	1.58	1.7
	µg l^{-1}	µg l^{-1}	
Total pigments (Chl. *a* + Phaeo.)	3.69	2.94	1.3
Chlorophyll *a*	0.84	1.08	0.8
Phaeophytin	2.85	1.86	1.5

water column volume of 197 km^3. According to their calculation, intruded waters contributed about 0.10 μM of NO_3^- increasing in water column. At almost all stations sampled across the shelf, much larger increases in nitrate concentration (average 0.4 μM) were observed as compared to the concentrations measured in normal summer time (0.15 μM)(M. Furnas and M. Mitchell, pers. comm.). Resuspended sediment contributed 0.11 μM of NO_3^- in the water column (Table 3.5). Therefore, there must be another source of increasing nitrate. The additional increases in nitrate observed likely occur via microbial-mediated nitrification. An attempt to quantify these processes is given in more detail in Chapter 4. Concentrations of PO_4^{3-} and $Si(OH)_4$ also increased with the magnitude of the increase declining as one moved offshore. Estimated inputs of PO_4^{3-} from intruded water were small (0.03 μM, as estimated from Furnas *et al.*, 1993's data) when compared to the amount of PO_4^{3-} (0.36 μM) derived from sediment resuspension process. Very high concentrations of chlorophyll *a* and phaeophytin were observed in surface waters across the shelf.

Marine sediments act as a storage reservoir of nutrient materials which exchange with the water column (Smith *et al.*, 1981; Val Klump and Martens, 1983). Results obtained in this study show that nutrient releases occurring during sediment resuspension events can be an important mechanism for returning nutrient stocks stored in the benthos back to the pelagic zone. By transferring nutrients from a benthic reservoir, sediment resuspension events actively contribute to increased primary production in the water column. (Fanning *et al.*, 1982). Results in this study showed that chlorophyll were increased following the resuspension of sediment. Increase in chlorophyll concentrations following storms were also observed in temperate regions (Zubkoff and Warinner, 1976; Loftus and Seliger, 1977; Zeeman, 1985).

Regenerated nitrogenous nutrients are regarded as the major source of nitrogen for oceanic primary producers (e.g. McCarthy, 1972; Eppley *et al.*, 1973; McCarthy *et al.*, 1977; Harrison, 1978; Glibert, 1982). The supply rate of "new" nitrogen ultimately determines the total amount of exportable production from particular systems. Benthic nitrogen regeneration has been shown to supply a major portion of phytoplankton N demand in some coastal environments (e.g. Nixon *et al.*, 1976; Blackburn and henriksen, 1983). Cyclonic resuspension of sediment are shown herein to be an important, though episodic, regional-scale contributor of nutrients to the pelagic system. Cyclonic events can resuspend sediments over the whole width of the shelf when compared to resuspension by the other processes (e.g.wind induced wave). Cyclones release nutrient not only from the wider area of sediment, but also from the deeper sediment. Cyclonic events

potentially stir the "new" nutrient in the deeper sediment back into the water column while the other processes could not.

Dissolved nutrients which are immediately returned back to water column would be used up by phytoplankton directly. Particulate nutrients which are remineralized to dissolved forms can be supplied to maintain the ongoing primary production in the water column. The water column remineralization of particulate nutrients which are a large part of nutrient releases is important as it supplies the nutrient after the cyclonic resuspension events.

Passing close to the central GBR coast approximately twice a year on a long-term average, cyclones and their associated strong winds stir sediments over an area in the order of several 1000's of km^2. Within a few days of cyclone "Winifred", a pronounced phytoplankton bloom with 3-fold higher levels of chlorophyll than normally observed in GBR waters (approximately 1 $\mu g\ l^{-1}$), had developed throughout the disturbed area. The significant input of nutrients from the sediment clearly contributed to the phytoplankton nutrient requirement as enhanced growth of the phytoplankton occurred within 2-3 days after the nutrient input (Furnas, 1989).

3.4.6 Contribution of nutrients from sediment resuspension to the shelf water

Phytoplankton biomass levels in GBR waters are normally nitrogen-limited (Furnas and Mitchell, 1986b). Levels of organic carbon, total nitrogen and total phosphorus in GBR shelf sediments are low compared to temperate shelf sediments (e.g. Tenore *et al.*, 1984; Aller *et al.*, 1985; Hopkinson, 1987). Alongi (1989c) has suggested that detrital inputs also appear to be low.

During calm conditions, nutrient fluxes from the sediments (Ullman and Sandstrom, 1987; Hansen *et al.*, 1987; Alongi, 1989c) and levels of bioturbation by infauna (Alongi, 1989c) in the central GBR are low compared to temperate benthic environments (e.g. Rhoads *et al.*, 1985; Yingst and Rhoads, 1985). Benthic nutrient fluxes in calm weather (Alongi, 1989c) are estimated to contribute 13 % of the annual N and 24 % of the annual P requirements of planktonic primary producers on the central shelf.

In GBR waters, nutrients derived from episodic cyclones contribute substantially to phytoplankton primary production. Primary production measured in central GBR shelf waters under normal conditions ranged between 129 and 1972 mg C $m^{-2}\ d^{-1}$ with an

overall mean of 620 mg C m^{-2} d^{-1} (Furnas and Mitchell, 1987). At a mid-shelf site (60 m) the mean was 509 $\pm$ 229 mg C m^{-2} d^{-1}. Using the Redfield ratio (C:N:P = 106:16:1) (Redfield, 1958), carbon production can be converted into nitrogen and phosphorus demand. When calculating the nutrient input by a cyclonic event, however, it is necessary to assume that the rate of these nutrient inputs occur in one day. Using the Redfield ratio and the assumption of a one day period of nutrient input, the estimated dissolved inorganic nitrogen and phosphorus promptly mixed into the water column by cyclonic resuspension can be estimated to add approximately 13 and 90 times more N and P, respectively than would be required by the daily demand under normal conditions. However, the production rate, and hence nutrient demand, increase exponentially with phytoplankton growth. Water column production rates measured at two sites one week after the disturbance of the GBR shelf by cyclone "Winifred" were 3400 and 4300 mg C m^{-2} d^{-1} (Furnas and Mitchell, 1988), respectively. With the nutrients provided, in part, by sediment resuspension, post-cyclone primary production rates were 6 to 8 times greater than the primary production measured under normal condition. By comparison with the maximum post-cyclone primary production rate (4300 mg C m^{-2} d^{-1}), dissolved inorganic N and P released from sediment resuspension still provided 2 and 11 times more N and P than the daily demand prior to the cyclonic event. However, enhanced nutrient levels from cyclones as generally limited to a short time periods (< 2 weeks) (Furnas, 1988; Liston, 1991). This indicates that phytoplankton are able used up to these large amounts of nutrient within a short time. Phytoplankton populations are able to taken nutrient rapidly (Goldman *et al.*, 1981; McCarthy *et al.*, 1984) and grow at rapid rates (> 1.5 doublings day^{-1}at normal nutrient levels; Furnas, 1988). As a result changes in pelagic biomass in the GBR remain nutrient, rather than kinetic limited.

Nutrient inputs to GBR shelf waters are derived from a number of sources. In the first instance, nitrogen and other nutrients derived in terrestrial runoff is largely restricted to the nearshore zone (Wolanski and van Senden, 1983). New nutrients in outer shelf waters are mainly derived from shelf break intrusion processes such as upwelling (e.g. Andrews and Gentien, 1982; Furnas *et al.*, 1993) over short time intervals. During normal conditions, nutrient stocks stored in the deeper sediments of shallow waters and deeper water shelf sediments, cannot readily recycle back to the water column. The resuspension of sediment by cyclones which pass through the central GBR region would therefore have a significant effect by remobilizing these nutrients from the less-often disturbed sediment back into the water. The definition of "new" production by Dugdale and Goering (1967) is that incremental primary production is associated with newly-available nitrogen or other nutrients. These less-often returned nutrients in the deeper

sediment to the water column which are episodically injected into the water column by cyclones can be provisionally considered as "new" nutrient sources to the pelagic system. Therefore, even though cyclones are a episodical source compared to other physical disturbances, it can provide a form of "new" nitrogen to the GBR water column.

Nutrient inputs from Coral Sea water due to upwelling is another episodic source which contribute to the shelf production. To date, evidence showed that occurrence of upwelling coincided with cyclonic event was not in a larger scale than that occur in other time (Furnas *et al.*, 1993). However, abnormally high nutrient concentrations measured in shelf waters following cyclonic event have not been recorded during upwelling phenomena in GBR area. Therefore, it can be implied that cyclone provide conditions for contributing nutrient and primary production in shelf scale. The new production creates the possibility of increased secondary and higher levels of production. The trophic status of a marine ecosystem is generally determined by the rates of introduction of new nitrogen (Glibert, 1988). The episodic supply of the nutrients by cyclones may be a regional contributor, recycling nutrient stocks stored in the deep layer of sediments back to the pelagic system. Cyclones are therefore an integral part of the GBR ecosystem which maintain the ongoing primary productivity of this region.

3.5 CONCLUSIONS

1. In most cases, the temporal changes in nutrient concentrations and speciation in water affected by a simulated resuspension event differed from water without resuspended sediment. Following prompt releases of nutrients by sediment resuspension, time-series experiments indicated that subsequent changes in concentration and speciation for 1-4 days were modest. As a consequence, measurements of nutrient concentrations in seawater for periods up to 1-4 days after a sediment resuspension event, should still represent the characteristics of the water column after a cyclonic event in terms of dissolved nutrient concentration and speciation.

2. The amounts of most nutrient species released from sediments were correlated with the amount of sediment resuspended into the water column. However, some individual nutrient species did not respond in the same pattern. This is most probably due to the patchy distribution of NH_4^+, NO_2^-, DOP in the sediments and the variability between sediment sites.

3. Variability in the amounts of nutrients released from sediment subsamples and the resulting concentrations in seawater occurred at a range of scales, from small scale effects related to water and sediment sampling (sediment subsamples within one grab) up to regional geographical scales (sites within shelf areas). The differences between the relative abundances of individual nutrient species and concentrations found in individual experiments are likely to be the result of the differing amounts of sediment used, the differences between porewater or solid-phase nutrients at each sediment site and possibly unresolved seasonal differences in sediment composition.

4. Resuspension of shelf sediments can contribute significant amounts of total nitrogen, particulate nitrogen (PN), ammonium (NH_4^+), pool of nitrate plus nitrite ($NO_3^- + NO_2^-$), total phosphorus, particulate phosphorus (PP), dissolved inorganic phosphorus (PO_4^{3-}), silicate ($Si(OH)_4$), chlorophyll *a* and phaeophytin to the overlying water column of the GBR shelf.

5. Statistically significant releases of dissolved organic nitrogen (DON), nitrate (NO_3^-), nitrite (NO_2^-), dissolved organic phosphorus (DOP) from resuspended sediment into the water column were not detected. The analytical sensitivity of analytical methods for oxidized nitrogen relative to small amounts released and low concentrations of NO_3^- and NO_2^- in porewater of sediment made changes difficult to detect. The high background levels for DON and DOP and variability of their chemical analyses by UV photo-oxidation method made it difficult to detect significant releases from the sediment. Variability associated with the concentrations in water, sediment subsampling and site levels adds to the problem and makes it difficult to detect the difference between particular experimental treatments.

6. With the exception of chlorophyll *a* , total pigments and total phosphorus, the quantities of individual nutrient species released from inner and outer shelf sediments were not significantly different. Greater levels of chlorophyll *a* and total pigments were released from inner shelf sediment than from outer shelf sediment. In contrast, more total phosphorus was released from outer shelf sediment, most likely because of the higher total phosphorus content of outer shelf sediment.

CHAPTER 4

TRANSFORMATIONS OF NITROGENOUS NUTRIENTS AND THE EFFECT OF CYCLONES

4.1 INTRODUCTION

It has long been recognised that nitrogen plays a central role in the nutrient dynamics of marine phytoplankton communities (reviewed by Glibert, 1988). Standing stocks of nitrogenous nutrients in coastal (e.g. Ryther and Dunstan, 1971; McCarthy *et al.*, 1977; Andrews, 1983); oceanic (e.g. Eppley *et al.*, 1973; Eppley and Peterson, 1979) and tropical shelf waters (e.g. Furnas and Mitchell, 1986b; Furnas *et al.*, 1990) are usually insufficient to support primary production rates for more than short periods. The cycling of nitrogen is, therefore, an important factor in the regulation of primary production.

Marine phytoplankton biomass is generally held to be limited by the amount of nitrogen available (Ryther and Dunstan, 1971, but see Smith 1984); however, the nature and extent of nitrogen limitation is avidly debated (Hecky and Kilham, 1988). In tropical shelf systems such as the GBR, nitrogen appears to limit phytoplankton biomass (Furnas and Mitchell, 1986b). Concentrations of dissolved inorganic nitrogen (ammonium, nitrate, nitrite) in GBR waters are normally low (e.g Ikeda *et al.*, 1980; Furnas and Mitchell, 1984), therefore additional inputs of nitrogen are important to the nitrogen dynamics of these waters. Owing to their central position in the transformation process, the recycling dynamics of ammonium, nitrite and nitrate are of importance in developing an understanding of the marine nitrogen cycle. Measurement of concentrations of these nitrogenous species is a relatively straightforward procedure. However, concentration measurements only describe an instantaneous state, without depicting the processes taking place within a system. More important is estimating the rates for uptake or transformation of these species, since this information permits a description of the dynamics of the system in question.

Higher concentrations of dissolved inorganic nitrogen are episodically found in the GBR due to intrusions of nutrient-enriched Coral Sea water (Andrews and Gentien,

1982; Furnas and Mitchell, 1986b) and after cyclonic events (Furnas, 1989). The observed increase in dissolved nitrogen concentrations after cyclone "Winifred" could not all be solely attributed to inputs from rainfall, porewater, remineralization process of organic nitrogen from resuspended sediment, river runoff (Furnas, 1989) or upwelling (Furnas *et al.*, 1993). Under normal conditions, the main source of nitrite in oxygenated water is through ammonium oxidation (Brandhorst, 1959; Olson, 1981a). However, following extreme storm conditions, higher than expected concentrations of nitrate and nitrite were measured (Furnas, 1989). It is believed that these higher concentrations resulted from enhanced nitrification, occurring after large amounts of ammonium from sediment porewaters were mixed into the water column. In support of this, simulated resuspension events (Chapter 3) demonstrated that nitrogen dynamics were characterized by decreases in ammonium while nitrate and nitrite increased.

Recent studies of nitrogen dynamics have emphasized the need to consider the full range of transformation processes operating in order to understand the balance between nitrogen fluxes and availability in a given system (Glibert *et al.*, 1982; Lipschultz *et al.*, 1985; Olson, 1981a; McCarthy *et al.*, 1984). Nitrogen transformation rates in shelf waters of the GBR have not been measured except in reef water (Ikeda *et al.*, 1982; Hopkinson *et al.*, 1987; Capone *et al.*, 1992). Two nitrogen transformation processes which would occur in seawater after a cyclonic disturbance event were investigated in this present study: 1) enhanced nitrification which was presumed to occur in GBR waters after cyclonic events (as suggested by the very high post-cyclone nitrate and nitrite concentration observed) and 2) uptake of dissolved inorganic nitrogen in water (ammonium, nitrite and nitrate). Fundamental information of nitrification and nitrogen uptake in the water column are briefly reviewed. As the methodology needed to address these aims is complex and required initial experimental work, the following section describes the methodologies involved.

4.1.1 Nitrification

Nitrification processes in the marine environment have been extensively reviewed by Kaplan (1983) and Henriksen and Kemp (1988). The biochemistry and physiology of nitrification have been covered in a number of reviews (Painter, 1970; Aleem, 1970; Kelly, 1971; Suzuki, 1974; Hooper, 1978). Briefly, nitrification occurs in two steps: primary and secondary (Kaplan, 1983). Primary nitrification is defined as the oxidation of ammonium to nitrite by bacteria. Secondary nitrification is the oxidation

of nitrite to nitrate (reviewed by Painter, 1970; Focht and Verstraete, 1977; Kaplan, 1983). The organisms capable of mediating these oxidations include both chemoautotrophs and heterotrophs. The bacterial genera *Nitrosomonas* and *Nitrobacter* are the principal organisms responsible for primary and secondary nitrification, respectively. The metabolic activity and growth rate of nitrifying bacteria are influenced by temperature (Berounsky and Nixon, 1990), pH (Jones and Hood, 1980), light (Horrigan *et al.*, 1981; Olson, 1981b; Ward, 1985), concentrations of ammonium, nitrite (Carlucci and McNally, 1969; Focht and Verstraete, 1977; Olson, 1981a; Berounsky and NIxon, 1990; Ward, 1985), and oxygen tension (Helder and de Vries, 1983).

The various techniques available for measurement of nitrification have been described (Schell, 1978; Kaplan, 1983). Briefly, four methods have previously been used to estimate or measure nitrification rates in marine water and sediment samples. They are 1) counts of nitrifying organisms (e.g. Ardakani *et al.*, 1974; Curtis *et al.*, 1975; Belser and Schmidt, 1978; Belser and Mays, 1980); 2) estimation of nitrogenous nitrogen production by measurement of changes in the concentrations of ammonium, nitrite or nitrate (e.g. Wafar *et al.*, 1990; Webb and Wiebe, 1975); 3) indirect measurement by dark anaplerotic[7] bicarbonate uptake attributed to nitrifying bacteria (e.g. Billen, 1975, 1976; Hall, 1982; Owens, 1986) and 4) direct measurements using nitrogen stable isotopes (e.g. Koike and Hattori, 1978b; Horrigan *et al.*, 1981; Olson, 1981a & b; Lipschultz, 1984; McCarthy *et al.*, 1984; Delaune and Smith, 1987).

Estimation of nitrification rates from counts of nitrifying organisms requires the use of specific nitrification activities determined in laboratory experiments using pure or enriched cultures (Ardakani *et al.*, 1974; Curtis *et al.*, 1975). The major shortcoming of this approach is that the influence of environmental factors on the activity of micro-organisms is not fully taken into account.

For this study, the remaining three methods listed above for measuring nitrification rate were chosen and will be discussed in more detail.

[7]Anaplerotic means filling up the Tricarboxylic acid (TCA) cycle with C4-compounds which are lost for synthesis.

a) Nitrification as estimated through net changes in ammonium, nitrite and nitrate concentrations

Estimations of nitrifying activity have been made by following net NO_2^- and NO_3^- production *in situ* (Webb and Wiebe, 1975; Wafar *et al.*, 1990). Unfortunately, this technique has a very low sensitivity and requires long incubation times (≥ 1 day). As a result, this procedure has the disadvantage that the rate obtained may not closely reflect rates under natural conditions. To circumvent this problem, Schwert and White (1974) proposed the use of an equilibration chamber incubated *in situ*, however, such a procedure remains experimentally tedious.

b) Nitrification as estimated by inhibitor sensitive dark ^{14}C-bicarbonate uptake

An alternative approach for estimating nitrification rates has been through measurement of dark (anaplerotic) ^{14}C-bicarbonate incorporation with and without specific nitrification inhibitors (e.g. Billen, 1976; Somville, 1978). While indirect, this approach has been used widely in terrestrial and aquatic systems as it is technically simple. An obvious advantage is that the N-substrates (e.g ammonium) can be maintained under near *in situ* concentrations during the incubation.

As it is believed that most nitrifying bacteria are obligate autotrophs (Painter, 1970) the incorporation of bicarbonate must play an important role in their metabolism. Secondary nitrification (nitrite oxidation) is known to be inhibit by light (e.g. Olson, 1981b; Lipschultz *et al.*, 1985). An underlying assumption behind the ^{14}C method is that there is a constant stoichiometric ratio between the ammonium oxidation rate and the bicarbonate uptake rate for a given species of nitrifier or assemblage of nitrifiers. Nitrification rates derived using the ratio of dark C uptake and nitrifying activity (expressed as oxidized nitrogen) were found to be consistent with measurements of NO_3^- concentration profiles in sediments (Billen, 1976) and with net NO_3^- production in water samples (Somville, 1978). However, Hall (1984) has questioned whether these ratios are constant. Various carbon uptake to nitrogen oxidation ratios have been presented, ranging between 0.01 and 0.18 moles of CO_2 reduced per mole of NH_4^+ oxidized and between 0.0022 and 0.04 moles of CO_2 reduced per mole of NO_2^- oxidized (Billen, 1976; Somville, 1978). To consider whether the dark ^{14}C uptake method can be used to reliably estimate nitrification rates, a direct comparison of methods was conducted by Enoksson (1986), who concluded that there was close

agreement between the rates estimated with the dark ^{14}C uptake method and with a $^{15}NO_3^-$ isotopic dilution method. Because of the range of carbon uptake to ammonium oxidation ratios, the estimation of nitrification rates by the dark ^{14}C uptake method remains controversial. Direct comparisons of ammonium and nitrite oxidation rates using the ^{15}N technique with measurements the ^{14}C method are therefore desirable.

A number of bacterial metabolic processes contribute to dark bicarbonate incorporation. To estimate the nitrification rate from dark ^{14}C-bicarbonate incorporation rates, a specific inhibitor of nitrifying activity is added. The difference between ^{14}C-bicarbonate incorporation measured in control samples and samples treated with inhibitors is used to estimate the nitrification rate (e.g. Goering, 1962a & b; Billen, 1976; Somville, 1978). Chemoautotrophic nitrification is inhibited by a number of specific chemical compounds. These compounds and their mode of action have been reviewed by Hauck (1980) and Henriksen and Kemp (1988). Nitrapyrin {2-chloro-6 (trichloromethyl pyridine; trade name: N-serve, Dow Chemical} is the most widely used. The effectiveness of this compound was first demonstrated by Goering (1962a & b) and has been confirmed by several soil studies (Bundy and Bremner, 1973, 1974; Bremner *et al.*, 1978). N-serve inhibits oxidation of ammonium to hydroxylamine by the nitrifying bacteria *Nitrosomonas* (Campbell and Aleem, 1965). However, doubt remains about its specificity (Billen, 1976; Ward, 1984) and efficiency in marine samples. An operational complication is that N-serve is only soluble in polar organic solvents (acetone, ethanol etc.) which may affect ^{14}C-bicarbonate incorporation (Henriksen, 1980; Hall, 1984; Hauck, 1980). However, Enoksson (1986) reported that the solvent carrier (ethanol) had no effect in blocking the nitrification process. The water soluble N-serve derivative "Hach2533" (Hach Chemical Company; Iowa, U.S.A.) is bonded onto an inorganic salt which serves as a carrier. "Hach2533" was considered for use in order to diminish the solvent effect in N-serve solutions. However, the inhibitory efficiency of "Hach2533" in marine nitrification studies has not been compared with other inhibitors. A third inhibitor, allylthiourea (ATU; Aldrich chemical company, USA) is also water-soluble and has been reported to give a higher efficient nitrification inhibition in lake sediment when compared to N-serve (Hall, 1984). In contrast, Henriksen and Kemp (1988) found that ATU gave lower and less consistent estimates of nitrification rates in marine sediments as compared to N-serve. In this study, comparison of the efficiency of three inhibitors (N-serve, ATU, Hach2533) in blocking the nitrification process is needed to assess which is the most efficient inhibitor for use with the dark ^{14}C uptake

method.

c) Nitrification as measured using nitrogen oxidation with ^{15}N isotopes

Nitrification rates can be directly estimated by measuring ammonium and nitrite oxidation processes with substrates labelled with ^{15}N isotopes. Techniques for the measurement of nitrification using ^{15}N isotopes have been described in detail by Schell (1978), Schmidt (1978) and Henriken and Kemp (1988). To measure nitrification in marine sediment, an ^{15}N isotope dilution technique is generally employed (e.g. Koike and Hattori, 1978; Chatarpaul *et al.*, 1980). The observed changes in concentration and atom % enrichment of NO_3^- over time are used to calculate nitrification. The sensitivity of the method, however, is low and highly dependent on the ambient pool concentrations of nitrite and nitrate. The method is straightforward in its application.

4.1.2 Nitrogen uptake measured by ^{15}N technique

The uptake of ammonium, nitrite and nitrate by natural populations of phytoplankton has been investigated in connection with primary productivity (e.g. Dugdale and Goering, 1967; MacIsaac and Dugdale, 1972; McCarthy, 1980; Harrison, 1983b; Glibert *et al.*, 1991). A variety of amino acids and urea are also used by phytoplankton, but this N source may only account for a fraction of the nitrogen used by primary producers (McCarthy, 1980). The important roles of ammonium and nitrate in the physiological ecology of marine phytoplankton have been well described (e.g. Morris, 1974; McCarthy, 1981, 1982; Goldman and Glibert, 1983). The dynamics of dissolved nitrogen uptake have been reviewed by Collos and Slawyk (1980), McCarthy (1980), Goldman and Glibert (1983) and Paul (1983).

The conversion of soluble nitrogen into particulate organic nitrogen by planktonic algae is usually referred to as nitrogen uptake (Paasche, 1988). The uptake rate can be estimated either from the net disappearance of substrate from the medium or from the increase of a tracer in cells (Collos, 1983). Quantification of the role of different nitrogenous nutrients in the ecology of phytoplankton can often only be made by the use of the stable isotope ^{15}N as a tracer. A particular advantage of the use of ^{15}N is that specific substrates labelled with ^{15}N can be used to evaluate all of the transformations in the nitrogen cycle. as a result, ^{15}N has been extensively used to

measure the assimilation of inorganic forms of nitrogen (NO_3^-, NO_2^-, NH_4^+) by phytoplankton (e.g. Goering *et al.*, 1964; Dugdale and Goering, 1967; Caperon *et al.*, 1979; Olson, 1981a; Garside and Glibert, 1984; LaRoche, 1983; McCarthy *et al.*, 1984).

In practice, however, it is sometimes difficult to apply particular ^{15}N-labelled substrates as true tracers of biological activity as the amount of tracer added significantly increases the ambient concentration of substrate in the system. Dugdale and Goering (1967) suggested that adding a mass of tracer equivalent to 10 percent of the ambient mass of the nutrient of interest. Fixed, small additions (0.1 μM) have been used as an alternative when substrate concentrations are not immediately known (e.g. Eppley *et al.*, 1973; 1979). The problem of determining how much labelled nutrient to add becomes increasingly difficult as ambient concentrations of the substrate approach the lower limits of analytical detection. In oligotrophic waters where ambient nutrient concentrations are very low, the concentrations of isotope needed to detect transformation processes are often far higher than natural concentrations. Transformation rates measured in samples where the amount of labelled compound added is high relative to ambient concentrations must therefore be considered as potential rather than actual rates.

To apply ^{15}N techniques, the extraction of uncontaminated ammonium from water samples for isotopic analysis is a major operational problem in the application of ^{15}N techniques. Three different approaches have previously been taken for the extraction of ammonium from the water sample for isotopic analysis: (i) distillation followed by Conway diffusion (Harrison, 1978); (ii) precipitation using mercuric chloride (Fisher and Morrissey, 1985); (iii) formation of the ammonium coupled organic dye, indophenol blue, with subsequent solvent extraction of the dye (e.g. Dudek *et al.*, 1986). A particular advantage of the latter approach is that once the indophenol derivative is formed, further contamination of the water sample by ammonium causes very little error in the final ^{15}N analysis (Selmer and Sørensson, 1986). The ammonium extraction procedures used herein were modified from Dudek *et al.* (1986) and Brzezinski (1987). The indophenol blue method is the most sensitive chemical method yet reported for the determination of ammonium in seawater, enabling measurement to nanomolar concentrations (Brzezinski, 1987). In addition, ammonium added to mixed reagents does not react to form indophenol and the extent and rates of the side reactions are not significantly affected by the procedure used to create reagent blanks in either seawater or double distilled water (Brzezinski, 1987).

Ammonium extraction using a polar solvent in this case (dichloromethane) is time-consuming. The alternative separation procedure involving the absorption of the indophenol blue dye onto an octadecylsilane (C-18) column, with subsequent elution and evaporation of the solvent was compared with solvent extraction.

Two types of octadecylsilane (C-18) columns were tested: separation phase extraction (SPE) columns (J.T. Baker Inc., NJ. USA) and Sep-Pak cartridges (Millipore Corporation, USA.) were tested. SPE columns are relatively expensive, therefore, the potential for reuse of columns was also evaluated to assess the extent of continued extraction efficiency and contamination problems.

STUDY OBJECTIVES

The goal of the work described in this chapter is to quantify the processes responsible for the elevated nitrate and nitrite concentrations observed following cyclones in GBR waters. Nitrogen transformation processes in shelf waters of the GBR have not been measured, especially under conditions of high particle-loading such as occurs during and after cyclonic disturbances. I have attempted to investigate and compare specific aspects of nitrogen transformation which pertained to GBR waters in both calm and post-cyclonic periods by using ^{14}C and ^{15}N tracer techniques.

In this present study, I have estimated nitrification rates i) directly through net changes in ammonium, nitrite and nitrate concentrations, ii) indirectly by inhibitor sensitive dark ^{14}C-bicarbonate uptake and iii) using ^{15}N tracer technique to directly measured by ammonium and nitrite oxidation. Potential nitrogen uptake rates were also measured using ^{15}N isotopes.

Ammonium oxidation rates, nitrite oxidation rates and the uptake of dissolved inorganic nitrogen (ammonium, nitrite and nitrate) by planktonic organisms were measured using ^{15}N isotope methods in control seawater and seawater with suspended sediment. Because Matulewich and Finstein (1978) showed that the number of nitrifying organisms is far higher in the sediment than in the water column, nitrification rates in seawater with frozen-thawed (normally abiotic) sediment were compared with rates measured in seawater with freshly collected (living) sediment added. This comparison was conducted to assess the effect of living organisms introduced into the water with the resuspended sediment as compared to rates due solely to bacteria present in the water column.

The specific objectives of the work described in this chapter are as follows:

1. To compare the efficiency of three nitrification inhibitors used in the dark ^{14}C uptake technique.

2. To assess the efficiency of organic solvent and organic columns for the extraction of ^{15}N labelled substrates.

3. To measure oxidation rates of inorganic nitrogen species ($NH_4^+ \rightarrow NO_2^-$; $NO_2^- \rightarrow NO_3^-$) in GBR water following simulated resuspension events and nutrient loading under aerobic condition.

4. To compare ammonium oxidation and nitrite oxidation rates measured using ^{15}N technique with measurement using the ^{14}C dark uptake method.

5. To compare nitrogen transformation rates in seawater with freshly collected sediment with rates based on frozen-thawed sediment.

6. To measure phytoplankton uptake rates of dissolved inorganic nitrogen (NH_4^+, NO_2^-, $NO_3^- \rightarrow$ PN) in GBR water following simulated resuspension events using ^{15}N techniques.

4.2 EXPERIMENTAL PROCEDURES AND RESULTS

4.2.1 Nitrification as estimated through net changes in ammonium, nitrite and nitrate concentrations.

In this study, nitrification over 24-h periods was estimated through net changes in ammonium, nitrite and nitrate concentrations in water samples with and without nitrification inhibitors. Nitrification could not be unambiguously detected from net changes in dissolved inorganic nitrogen concentrations (Appendix IV: Table IV-1). Overall changes in the concentrations of ammonium, nitrate and nitrite with time were small in relation to the absolute concentrations. Concentrations of nitrite, the direct product of ammonium oxidation, were very low and remained near the detection limits of standard analytical methods (< 0.02 μM). Relative variability of concentrations

within sampling periods was quite high. Further tests with standard solutions showed that the inhibitors or impurities associated with them affected the measurement of ammonium, nitrate and nitrite species (Appendix IV: Table IV-2). This method therefore was not pursued further.

4.2.2 Nitrification as estimated by inhibitor sensitive dark ^{14}C-bicarbonate uptake.

The nitrification experiment estimated by inhibitor sensitive dark ^{14}C-bicarbonate uptake is in turn divided into seven individual trials. Theses trials were conducted to estimate nitrification rates in GBR waters, following cyclonic disturbances. These trials addressed the following considerations:

i) do ambient ammonium concentrations affect dark ^{14}C-bicarbonate uptake rates? (Morris *et al.*, 1971a &b)

ii) what are the relative efficiencies of the three nitrification inhibitors for GBR waters and sediment?

iii) how do nitrification rates estimated from dark ^{14}C uptake compare to ammonium oxidation rates directly measured by ^{15}N methods in seawater with and without suspended sediment?

iv) what are the estimated nitrification rates in central GBR seawater with and without suspended sediment?

a) Experimental procedures

To derive a dark C uptake/ N oxidation ratio for GBR plankton populations and sediments, experimental measurements of dark ^{14}C-bicarbonate uptake and ^{15}N-ammonium oxidation rates were conducted in parallel. Comparisons were made between control seawater and seawater with sediment added. All ^{14}C-bicarbonate uptake trials were conducted in a controlled temperature room (27° C). One trial was carried out on board ship. Seawater used for the trials was collected from the surface at inshore or mid-shelf sites with an acid-cleaned plastic bucket and screened through a plankton net (mesh size 20 μm) to exclude large zooplankton. Sediment used in the laboratory trials was collected from an inner shelf site (IS3; Figure 2.1). For the trial conducted on board ship, fresh sediment was collected at nine sites across the shelf. The experimental design and analytical procedures are shown schematically in Figure 4.1.

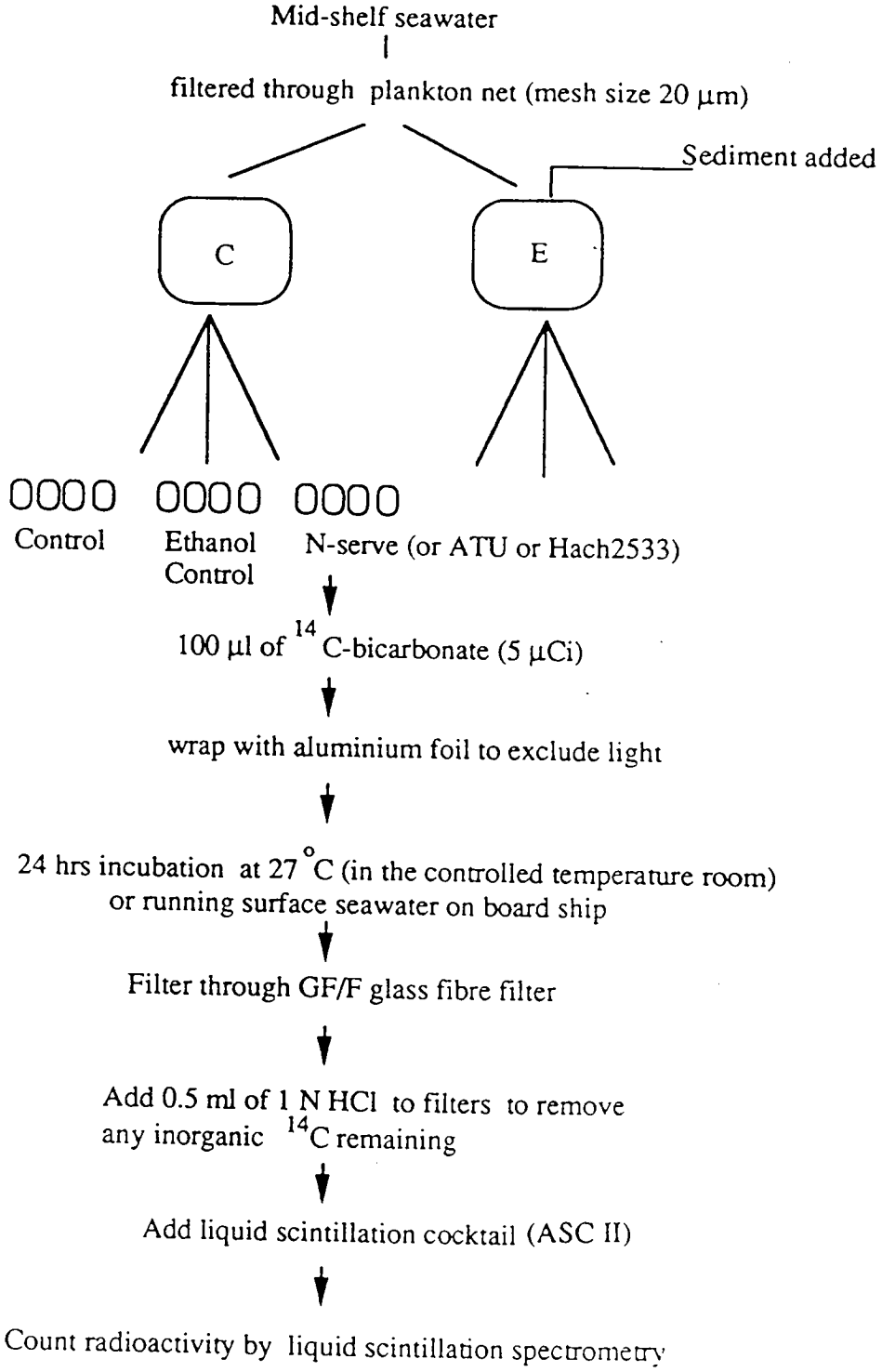


Figure 4.2 Experimental design for ^{14}C-bicarbonate dark uptake experiment and analytical procedure to determine CPM (count per minute)

Twelve 100 ml replicate aliquots of seawater were dispensed into 150-ml polycarbonate bottles. A small amount of inhibitor solution (25 µl) was added to four bottles while absolute ethanol (25 µl) was added to each of another four bottles. Neither inhibitor nor ethanol were added to the remaining four bottles. Final concentrations of the nitrification inhibitor and ethanol are shown for each trial (see Table 4.1). The N-serve stock solution was prepared either immediately before use or was stored under refrigeration in order to reduce hydrolysis of nitrapyrin to 6-chloropicolinic acid (Bremner *et al.*, 1978). N-serve was dissolved in absolute ethanol, while ATU and Hach2533 were dissolved in deionized water.

The effect of suspended sediment on the efficiency of the three inhibitors in seawater was tested at various concentrations of ammonium. Ammonium standard (0-18 µM) solutions were added prior to addition of the nitrification inhibitor. Five microcuries (185 kBq) of ^{14}C-bicarbonate (Amersham) was added to each 100-ml sample. The bottles were wrapped in aluminium foil to exclude light and incubated in a controlled temperature room (27 °C) for 24 h. At the end of incubation, the contents of each bottle was filtered onto a Whatman GF/F glass fibre filter, which were rinsed with filtered seawater and dried. The dried filters were placed in scintillation vials and acidified with 0.1 ml of 1 N HCl to remove radioactivity associated with precipitated carbonates and inorganic carbon (Hitchcock, 1986). Ten millilitre of scintillation cocktail (ASC II) were added. The solution was then mixed with a "vortex" mixer for 5 seconds. Radioactivity on the filters was quantified by liquid scintillation spectrometry (Beckman LS 2800, USA). CPM values (count per minute) were converted to DPM (disintegration per minute) using the external standards ratio method (approximately 97% efficiency).

The hourly dark ^{14}C uptake rate in samples with and without nitrification inhibitors was calculated using the equations of Strickland and Parson (1972) as follows:

$$Dark\ uptake\ rate\ (nmol\ C\ l^{-1}hr^{-1}) = \frac{R_s \times W}{R \times N} \quad \ldots(4.1)$$

R_s = Sample count (DPM) corrected for quenching
R = Total activity of bicarbonate added (5 µCi = 1.11 x 10^7 DPM)
W = Weight of total carbon dioxide = 1.8885 x 10^6 nmol C l^{-1}
N = Number of hours incubation

The amount of C incorporated due to nitrification was taken as the difference between the amount of dark ^{14}C-bicarbonate uptake in samples with and without inhibitors. This difference is defined as inhibitor sensitive dark ^{14}C-bicarbonate uptake (hereafter ISDCBU).

The ethanol used as the N-serve solvent (393 mg l^{-1} from 25 µl in 100 ml seawater) inhibited dark ^{14}C-bicarbonate incorporation in both control seawater and seawater with suspended sediment (T-test, $P < 0.05$). Samples with ethanol only added were used as an additional control.

Dark uptake rates were measured at sea using freshly collected seawater and sediment from three sites within each of the inner shelf, mid shelf and outer shelf regions (see Figure 4.5). At each site, seawater (5 m depth) was collected by Nisken bottles. Bulk sediment was collected with a Smith-McIntyre grab (see Chapter 2). Sediment subsamples (approximately 6 cm^3) were added to two litres of seawater which had been screened through nylon net (20 µm mesh size). Four 135 ml replicates of seawater, with and without sediment added, were dispensed into eight 150-ml polycarbonate bottles. Absolute ethanol (0.1 ml) was added to four bottles (controls) while 0.1 ml of an N-serve stock solution (final concentration 50 mg l^{-1}) were added to the other four bottles. All bottles were wrapped with aluminium foil to exclude light. Samples were incubated for 24 hours on board ship in a tank filled with flowing surface seawater. The CPM values measured in the filtered material were converted to DPM values using internal standards (Strickland and Parsons, 1972).

b) Results

Effectiveness of inhibitors

The results of all trials testing the effectiveness of the three nitrification inhibitors: N-serve; ATU and Hach2533 on dark bicarbonate uptake in control seawater and seawater with sediment added are shown in Table 4.1 and Figure 4.2. N-serve blocked dark ^{14}C-bicarbonate uptake in control seawater samples at concentrations ≥ 5 mg l^{-1} (T-test, $P < 0.05$), but not in the seawater with suspended sediment (T-test, $P > 0.05$) and was less effective in the presence of suspended sediment when compared to Hach2533 and ATU at concentrations < 50 mg l^{-1}.

Amongst the three inhibitors the highest inhibitor-sensitive dark ^{14}C-bicarbonate

uptake (ISDCBU) rates were obtained by using N-serve at a concentration of 50 mg l^{-1} (Appendix Table VI-1). ATU (50 mg l^{-1}) and Hach2533 (100 mg l^{-1}) did not efficiently block the dark C-bicarbonate uptake in seawater with sediment added. The ISDCBU rates (obtained from both N-serve and ATU) were significantly higher in the seawater with sediment added than in the control seawater (Two-way ANOVA, Appendix VI: Table VI-1). The efficiency of N-serve relative to Hach2533 was not resolved since the concentrations of the two inhibitors were different.

Overall, the three nitrification inhibitors (N-serve, ATU and Hach2533) blocked dark ^{14}C-bicarbonate uptake in control seawater samples but were less efficient in seawater samples with sediment added. At equivalent concentrations $\geq$ 50 mg l^{-1}, N-serve was judged to be more efficient than ATU in blocking dark ^{14}C-bicarbonate incorporation.

Relationship between ammonium concentration and dark ^{14}C-bicarbonate uptake

Dark ^{14}C-bicarbonate uptake rates in seawater (with and without suspended sediment) increased with increasing concentrations of ammonium (Figure 4.3) though the increase was relatively small. The efficiency of inhibitors was checked at various concentrations of ammonium in seawater with suspended sediment. In seawater with ammonium added, dark uptake was less efficiently blocked by ATU, excepting the samples with ammonium concentration set at 9 µM (Figure 4.4).

N-serve sensitive dark ^{14}C uptake rates in central GBR waters

Dark ^{14}C bicarbonate uptake rates measured in fresh seawater with sediments freshly collected from inner-, mid- and outer-shelf areas were compared in a pairwise manner with rates measured in natural seawater (without sediment added), (Trial C.7, Table 4.1). Measured rates of dark ^{14}C-bicarbonate uptake (in seawater both with and without suspended sediment) varied between sites (Figure 4.5). The dark ^{14}C-bicarbonate rates showed no clear pattern between controls (without sediment added) and water with suspended sediment regardless of its origin. N-serve sensitive dark C-bicarbonate uptake (NSDCBU) rates for seawater with suspended sediment collected from six sites (IS7, IS9, MS3, MS4, OS7, OS8) were higher than rate in the control seawater, whereas rate estimates from three sites (IS8, MS2, OS6) were lower. Mean NSDCBU rates in seawater with added sediment (3.18 nmol C l^{-1} h^{-1}) were higher than mean rates measured in control seawater (1.79 nmol C l^{-1} h^{-1}). .

Table 4.1

Effects of ammonium, ethanol and nitrification inhibitors on dark ^{14}C bicarbonate uptake rate (nmol C l^{-1} hr^{-1}) in the seawater with and without suspended sediment added.

Trial	Final concentration in solution				Dark incorporation rate in samples									
					Without sediment					With suspended sediment				
	[NH4] added µM	[Ethanol] mg/l	[N-serve] [ATU] mg/l	[Hach2533] mg/l	Control	Ethanol	N-serve	ATU	Hach2533	Control	Ethanol	N-serve	ATU	Hach2533
C.1: Test	0	393	5		5.8	4.9	4.4			13.1	12.6	12.6		
C.2:Substrate	0	393	10		9.0	8.2	5.4			11.1	10.8	7.3		
	1.5				11.0	10.7	10.7			17.2	16.1	16.5		
	3				19.6	18.8	14.1			23.5	22.9	18.5		
	6				26.3	20.7	25.8			26.1	23.6	25.9		
	12				23.5	21.8	22.7			42.6	34.1	41.0		
	18				28.1	20.6	24.3			61.3	59.9	24.9		
*C.3:N-serve	0	393	0	0		5.2		5.6	6.1		11.7		9.5	12.0
*C.4:ATU			5	25			4.7	5.1	5.7			10.6	8.6	9.9
*C.5:Hach2533			10	50			4.0	5.3	5.9			9.0	8.6	9.6
			20	100			4.1	4.8	5.7			10.5	8.6	10.3
			30				3.8	4.8				8.5	8.0	
			50				3.8	5.1				5.2	7.4	
	3		0	0						11.4	25.9		11.8	
			5	50									11.2	13.3
			10	100								29.9	12.0	9.7
			20									28.6	8.4	
			30									25.1	10.1	
	6		0	0						8.9	50.8		9.2	
			5	50									9.2	16.7
			10	100								62.3	10.4	16.8
			20									55.3	12.9	
			30									66.4	13.2	
	9		0							11.1			11.5	
			5										15.5	
			10										30.3	
			20										20.9	
			30										15.8	
	12		0								71.4			
			5											
			10									90.3		
			20									89.1		
			30									92.7		
C.6:Effectiveness		393	30	50	6.7	5.9	3.8	5.3	4.4	10.0	8.4	7.5	10.0	10.3
			50	100			3.6	5.5	4.4			5.2	10.2	9.1
C.7:GBR waters														
IS7		291	50			9.5	8.6				14.3	5.7		
IS8						6.1	3.5				10.5	9.4		
IS9						6.8	6.4				8.9	6.0		
MS2						4.4	0.9				5.9	4.1		
MS3						4.9	3.6				5.5	3.2		
MS4						4.8	2.7				12.3	10.1		
OS6						5.4	2.5				9.7	7.7		
OS7						2.9	2.5				11.2	4.4		
OS8						2.9	2.2				5.4	4.4		

* Trials C.3, C.4 and C.5 were carried out at different times using different batches of seawater

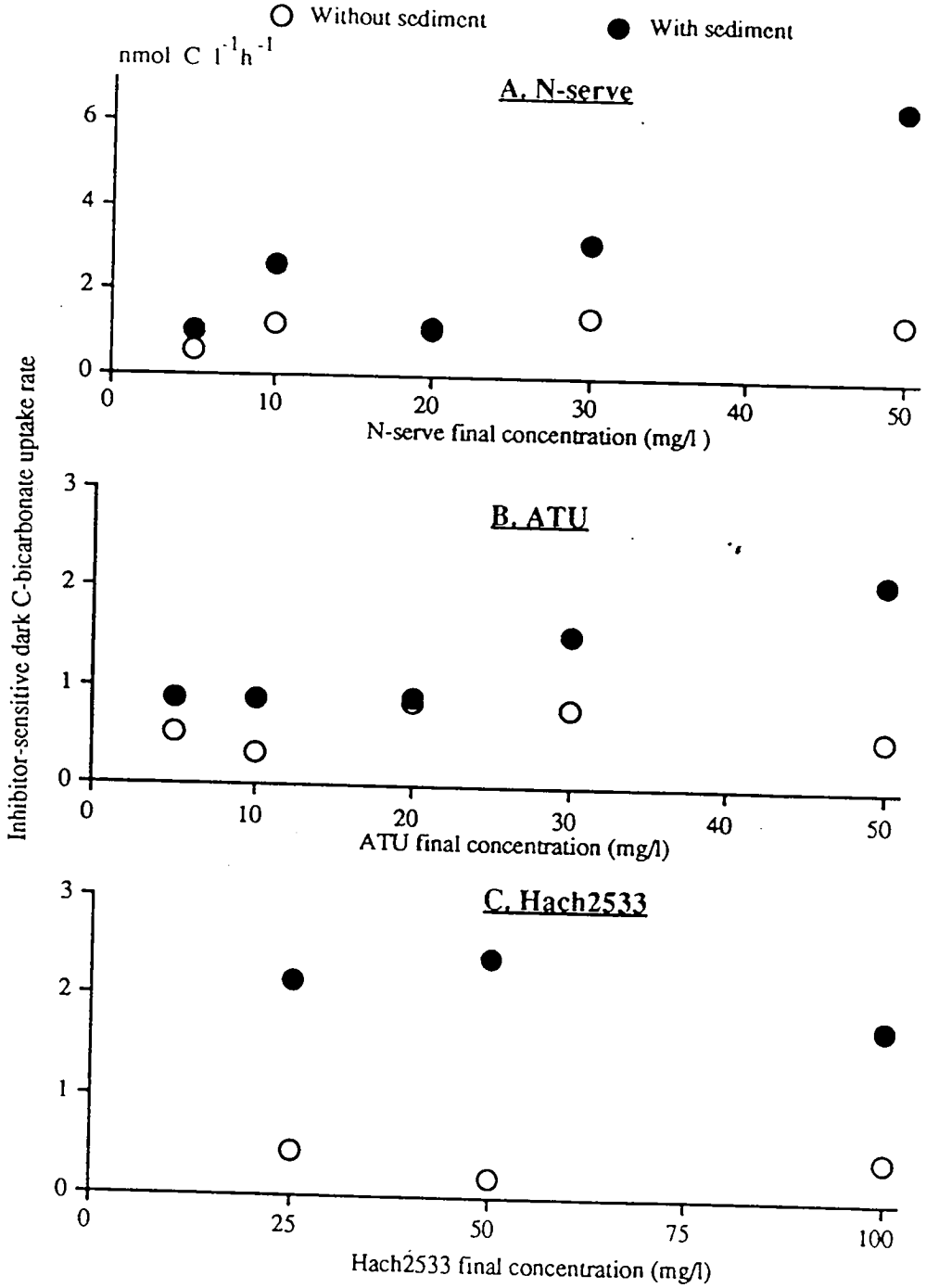


Figure 4.2 Inhibitor-sensitive dark C-bicarbonate uptake (ISDCBU) rates at various concentrations of N-serve (A), ATU (B) and Hach2533 (C) in seawater with and without sediment.

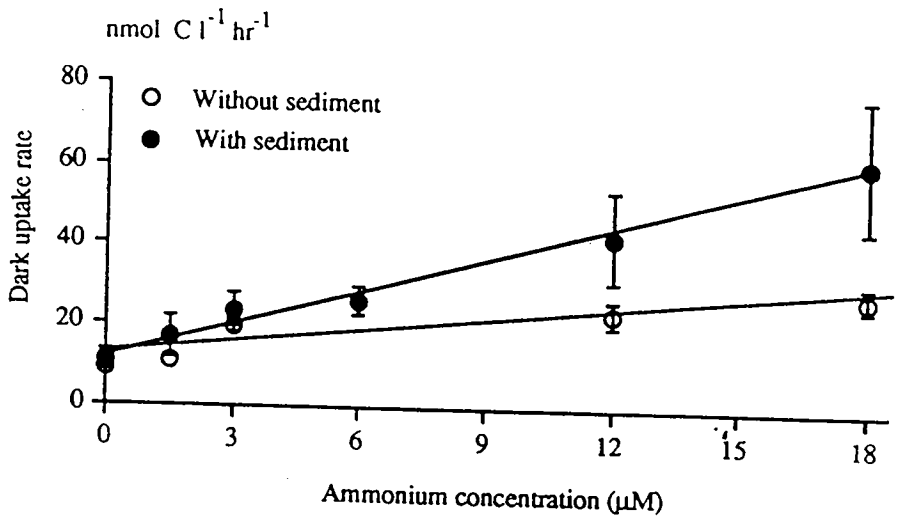


Figure 4.3 Effects of ammonium concentration on dark bicarbonate uptake rates in the seawater with and without suspended sediment.

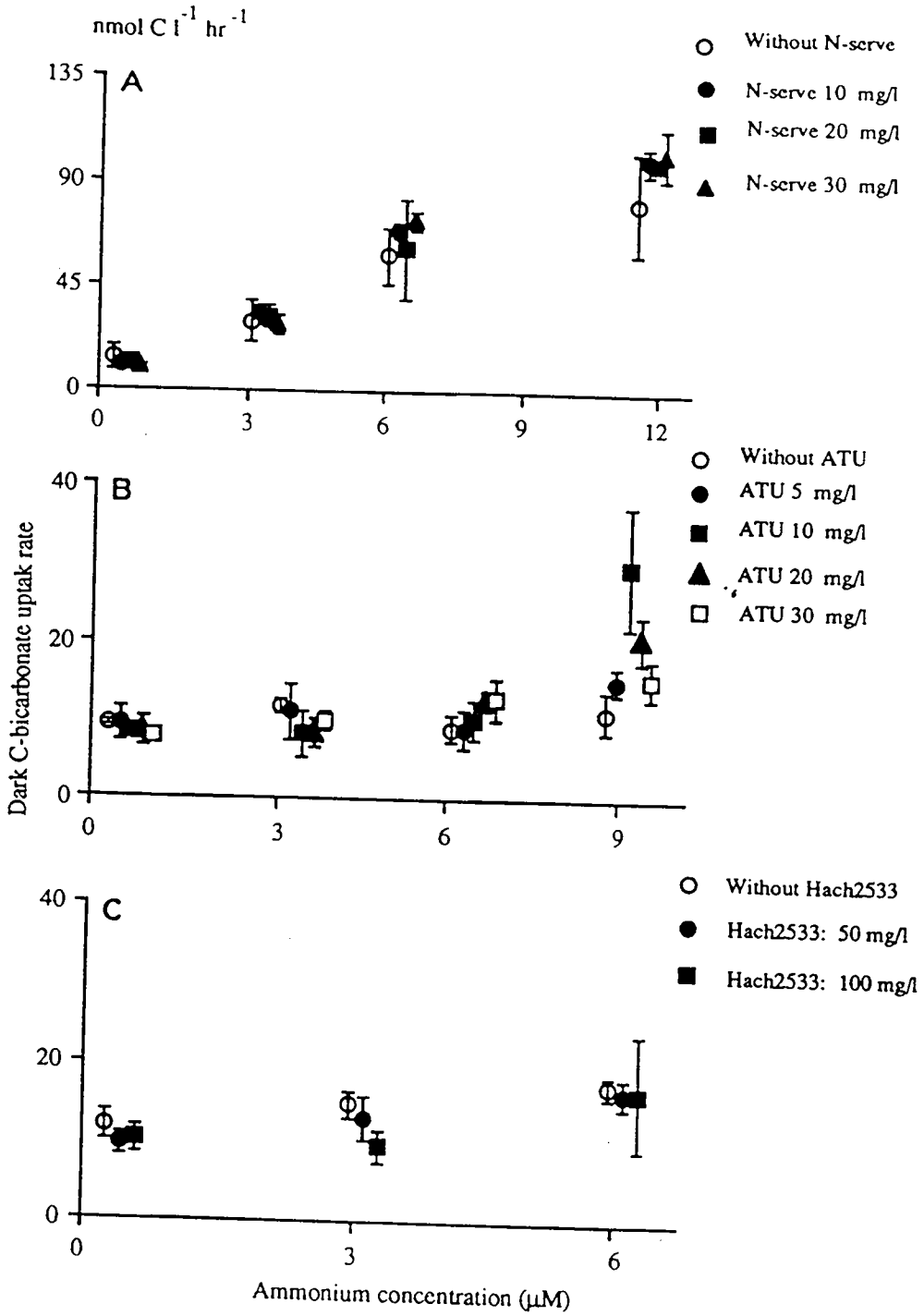


Figure 4.4 Dark bicarbonate uptake rates related to ammonium concentrations in the experimental seawater (with suspended sediment) with and without inhibitors: A) N-serve; B) ATU; C) Hach2533.

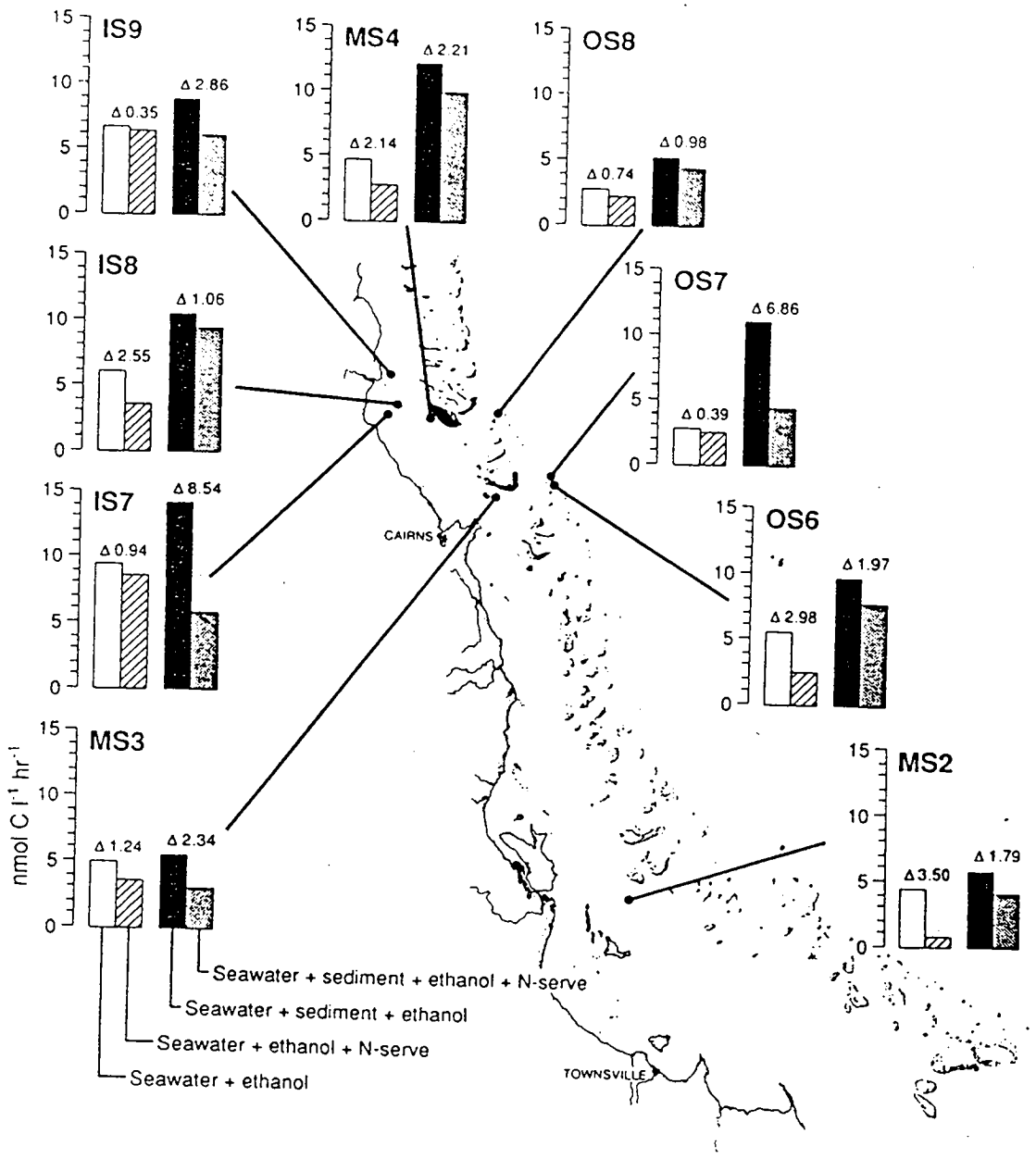


Figure 4.5 Dark ^{14}C-bicarbonate uptake (nmol C l^{-1} hr^{-1}) in seawater and seawater with added sediment freshly collected at inner shelf (IS), mid-shelf (MS) and outer shelf (OS) sites in GBR. Samples are treated and untreated by N-serve (final concentration = 50 mg l^{-1}). The measured rates are based on 6 cm^3 of sediment being suspended in 2 litres of seawater.

4.2.3 Nitrification and nitrogen uptake rates measured by using ^{15}N isotopes

Five trials were conducted in this ^{15}N experiment. The first trial was carried out to assess the relative extraction efficiencies of organic solvents (dichlomethane; Dudek *et al.*, 1986) and octadecylsilane columns (SPE and Sek-Pak; Selmer and Sørensson, 1986). The other four trials were to measure ammonium and nitrite oxidation rates and nitorgen (ammonium, nitrite and nitrate) uptake rates by using ^{15}N isotopes.

a) Experimental procedure

The first trial was carried out using nearshore seawater (collected from the AIMS jetty). The remaining four trials were carried out using different batches of mid-shelf water and inner shelf sediment from different sites (Table 2.1). The experimental design for the ^{15}N experiments is shown schematically in Figure 4.6. One hundred twenty litre batches of seawater were filtered through a plankton net (20 µm mesh size). The water was used to fill six 20-litre carboys. Three carboys contained 20 litres of seawater (without sediment addition: controls) and the other three carboys contained 20 litres of seawater which had been mixed with sediment (experimental water). Pairs of carboys (one contained control water and the other contained experimental water) were inoculated with $^{15}NH_4Cl$ (99 atom % enriched; SIGMA, USA), $Na^{15}NO_2$ (99 atom % enriched; MSD Isotopes, MERCK, Canada) or $K^{15}NO_3$ (99 atom % enriched; SIGMA, USA). The final concentration of isotopes in each trial are presented in Tables 4.2 and 4.4. Replicate subsamples for analysis of substrate concentrations and isotopic content were collected at 'time zero' (through not every trial) and thereafter at 3 or 4 and 6 h after inoculation. These time points were chosen as the incubation periods needed to be long enough to allow measurable nitrogen transformations to occur, but short enough to preclude significant recycling of the ^{15}N substrate (e.g. Glibert *et al.*, 1982; Harrison, 1983a; Laws, 1984; Dugdale and Wilkerson, 1986).

Trial N.1 was carried out in parallel with dark ^{14}C-bicarbonate uptake trial C.6. At each time point water samples were collected from each carboy and filtered through precombusted Whatman GF/F glass fibre filters. The filtrates were analysed for ammonium, nitrite and nitrate. The filters were retained for analysis of particulate nitrogen. The handling procedure for processing ^{15}N water samples is schematically

illustrated in Figure 4.7 and the individual analytical procedures for each nitrogen species are described as follows:

Ammonium

The ammonium extraction procedure was modified from Dudek *et al.* (1986) and Brzezinski (1987). Four hundred (400) ml of sample was mixed with 5.6 ml of AR grade phenol (10 gm in 100 ml of 95% ethanol), 5.6 ml of sodium aquapentacyanoferrate (AqF),(300 mg in 250 ml DIW), and 14 ml of oxidizing reagent. Sodium aquapentacyanoferrate was used instead of sodium nitroprusside as the catalyst to enhance the reaction rates and reduce blanks (Dudek *et al.*, 1986). The oxidizing reagent was made by mixing 2.3 ml of 3.5 % hypochlorite solution (commercial Sno-Wite bleach solution) with 50 ml 0.25 M NaOH. Heating (60° C for 20 minutes) has been suggested to speed the indophenol blue development (Dudek *et al.*, 1986). Higher recoveries of ammonium were observed in heated seawater samples but not in standard solution made up in deionized water. This may be due to the degradation of urea (Brzezinski, 1987) or dissolved organic nitrogen compounds in seawater. The sample was therefore stored in the dark at room temperature (approximately 20° C) for four hours to allow the indophenol blue color to develop.

After the indophenol blue development, samples were acidified to pH 6.3 by adding 4 ml of 1 M phosphoric acid, changing the color from the oxidized indophenol dye (blue) to a reduced form (red). The indophenol solution was then passed through activated SPE columns at approximately 4 ml min^{-1}. The SPE columns were activated by sequential rinses with 10 ml of methanol and 5 ml of deionized water according to Selmer and Sørensson (1986). The indophenol dye was retained on the column and the water was discarded. Contaminating compounds retained on the column with a polarity higher than that of indophenol were removed by passing 5 ml of an alkaline (pH 10) 1% (vol/vol) methanol-water mixture through the SPE column. No indophenol was eluted by this process. The red indophenol retained on the column was quantitatively eluted by 2 x 0.5 ml rinses of absolute methanol instead of the 10% (v/v) methanol-water mixture proposed by Selmer and Sørensson (1986). The indophenol was collected in a precombusted borosilicate glass (pyrex) tube containing a 25 mm precombusted Whatman GF/F glass fibre filter. The methanol solvent was then evaporated by a helium gas stream, leaving the indophenol on the glass fibre filter. The filter was dried for at least 12 h in a vacuum desiccator and stored under vacuum until isotopic analysis.

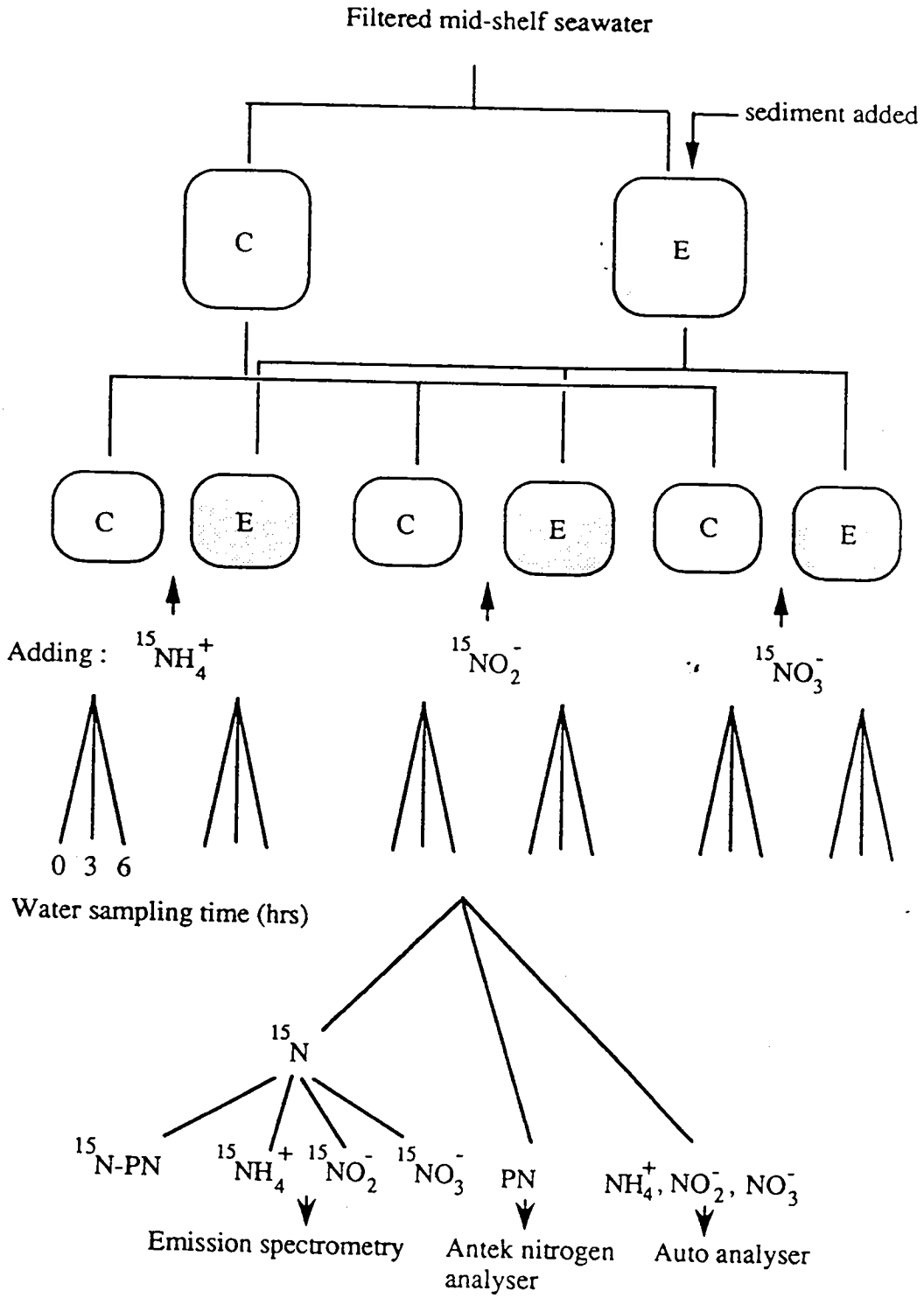


Figure 4.6 Design of ^{15}N isotope experiments. C = control seawater, E = seawater with suspended sediment.

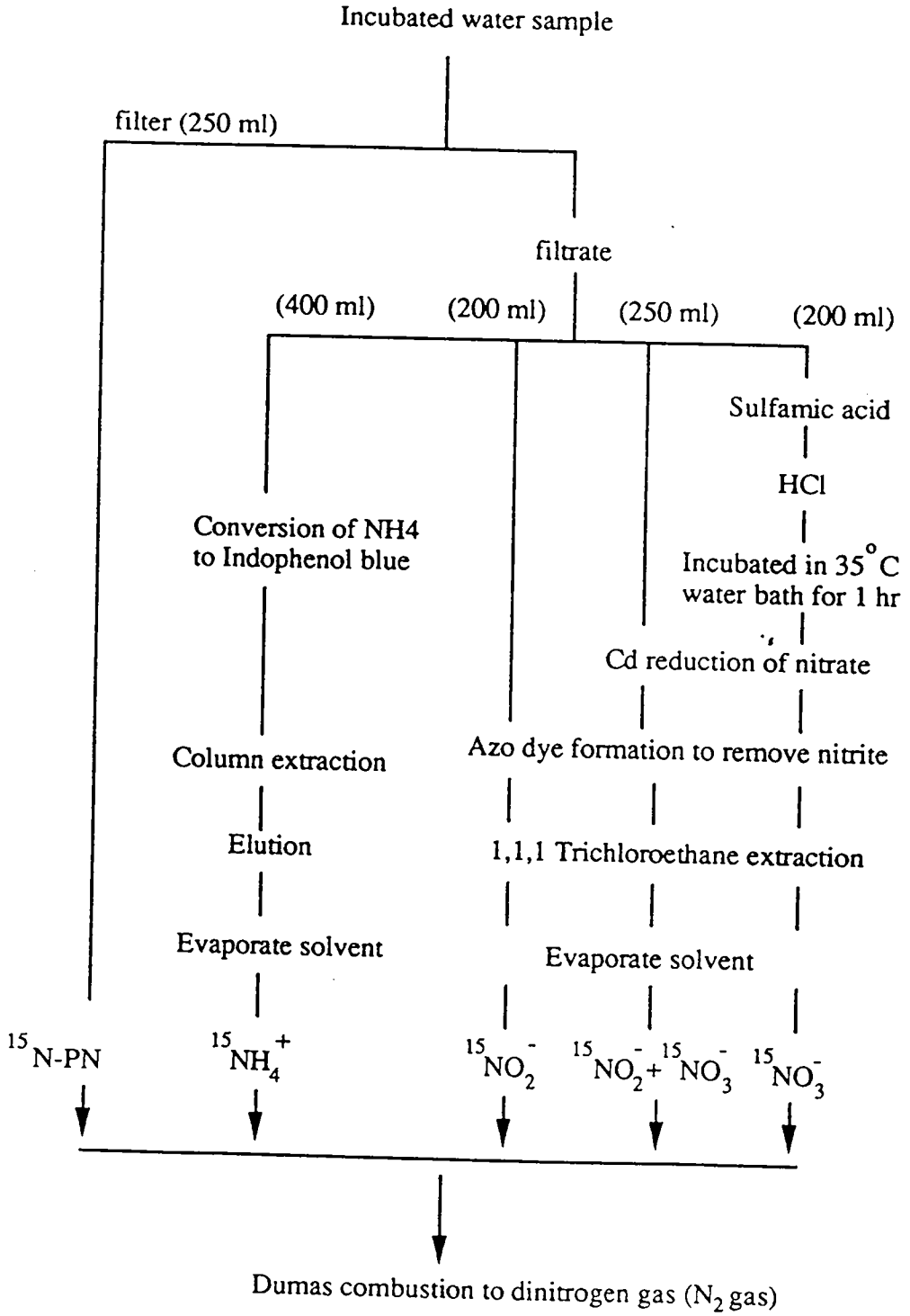


Figure 4.7 Analytical procedures to recovery soluble and particulate isotopic species (ammonium, nitrite, nitrate and PN) in individual water samples.

Nitrate and Nitrite

The basic procedure for the separation of nitrite from natural seawater by formation and organic extraction of the azo dye was introduced by Schell (1978). The analysis of nitrate after reduction to nitrite (Strickland and Parsons, 1972) is complicated by the presence of pre-existing nitrite. In addition, quantitative conversion of NO_3^- to NO_2^- is difficult to obtain. The effectiveness of the nitrate reduction procedure is dependent on copper-cadmium preparation procedures (Margeson *et al.*, 1980). Alternatives (Margerson *et al.*, 1980; Jones, 1984) to the cadmium column reduction method failed to give high and consistent conversions of NO_3^- to NO_2^- (data not shown). Analytical errors for nitrate determination by cadmium column reduction are additive in the presence of nitrite, reducing precision. However, procedures for destroying nitrite prior to nitrate reduction with sulfamic acid (NH_2SO_3H) as adapted by Lipschultz (1984) are also complicated. Competition between sulfamic acid and the azo dye formation process can be minimized by the appropriate choice of pH, temperature, and sulfamic acid concentration (Lipschultz, 1984). In the first three trials (N.1, N.2 and N.3), without destruction of pre-existing nitrite, apparent yields of NO_3^- in samples with $^{15}NO_2^-$ added were abnormally high, resulting in very high apparent (20-fold) nitrite oxidation rates (data not shown) as compared to rates measured in the samples added with $^{15}NH_4^+$ isotopes. Therefore, nitrite was removed by sulfamic acid before nitrate reduction was carried out in trial N.4.

At each sampling point, water samples were first filtered through Whatman GF/F glass fibre filters. Nitrite in subsamples of the filtrate was extracted by the azo dye procedure following Lipschultz (1984). For nitrate measurement without destruction of pre-existing nitrite, nitrate in the filtrate was reduced to nitrite using cadmium columns (Strickland and Parsons, 1972) and re-extracted using the azo dye procedure. To speed processing, several cadmium columns were run in parallel. Nitrate and nitrite standard solutions were run to correct for column-specific variations in nitrate recovery and nitrite destruction. The calculated recovery of nitrate from columns varied between 70 and 112 percent. Up to 23 percent of the nitrite in samples was destroyed when passed through the cadmium columns. Calculated nitrite and nitrate concentrations were corrected for this destruction. Before the azo dye extraction step, carrier nitrite ($^{14}NO_2^-$ standard solution) was added to provide sufficient mass to carry out the isotopic analyses with reasonable precision. The amounts of carrier added are shown in Appendix V: Tables V-1, V-2.

To destroy pre-existing nitrite prior to nitrate reduction, cold concentrated sulfamic acid (NH_2SO_3H; 0.2 ml) and 1 ml of concentrated hydrochloric acid (HCl) were added to water samples (Lipschultz, 1984). These amounts of sulfamic acid and HCl completely destroyed the nitrite present and gave a high recovery of nitrate. Samples were then incubated at 35° C for 1 h. Nitrite concentrations in incubated samples were measured by manual colorimetric methods (Strickland and Parson, 1972) to ensure that pre-existing nitrite was completely destroyed. The acid in the samples was then neutralized to pH 7 with sodium hydroxide (NaOH) to permit efficient cadmium reduction of nitrate to nitrite. The neutralized samples were passed through cadmium reduction columns to reduce the nitrate to nitrite. Samples were then processed in the same manner previously given for nitrite. Filters with extracted nitrite were stored in precombusted borosilicate glass tubes in a desiccator until nitrogen isotopic analysis.

Particulate nitrogen (PN)

Four 250-ml water samples were filtered through precombusted (450° C for 12 h) Whatman GF/F glass fibre filters. The filters were dried at 60° C under vacuum. Two filters were analysed for PN content using an ANTEK Nitrogen analyzer (Furnas *et al.*, 1990). The other two filters were stored in precombusted borosilicate glass tubes until isotopic analysis.

Nitrogen isotopic analysis

The filters containing indophenol, azo dye and particulate nitrogen were placed in 10 mm o.d. borosilicate glass tubes. A micro-Dumas conversion of the fixed N to N_2 gas (Kristiansen and Paasche, 1982) was performed by adding 1-1.2 gm of 1:1 mixture (by weight) of precombusted CaO (800° C) and cuprox Coleman reagent with platinum catalyst (CuO) which had been precombusted to 530° C. The tubes were evacuated to a pressure between 10^{-3}-10^{-4} torr (0.1-1 mm Hg), sealed under vacuum and combusted at 530° C for 12 h to convert the ammonium, nitrite or particulate organic nitrogen compound to dinitrogen gas. The $^{15}N/^{14}N$ ratios of the combusted samples were determined by optical emission spectrometry (N-150, JASCO, Fiedler and Proksch, 1975). The spectrometer was interfaced to a microcomputer for data logging and isotopic calculations (P. Liston per comm.).

Dissolved inorganic nitrogen

Concentrations of dissolved inorganic nitrogen (DIN) species (ammonium, nitrate and nitrite) were measured at each sampling period in trial N.1 (5 μM isotope addition) segmented flow analyses using an AutoAnalyser (Skalar Analytical SA 20/40 analyser). Thereafter, DIN concentrations (trials N.2, N.3 and N.4) were analysed immediately by manual colorimetric methods (Strickland and Parsons, 1972).

Calculation of transformation rates

The atom % abundance of ^{15}N can be calculated from isotopic emission spectra by using the relative emission peaks produced by dinitrogen gas in the forms of $^{15}N^{15}N$ (mass 30), $^{15}N^{14}N$ (mass 29) and $^{14}N^{14}N$ (mass 28). The measured atom % abundances of individual samples were calculated against a standard curve relating measured against actual atom % abundances (Figure 4.8). The value of ^{15}N (atom %) is evaluated on the assumption that, for the N_2 gas in the discharge tube, the ^{14}N and ^{15}N atoms are in a perfect statistical combination with respect to the production of molecules; for the equilibrium:

$$^{14}N^{14}N + {}^{15}N^{15}N \rightleftharpoons 2\,{}^{14}N^{15}N \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

The atom percent of a given sample is calculated by the equation:

$$Atom\ \%\ of\ {}^{15}N = \frac{2(mass\ 30) + mass\ 29}{2(mass\ 28 + mass\ 29 + mass\ 30)} \quad \ldots\ldots (4.3)$$

When the level of mass 30 is too low to be measured accurately, the full equation can be replaced by the equation:

$$Atom\ \%\ of\ {}^{15}N = \frac{100}{2R+1} \quad when \quad R = \frac{mass\ 28}{mass\ 29} \quad \ldots\ldots (4.4)$$

Atom % excess is the measured atom % ^{15}N abundance subtracted by the natural atom % ^{15}N abundance. The natural abundance of ^{15}N is approximately 0.366% (Fiedler and Proksch, 1975). Transformation rates were calculated over the sampling intervals of the 0-3 or 0-4 h and 0-6 h incubation periods. It was assumed that the transformation processes were linear over the sampling interval.

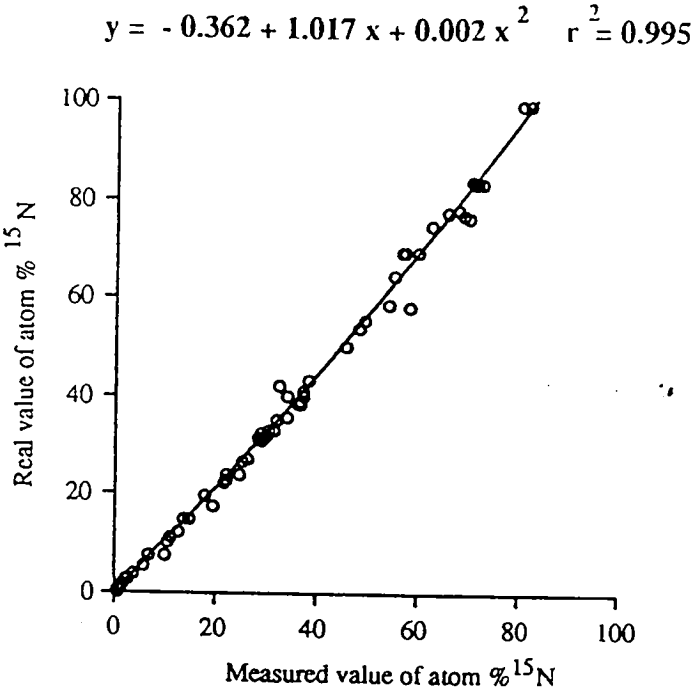


Figure 4.8 Standard curve for isotopic ratio analyses.

Ammonium oxidation rate

As ammonium and nitrite oxidation rates are influenced by the same tracer ($^{15}NH_4^+$) addition, the total ammonium oxidation rate is the sum of nitrite accumulated, nitrate produced and some proportion of nitrite taken up by phytoplankton in the water sample. The ammonium oxidation rate was calculated from the sum of the net nitrite accumulation rate and nitrite oxidation rate. The nitrite accumulation rate was calculated directly from the yield of nitrite measured in the samples. As the product of nitrite and aniline is benzene-diazonium chloride, which contains one nitrogen atom from the sample nitrite and one nitrogen atom from reagent aniline (Figure 4.9), the atom % $^{15}NO_2^-$ abundance of nitrite in the sample is diluted by the factor of two. The mass of oxidized ^{15}N can then be calculated by the following equation (Hashimoto, 1981):

$$NO_2^-{}_{(yield)} = \frac{(NO_2^-{}_{(ambient)} + NO_2^-{}_{(carrier)})\,(atom\%\,of\,^{15}NO_2^-{}_{(sample)} - 0.00366)}{(0.5 - 0.00366)\;V\;T\;R} \quad ..(4.5)$$

$NO_2^-{}_{carrier}$ = $^{14}NO_2^-$ addition to sample

$NO_2^-{}_{ambient}$ = concentration of NO_2^- or NO_3^- in samples

0.5 = the molar fraction of ^{15}N in sample nitrogen resulting from oxidation of ^{15}N, is approximately 0.5, since each atom of N from labelled NH_4^+ is coupled with an atom of N from aniline during the dye forming reaction

0.00366 = natural abundance of ^{15}N

V = volume of extracted samples

T = incubation time

R = atom % enrichment (dilution factor): in cases where the $^{15}NH_4^+$ (or $^{15}NO_2^-$or $^{15}NO_3^-$) added to the incubation container was diluted by the presence of pre-existing ambient NH_4^+ (or NO_2^- or NO_3^-) of natural isotopic content, $N_{yield\ or\ uptake}$ must be corrected by a dilution factor. The dilution factor can be either measured directly from initial enrichment of $^{15}NH_4^+$ or $^{15}NO_2^-$ or $^{15}NO_3^-$ in the medium (trials N.1 and N.4) or calculated from the ^{15}N addition (trials N.2 and N.3) as following equation (Dugdale and Goering, 1967):

$$R = \frac{(atom\%_{added} \times [NH_4^+]_{added}) + (atom\%_{ambient} \times [NH_4^+]_{ambient})}{[NH_4^+]_{added} + [NH_4^+]_{ambient}} \quad ..(4.6)$$

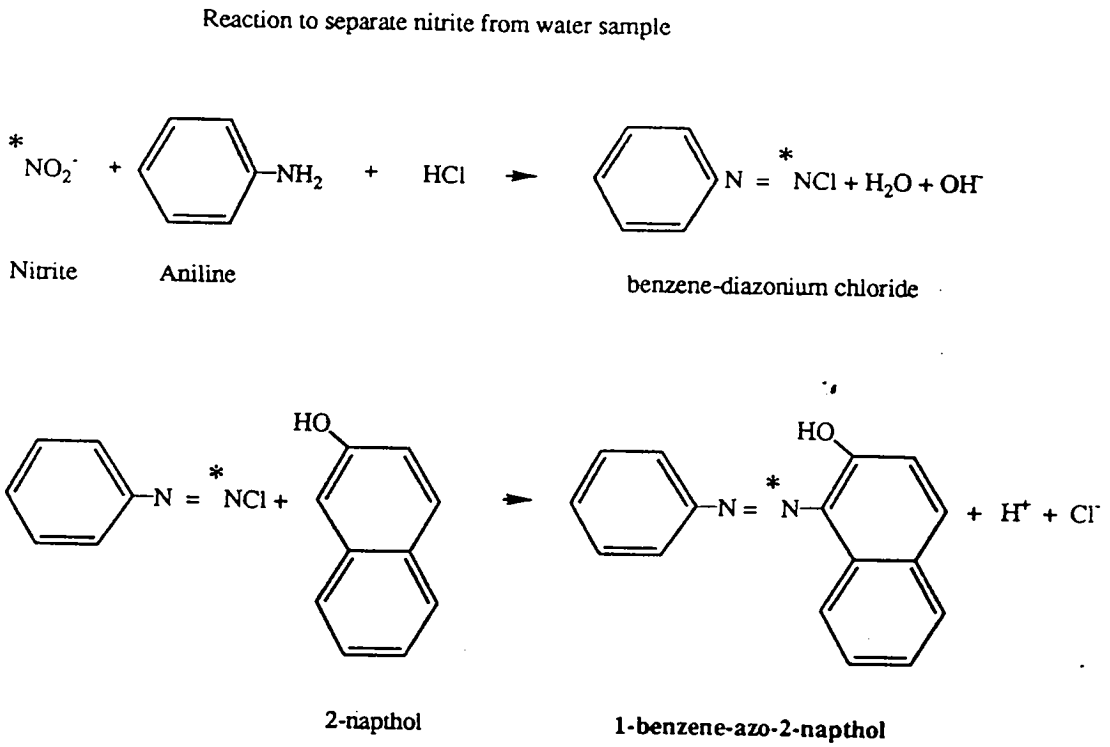


Figure 4.9 Reaction of dye azo and $^{15}NO_2^-$ position (from Hashimoto, 1981).

Calculated R values from each trial are summarized in Appendix V: Table V-1. The values of $NO_2^-{}_{yield}$ and the calculated rates of nitrite accumulation rates are listed in Appendix V: Table A-2.

Nitrite oxidation rates

Nitrite oxidation rates can be measured using either $^{15}NH_4^+$ or $^{15}NO_2^-$ additions. In the samples pre-existing nitrite was destroyed, $NO_3^-{}_{yield}$ after cadmium reduction to nitrite was calculated using equation 5 following adjustment of column reduction recoveries of NO_3^-.

$$NO_3^-{}_{(yield)} = \frac{(NO_3^-{}_{(a)} + NO_2^-{}_{(c)})\,(atom\ \%of\ ^{15}NO_2^-{}_{(s)} - 0.00366)}{(0.5-0.00366)\ V\ T\ R} * CX \quad \ldots (4.7)$$

$NO_3^-{}_{(a)} = NO_3^-{}_{(ambient)}$
$NO_2^-{}_{(c)} = NO_2^-{}_{(carrier)}$
$^{15}NO_2^-{}_{(s)} = {}^{15}NO_2^-{}_{(sample)}$
CX = Recovery of NO_3^- reduced to NO_2^- using cadmium column

In the samples where pre-existing nitrite was not destroyed, yield of NO_2^- was subtracted from the aggregate yield of ($NO_3^- + NO_2^-$).

$$NO_3^-{}_{(yield)} = \frac{([(NO_3^-{}_{(ambient)} * CX] + [NO_2^-{}_{(ambient)}] * CY] + [NO_2^-{}_{(carrier)}])}{(0.5-0.00366)\ V\ R\ T}$$

$$* (atom\%of\ ^{15}NO_2^-{}_{(sample)} - 0.00366) * CX - NO_2^-{}_{(yield)} \quad \ldots (4.8)$$

CX = Recovery of NO_3^- reduced to NO_2^- using a cadmium column
CY = Recovery of NO_2^- destroyed when passing through the cadmium column

The values of $NO_3^-{}_{yield}$ and the calculated rates are shown in Appendix V: Table V-3).

Nitrogen uptake rate

The uptake of ammonium, nitrite or nitrate into the particulate fraction was calculated from the atom % excess of PN at each sampling point, divided by the incubation period, as follows:

$$Uptake\ rate = \frac{atom\%\ ^{15}N\text{-}PN_a \times PN_c}{T \times R} \quad \ldots\ldots\ldots (4.9)$$

Atom % ^{15}N-PN$_a$ = atom % excess of ^{15}N-PN from each $^{15}NH_4^+$, $^{15}NO_2^-$, $^{15}NO_3^-$ addition

PN_c = concentration of particulate inorganic nitrogen

T = incubation time

R = atom % enrichment (described as above)

The values of ammonium, nitrite and nitrate in the particulate fraction and the calculated rates of uptake are listed in Appendix V: Table V-4.

Analysis of transformation rates

Differences in rates of ammonium oxidation, nitrite oxidation and inorganic nitrogen uptake between trials, treatments (control seawater, seawater with frozen-thawed sediment added, seawater with freshly collected sediment added) were compared by two-way ANOVA. Prior to the analysis of variance, rates calculated over 0-3 h and 0-6 h intervals were compared by Paired t-test. Multiple comparison tests (Tukey test, Zar, 1984) were used to carry out *a posteriori* comparisons of mean rates across factors found to be significant. The different rates of nitrite oxidation measured with $^{15}NH_4^+$ and $^{15}NO_2^-$ additions were analysed by two-way ANOVA. Summary of ANOVA and Tukey test results is shown in Appendix VI.

b) Results

Extraction efficiency of organic solvent and octadelcyisilane columns

The efficiency of $^{15}NH_4^+$ extraction using the Baker SPE columns was slightly, but not significantly ($\underline{P} > 0.05$) higher than $^{15}NH_4^+$ extraction using Sep-Pak columns (Figure 4.10). One advantage of the SPE column was that the amount of methanol required for efficient elution (2 x 0.5 ml) is less than that required to elute the indophenol from Sep-Pak column. This smaller volume is more quickly evaporated. Solvent extraction of indophenol by dichloromethane (0.004 for distrilled water blank, 0.002 for reagent blank) yielded significantly lower blanks (T-test, $\underline{P} < 0.05$)

compared to the column extraction procedure (0.022 for blank, 0.010 for reagent blank). However, recovery efficiency by solvent extraction of standard samples was low compared to those obtained with columns (Figure 4.10). The difference in recovery between column extraction and solvent extraction was similar to that found by Brzezinski (1987).

The presence of NO_3^- and NO_2^- in NH_4^+ standard samples (< 5 μM) did not significantly affect the efficiency of the ammonium extraction by columns (T-test, $\underline{P} > 0.05$). Blanks were found to be slightly higher in used columns washed with absolute methanol. Recoveries of ammonium from standard samples using reused columns were slightly, but not significantly ($\underline{P} > 0.05$) lower than recoveries using new columns. Absorbances of the blank samples were not significantly different ($\underline{P} > 0.05$). However small they were, however absorbance of the blanks from recycled columns were too high to permit re-use in blank and low NH_4^+ samples. Therefore only new SPE columns were used to extract ammonium in the ^{15}N experiments.

Ammonium oxidation rates

Nitrogen oxidation and uptake rates calculated over 0-3 h and 0-6 h time periods did not significantly differ (Appendix VI: Table VI-2); therefore rates calculated from the two time periods were used to analyse differences in rates among trials (trials N.1, N.2 with 2 μM, N.2 with 0.5 μM, N.3, N.4) and treatments (control, seawater with frozen-thawed sediment, seawater with freshly collected sediment).

Ammonium oxidation rates and nitrite accumulation rates calculated over various time periods within trials are summarized in Table 4.2. Ammonium oxidation rates ranged from 0.4 nmol N l^{-1} h^{-1} to 6.0 nmol N l^{-1} h^{-1}. The highest ammonium oxidation rates were obtained in trial N.1 where the seawater was spiked with 5 μM $^{15}NH_4^+$. Ammonium oxidation rates measured in trials N.2, N.3 and N.4 were not significantly different (Tukey test, Two-way ANOVA, Appendix VI: Table VI-3). The high rate observed in trial N.1 is likely the result of the higher concentration of $^{15}NH_4^+$ added. Ammonium oxidation rates in seawater with either freshly collected sediment (range 1.2-6.0 nmol N l^{-1} h^{-1}) or frozen-thawed sediment (0.9-4.7 nmol N l^{-1} h^{-1}) were significantly higher than rates in the control seawater (range 0.4-3.9 nmol N l^{-1} h^{-1}) (Tukey test, $\underline{P} < 0.05$).

Ammonium oxidation rates in the seawater with frozen-thawed sediment did not differ

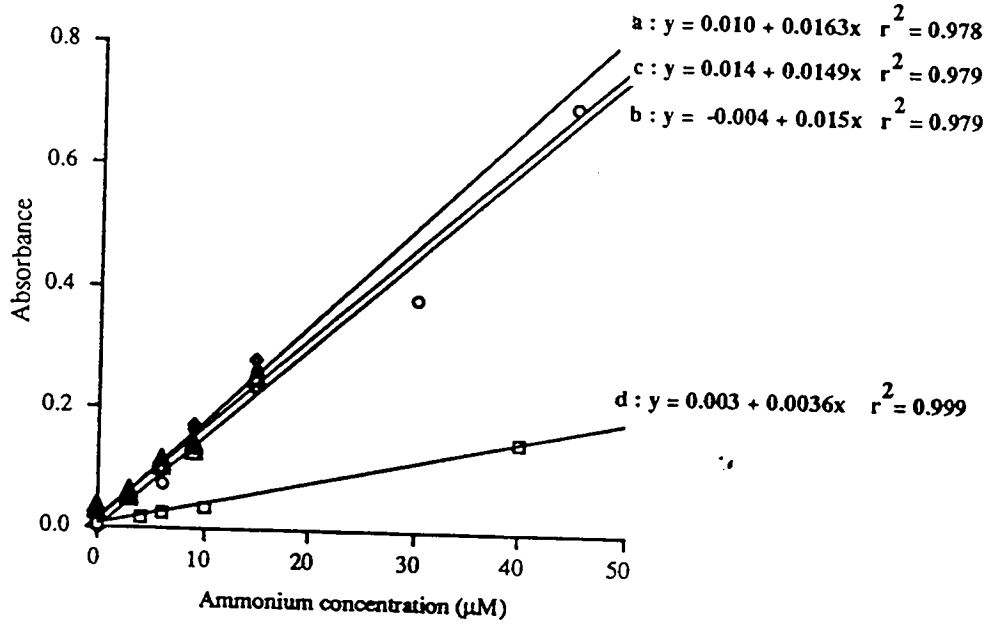


Figure 4.10 Absorbance versus ammonium concentrations after extraction procedure.

(a) : New SPE column ◇

(b) : Sep-Pak cartridge ▲

(c) : Reused SPE column O

(d) : Solvent extraction □

from rates measured in seawater mixed with freshly collected sediment. Though ammonium oxidation rates measured in seawater with freshly collected sediment added were between 0.7- and 5-fold higher than rates in seawater with frozen-thawed sediment added. There was no statistical difference when the rates were compared on a pair-wise basis (Paired T-test, $\underline{P} < 0.05$). Whether a significant difference occurred could not be detected due to the low number of replicates which reduce the power of the test.

The amount of nitrite accumulation measured at each sampling time during the four trials are shown in Figure 4.11. Rates of nitrite accumulation as a result of ammonium oxidation differed within and between trials. The differences in temporal pattern indicate that ammonium oxidation rates or nitrite oxidation rates are not uniform over even short incubation periods (6 h). In trial N.1 where the initial samples were collected immediately after $^{15}NH_4^+$ additions and designated as "time 0", significant amounts of $^{15}NO_2^-$ were detected. These "Time 0" $^{15}NO_2^-$ productions may either be the result of an error in the chemical analysis procedure or very fast ammonium oxidation rates occurring within the first 10 minutes. Some production of nitrite before "Time 0" may have resulted since it takes a finite time period for water sampling and filtration before the samples can be extracted or refrigerated.

Comparison of ammonium oxidation rates estimated by ^{14}C and ^{15}N techniques

The rate of ammonium oxidation was indirectly estimated by the dark anaplerotic uptake of ^{14}C-bicarbonate in samples with and without added nitrapyrine (N-serve). The NSDCBU rate was taken as the difference between the dark ^{14}C-bicarbonate uptake by N-serve treated and untreated (control) samples (Table 4.1, trial C.6). The NSDCBU rates, based on 24 h incubations were 2.3 and 3.2 nmol C l^{-1} h^{-1} in the control seawater and seawater with suspended sediment added, respectively (Table 4.3). In comparison, ammonium oxidation rates obtained in parallel over 6 h incubation with ^{15}N tracers were 3.9 and 4.4 nmol N l^{-1} h^{-1} in the control and experimental seawater, respectively. Thus, the C uptake/N oxidation ratios (by atoms) were 0.59 in the control and 0.73 in seawater with suspended sediment, respectively with an overall average ratio of 0.66 nmol C taken up per nmol of NH_4^+ oxidized (Table 4.3).

Table 4.2

Ammonium oxidation rates, nitrite accumulation and nitrite oxidation rates (nmol N l^{-1} hr^{-1}) measured in the samples spiked with $^{15}NH_4^+$ or $^{15}NO_2^-$.

Experimental trial	Isotope additions	Sediment site	Seawater site	Ammonium oxidation rates: Control seawater	Ammonium oxidation rates: Seawater with sediment: Frozen sediment	Ammonium oxidation rates: Seawater with sediment: Fresh sediment	Ammonium oxidation rates: Ratio of fresh: frozen sediment rates	Nitrite accumulation rates: Control seawater	Nitrite accumulation rates: Seawater with sediment: Frozen sediment	Nitrite accumulation rates: Seawater with sediment: Fresh sediment	Nitrite accumulation rates: Ratio of fresh: frozen sediment rates	Nitrite oxidation rates: Control seawater	Nitrite oxidation rates: Seawater with sediment: Frozen sediment	Nitrite oxidation rates: Seawater with sediment: Fresh sediment	Nitrite oxidation rates: Ratio of fresh: frozen sediment rates
1: Trial N.1															
Rate over 0-4 hr period	5 µM	IS3	SW6	>2.47	4.69			2.47	2.58			-	2.11		
Rate over 0-6 hr period	$^{15}NH_4^+$			3.89	4.41			3.21	3.33			0.68	1.08		
2: Trial N.2															
A:	2 µM	IS3	SW7												
Rate over 0-3 hr period	$^{15}NH_4^+$			1.36	1.72			1.08	1.25			0.28	0.47		
Rate over 0-6 hr period				0.99	1.86			0.82	1.39			0.17	0.22		
B:	0.5 µM	IS3	SW7												
Rate over 0-3 hr period	$^{15}NH_4^+$			2.81	3.70			1.64	2.41			1.17	1.29		
Rate over 0-6 hr period				1.42	1.78			0.71	1.31			0.71	0.47		
3:Trial N.3															
Rate over 0-3 hr period	0.5 µM	IS5	SW8	0.58	2.81	1.88	0.7	0.29	1.46	1.75	1.2	0.29	1.35	0.13	0.09
Rate over 0-6 hr period	$^{15}NH_4^+$			0.42	1.19	1.23	1.0	0.10	0.33	0.95	2.9	0.32	0.86	0.28	0.33
4: Trial N.4															
Rate over 0-3 hr period	0.5 µM	IS6	SW9	0.68	0.91	4.35	4.8	0.39	0.40	3.76	9.4	0.09	0.51	0.59	1.15
Rate over 0-6 hr period	$^{15}NH_4^+$			0.99	2.41	6.01	2.5	0.52	0.94	5.44	5.8	0.47	1.47	0.57	0.39
Rate over 0-3 hr period	0.5 µM											0.76	2.55	4.86	1.91
Rate over 0-6 hr period	$^{15}NO_2^-$											0.51	0.83	2.41	2.92

Ammonium oxidation rates are calculated from the sum of nitrite accumulation rates and nitrite oxidation rates.

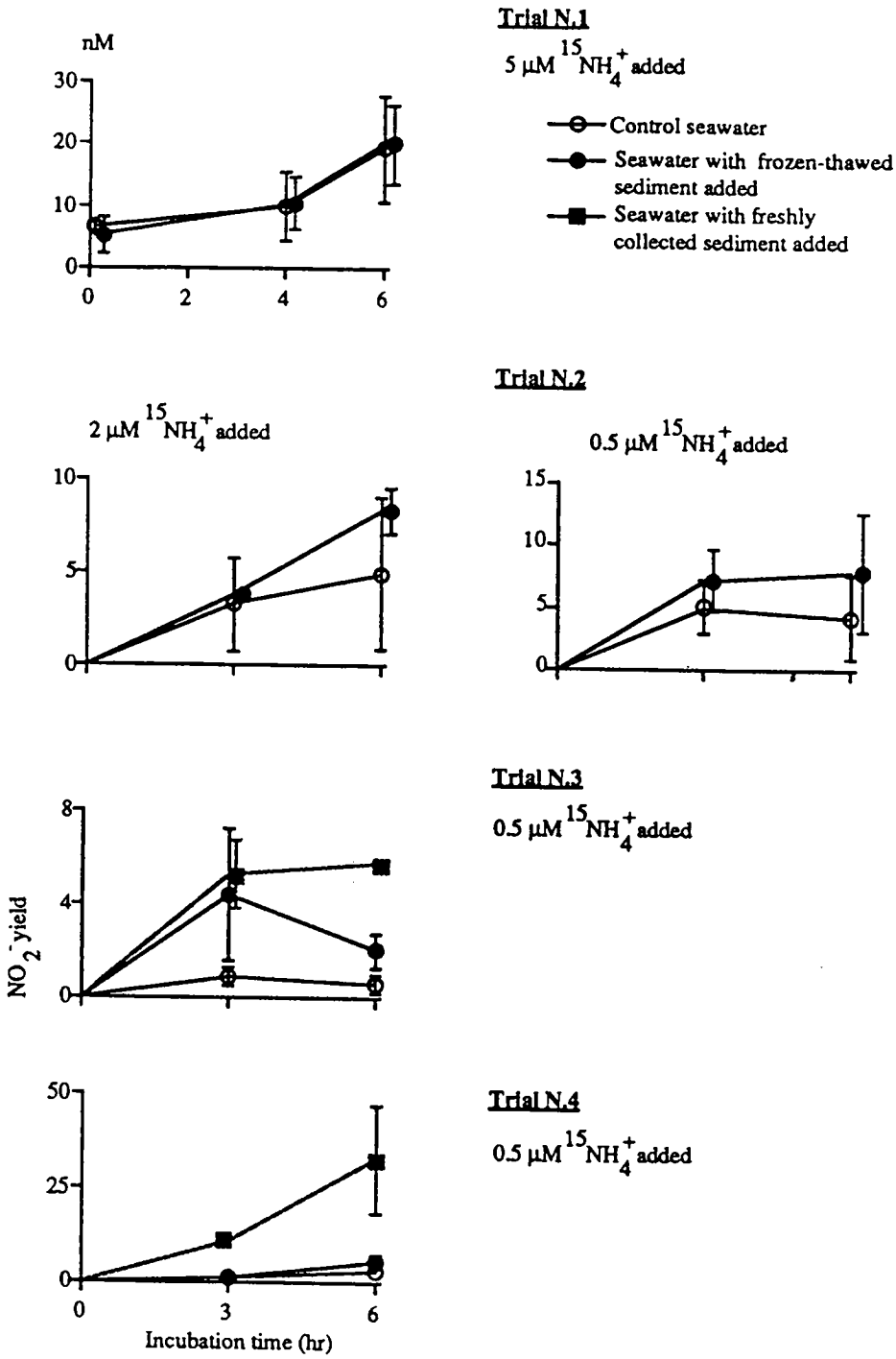


Figure 4.11 Temporal changes in nitrite accumulated from input of oxidaized ammonium and outputs by nitrite oxidation as determined with $^{15}NH_4^+$ additions. Error bars (1 SD) are smaller than symbols when absent.

Table 4.3

Comparison of ratios between N-serve sensitive dark ^{14}C-bicarbonate uptake (NSDCBU) rates (nmol C l^{-1} h^{-1}) and ammonium oxidation rates (nmol N l^{-1} h^{-1}) determined by ^{15}N techniques (C uptake/ N oxidation). The NSDCBU rates were calculated from 24 hours incubation while 6 hour incubations were used for determining ammonium oxidation rates. N = number of replicates.

Control seawater					Seawater with suspended sediemnt				
NSDCBU rate	N	Ammonium oxidation rate	N	C:N ratio	NSDCBU rate	N	Ammonium oxidation rate	N	C:N ratio
2.3	4	3.88	4	0.59	3.2	4	4.4	4	0.73

Nitrite oxidation rates

Nitrite oxidation rates were measured in trials involving both $^{15}NH_4^+$ and $^{15}NO_2^-$ additions. Mean changes in the concentration of nitrate derived from $^{15}NH_4^+$ and $^{15}NO_2^-$ are shown in Figure 4.12. Nitrite oxidation rates are summarized in Table 4.2. In four trials with $^{15}NH_4^+$ addition, nitrite oxidation rates did not significantly differ between trials (Appendix VI: Table VI-4). The nitrite oxidation rates obtained from trails with $^{15}NO_2^-$ additions were always higher than the rates obtained with $^{15}NH_4^+$ addition (Table 4.2). The very large differences (10 to 20-fold) resulting from $^{15}NO_2^-$ additions compared to $^{15}NH_4^+$ additions in trials N.1, N.2 and N.3 (data not shown) are most likely due to contamination of the nitrate samples by pre-existing nitrite. Therefore, nitrite oxidation rates obtained in samples without destruction of pre-existing nitrite cannot be used. In trial N.4 pre-existing nitrite was destroyed from the samples before cadmium reduction. The nitrite oxidation rates measured in samples with $^{15}NO_2^-$ addition were still significantly higher than those measured in samples with $^{15}NH_4^+$ additions (Tukey test, Appendix VI: Table VI-4). This may be due to fact that the existing nitrite was not completely destroyed. Nitrite oxidation rates measured in samples with freshly collected sediment added were 2- to 3-fold higher than rates in seawater with frozen-thawed sediment added where $^{15}NO_2^-$ was used as the ^{15}N source.

Nitrite oxidation rates measured in trials with $^{15}NH_4^+$ additions (range = 0.2 to 1.5 nmol N l^{-1} h^{-1}) in seawater with sediment added were significantly higher than rates in control seawater (0.2 to 1.2 nmol N l^{-1} h^{-1}). Although, nitrite oxidation rates (with $^{15}NH_4^+$ addition) measured in seawater with freshly collected sediment differed from rates measured in seawater with frozen-thawed sediment (by a factor of 0.1-1.2, Table 4.2), these differences were not statistically significant (Tukey test, Appendix VI: Table VI-3).

Nitrate production rates were usually higher in the first 0-3 h or 0-4 h time period compared to rates over 3-6 h or 4-6 h time periods though this was not statistically significant. The differences in temporal patterns indicate that nitrite oxidation rates may not be constant over the incubation period. This temporal pattern is similar to the ammonium oxidation measurement where amounts of $^{15}NO_3^-$ were detected at "time 0" (samples points collected immediatedly after $^{15}NH_4^+$ additions) (Figure 4.12).

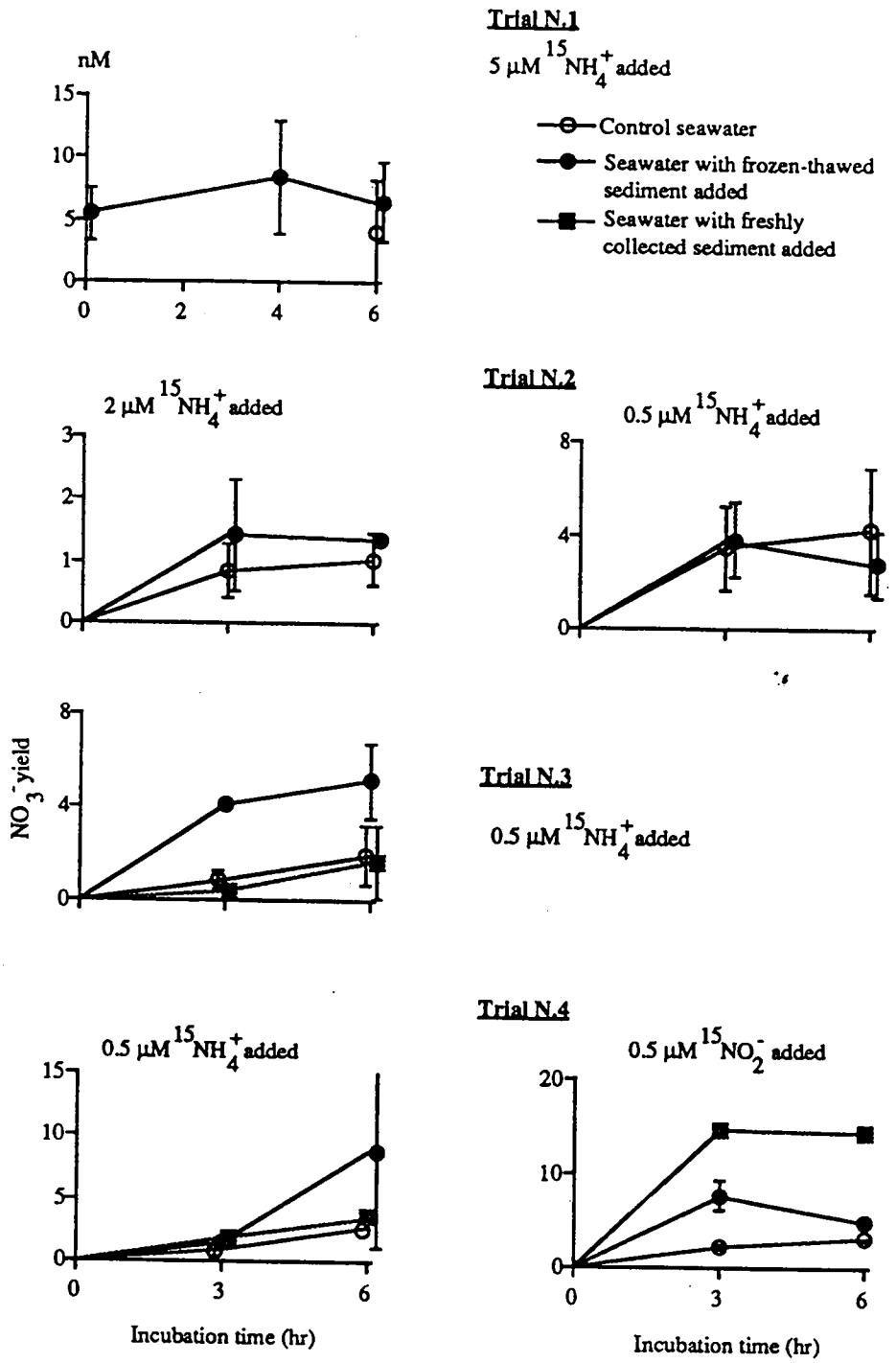


Figure 4.12 Temporal changes in nitrate yield produced from oxidation of nitrite during incubation with $^{15}NH_4^+$ and $^{15}NO_2^-$ additions. Error bars (1 SD) are smaller than symbols when absent.

Nitrogen uptake rates

Uptake rates of ammonium, nitrite and nitrate measured in the four trials (N.1- N.4) are summarized in Table 4.4. Nitrate uptake was only measured in trials N.1 and N.4. Overall, ammonium uptake rates were higher (2.6-82.2 nmol N l^{-1} h^{-1}) than uptake of either nitrate (0.3-16.8 nmol N l^{-1} h^{-1}) or nitrite (0.1-9.8 nmol N l^{-1} h^{-1}). There were no significant differences in ammonium and nitrite uptake rates between the four trials (Appendix VI: Tables VI-5 & VI-6). The nitrate uptake rates in trial N.4 were significantly higher than trial N.1 (Appendix VI: Table VI-7).

Ammonium uptake rates in seawater with freshly collected sediment added (37.7-82.2 nmol N l^{-1} h^{-1}) were significantly higher than rates measured in seawater with frozen-thawed sediment (4.3-57.0 nmol N l^{-1} h^{-1}) and in the control (2.6-39.1 nmol N l^{-1} h^{-1}) (Appendix VI: Table VI-5) (Tukey test, $P < 0.05$). Likewise, nitrate uptake rates in seawater with the freshly collected sediment added were significantly higher than rates measured in the control (0.3-1.0 nmol N l^{-1} h^{-1}). The nitrate uptake rates measured in seawater with freshly collected sediment (9.7-16.8 nmol N l^{-1} h^{-1}) did not differ from rates measured in seawater mixed with frozen-thawed sediment (8.7-16.5 nmol N l^{-1} h^{-1})(Appendix VI: Table VI-7). In contrast, nitrite uptake rates in seawater with frozen-thawed sediment added were significantly higher than control seawater (0.1-1.33 nmol N l^{-1} h^{-1}). The rates with frozen-thawed sediment (0.3-9.8 nmol N l^{-1} h^{-1}) did not differ from rates measured in seawater with freshly collected sediment added (2.8-3.0 nmol N l^{-1} h^{-1}) (Appendix VI: Table VI-6).

Uptake rates of ammonium, nitrite and nitrate varied with time. Rapid nitrogen uptake with isotope addition. A significant amount of ^{15}N-PN was detected in the "time 0" samples in trials N.1, N.2 and N.3. The "time 0" samples can be considered to be "time 0.25 h" as it took approximately 15 minutes to finish filtering the samples. Analytical error could not account for the amount of ^{15}N-PN measured in time-zero samples. The measured ^{15}N-PN was probably due to the rapid uptake processes or adsorption onto particles (Goldman *et al.*, 1981). In some cases (trials N.1, N.2 with 0.5 μM addition and N.4), ammonium uptake rates were higher during 3-6 h or 4-6 h time periods while in trial N.3 higher rates were obtained in the beginning period (0-3 h) of incubation (Figure 4.13). Nitrate (Figure 4.14) and nitrite uptake rates (Figure 4.15) were consistenly higher during 0-3 or 0-4 h incubation time period.

Table 4.4

Ammonium, nitrite and nitrate uptake rates (nmol N l^{-1} hr^{-1}) measured in the samples spiked with $^{15}NH_4^+$, $^{15}NO_2^-$ and $^{15}NO_3^-$.

Experimental trial	^{15}N addition	Sediment site	Seawater site	Ammonium uptake			Nitrite uptake			Nitrate uptake		
				Control seawater	Seawater with sediment		Control seawater	Seawater with sediment		Control seawater	Seawater with sediment	
					Frozen sediment	Fresh sediment		Frozen sediment	Fresh sediment		Frozen sediment	Fresh sediment
1: Trial N.1												
Rate over 0-4 hr period	5 µM	IS3	SW6	2.56	4.28		0.16	0.35		0.40	1.07	
Rate over 0-6 hr period				4.07	5.68		0.10	0.29		0.25	0.72	
2: Trial N.2												
A:	2 µM	IS3	SW7	8.03	33.56		1.33	9.84				
Rate over 0-3 hr period				7.22	16.34		0.44	3.41				
Rate over 0-6 hr period												
B:	0.5 µM			9.53	24.30		1.15	8.12				
Rate over 0-3 hr period				9.61	16.61		0.60	5.47				
Rate over 0-6 hr period												
3:Trial N.3												
Rate over 0-3 hr period	0.5 µM	IS5	SW8	5.48	44.12	76.36		8.02				
Rate over 0-6 hr period				5.24	23.10	41.55		5.64				
4: Trial N.4												
Rate over 0-3 hr period	0.5 µM	IS6	SW9	22.28	35.25	37.68	0.59	6.49	3.03	1.03	16.53	16.83
Rate over 0-6 hr period				39.08	56.98	82.24	0.39	3.77	2.79	0.80	8.72	9.71

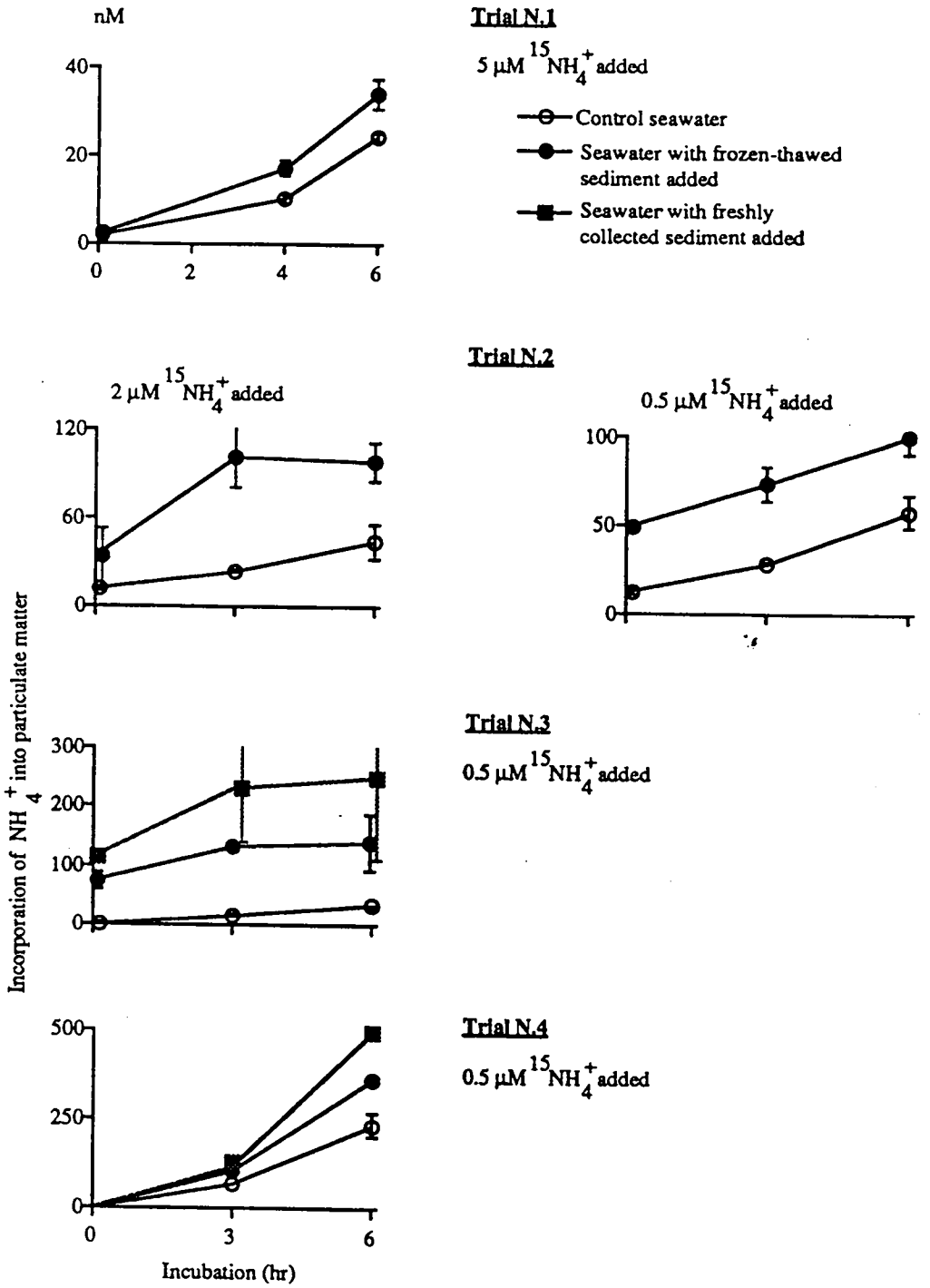


Figure 4.13 Incorporation of ammonium into particulate matter during the four experimental trials with $^{15}NH_4^+$ additions. Error bars (1 SD) are smaller than symbols when absent.

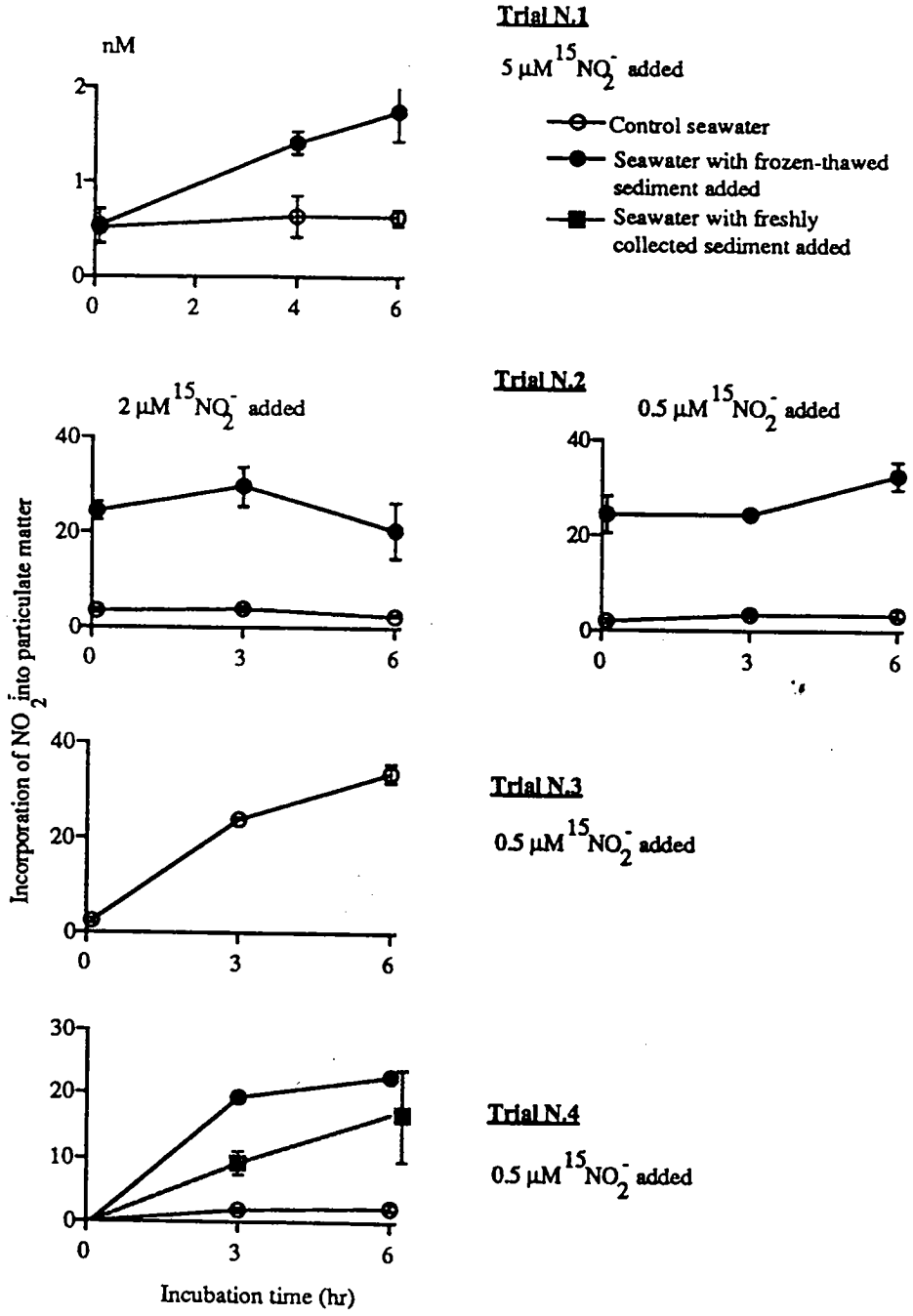


Figure 4.14 Incorporation of nitrite into particulate matter during the four experimental trials with $^{15}NO_2^-$ addition. Error bars (1 SD) are smaller than symbols when absent.

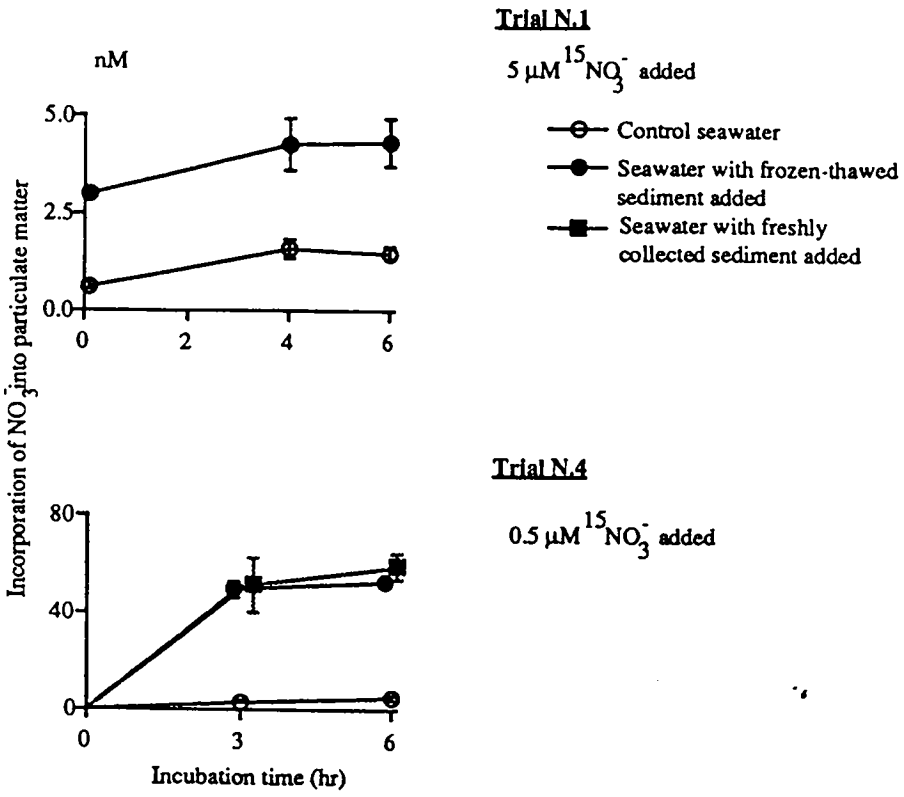


Figure 4.15 Incorporation of nitrate into particulate matter during the two experimental trials with $^{15}NO_3^-$ addition. Error bars(1 SD) are smaller than symbols when absent.

4.3 DISCUSSION

4.3.1 Cyclone disturbances and nitrogen transformation processes in GBR waters

Dissolved nutrient concentrations and related environmental factors measured a week following the passage of a tropical cyclone ("Winifred") and during a 'normal' summer condition (Figure 3.39), clearly indicated the effect of cyclonic disturbance on nutrient concentrations in GBR shelf waters. Increases in water column nutrient concentrations as a result of cyclonic disturbance can be attributed to four possible sources, enhanced river runoff (e.g. Mitchell, *et al.*, 1990), rainfall (e.g. Paerl *et al.*, 1990), sediment resuspension (Chapter 3) and Coral Sea upwelling (Furnas *et al.*, 1993). In Chapter 3, the sediment resuspension process was shown to have the potential to introduce significant amounts of dissolved and particulate nutrients into the water column. However, the magnitude of nitrite and nitrate inputs from sediment resuspension and the above sources could not fully account for the increase in these nitrogen species measured one week following cyclone "Winifred" (Furnas, 1989). It was hypothesized that water column nitrification processes were responsible for the enhanced concentrations of nitrate and nitrite measured in the water column (Furnas, 1989).

Experimental studies herein show that rates of nitrogen transformation, measured either by ^{14}C and ^{15}N tracer methods support this hypothesis. Estimated nitrification rates (whether by N-serve sensitive dark ^{14}C-bicarbonate uptake), ammonium oxidation, nitrite oxidation and inorganic nitrogen uptake were higher in seawater with sediment added. Increased in *in situ* nitrate and nitrite concentrations reflect the higher ammonium oxidation and nitrite oxidation rates caused by a combination of higher levels of the ammonium substrate, optimal conditions for oxidation processes by bacteria (namely, the low light intensity and high water temperature associated with aftermath of tropical cyclones) and increases in populations of nitrifying bacteria, both associated with the resuspended sediment or those which were released into the water column (Matulewich and Finstein, 1978).

a) Ammonium oxidation and nitrite oxidation rates

The higher rates of ammonium and nitrite oxidation measured in seawater with suspended sediment can be attributed to these following factors.

Substrate

Experimental results showed that significantly higher ammonium (1.2-7.9 nmol N l^{-1} h^{-1}) and nitrite oxidation rates (0.2-4.9 nmol N l^{-1} h^{-1}) were observed in the seawater with suspended sediment added as compared to the control seawater without sediment. This is due to the higher ammonium concentration in the water with suspended sediment (Chapter 3). Measurement of nitrification processes in marine environments have shown that the distribution and magnitude of the rates are influenced by ammonium concentration (Hashimoto *et al.*, 1983; Ward *et al.*, 1984). Increases in ammonium concentration increase ammonium oxidation rate (e.g. Wada and Hattori, 1971a; Mevel and Chamroux, 1981) and nitrate production also increases in a positive manner with nitrite concentrations (e.g. Olson, 1981a). Generally, nitrifying bacteria require three main substrates: carbon dioxide, oxygen and ammonium (or nitrite). It is unlikely that carbon dioxide is limiting in most marine environments, but potentially either oxygen or ammonium are deficient in supply (Fenchel and Blackburn, 1979). However oxygen is not limiting in disturbed seawater during aeration in the experimental carboy or during cyclonic events.

On the GBR shelf, tropical cyclones are dramatic events, which resuspend sediment particles and associated porewater into the water column over wide areas, giving rise to both high turbidity and higher dissolved inorganic nitrogen concentration, particularly of ammonium. Ammonium in the water column following the cyclone can arise indirectly from the remineralization of particulate nitrogen (e.g. Val Klump and Martens, 1983; Furnas, 1988), which is supplied from sediment resupension (Table 3.5) or river runoff (e.g Mitchell *et al.*, 1990). Organic matter from the sediment can be mineralized to ammonium and then be available to be oxidized by nitrifying bacteria (McLaren, 1971; Ardakani *et al.*, 1974; Rajendran and Venugopalan, 1977; Mevel and Chamroux, 1981).

Similarly, experimental results showed that nitrite oxidation rates were higher in seawater with suspended sediment (0.5 - 1.5 nmol N l^{-1} h^{-1}) than those in the control seawater (0.3 - 0.5 nmol N l^{-1} h^{-1}). Nitrite oxidation rates are regulated by the ammonium oxidation rate if the ammonium oxidation rate *in situ* is lower than the potential nitrite oxidation rate. In such cases, nitrite oxidizing bacteria are substrate dependent as the process is the second step from ammonium oxidation process. The experimental results showed that nitrite oxidation rates measured in the samples with direct $^{15}NO_2^-$ additions were significantly higher than rates measured in the samples

with $^{15}NH_4^+$ addition (Table 4.2). This was due to the greater availability of NO_2^- for the nitrite oxidation (Olson, 1981a) in the samples spiked with $^{15}NO_2^-$. The experimental results suggest that the high levels of nitrite found in the water column following cyclonic events would readily be available for nitrite oxidation, resulting in high levels of nitrate.

Increased ammonium (nitrite) concentrations as a result of sediment resuspension events would result in an increasing rate of ammonium (nitrite) oxidation. Higher rates of ammonium and nitrite oxidation were also measured in Chesapeake Bay following a storm (Horrigan *et al.*, 1990). McCarthy *et al.* (1984) suggested that the primary source of nitrate and nitrite in Chesapeake Bay derived from nitrification in the water rather than in the sediments. This reasoning is almost certainly related to the fact that nitrate and nitrite in the sediment do not accumulate but are readily transformed to ammonium (reduction process) or dinitrogen gas (denitrification).

Availability of nitrifying bacteria

The enhanced population of nitrifying bacteria within sediment may increase ammonium oxidation rates. Sightly higher (though not significantly) rates of ammonium oxidation were measured in seawater when freshly collected sediment was added as compared to those rates measured in seawater with frozen-thawed sediment. It is not clear whether freezing and thawing of sediment killed all nitrifying organisms (Ingraham, 1962; Rheinheimer, 1991) and may increase ammonium from particulate sources (Yamada *et al.*, 1990) which would also be available for oxidization. The nitrifying bacteria living within sediment porewater or in association with sediment particles, will be released into the water column during sediment resuspension events. These nitrifiers are an additional source of the bacterial populations responsible for enhancing the nitrification rate in the water column following resuspension events (Carey, 1938; Matulewich and Finstein, 1978).

Low light intensity

It is known that nitrifying bacteria are inhibited by light (Müller-Neuglück and Engel, 1961; Olson, 1981b; Harrison *et al.*, 1981; Horrigan *et al.*, 1981; Lipschultz, 1984; Vanzella *et al.*, 1989). The low *in situ* light intensities created by sediment particles following resuspension events may provide a more favourable condition for nitrifying organisms when compared to normal clear reef waters. The lower *in situ* light

intensities occurring during cyclonic events (Furnas, 1989) are favourable for nitrifying bacteria to oxidize ammonium to nitrite and nitrate.

Optimum temperature

Nitrification rates are directly correlated with temperature (Berounsky and Nixon, 1990). The nitrifying bacteria *Nitrosomonas* has an optimum growth temperature between 25° C and 35° C, while for *Nitrobacter* , the optimum growth temperature lies between 25° C and 30° C (Helder and de Vries, 1983). At temperatures below 35° C cultures of marine and freshwater nitrifiers show an exponential increase in the rate of nitrification with increasing temperature; however above 35° C, rates decline (Carlucci and Strickland, 1968; Jones and Hood, 1980; Helder and de Vries, 1983). During the austral summer when cyclones occur in the GBR, water temperature generally exceeds 27° C, which in association with suspended particle matter, low *in situ* light intensity and higher substrate concentration, promote water column nitrification.

b) Preference of phytoplankton utilization

Another factor contributing to the observed high levels of nitrate and nitrite in the water column following cyclonic events is the accumulation of nitrate and nitrite due to preferential uptake of ammonium by phytoplankton. Ammonium is generally utilized in preference to nitrate in both phytoplankton cultures and natural phytoplankton populations (e.g. Eppley *et al.*, 1969; McCarthy and Eppley, 1972; MacIsaac and Dugdale, 1972; Conway and Whitledge, 1979; McCarthy *et al.*, 1977). Experimental measurements of nitrogen uptake in seawater with suspended sediment (Table 4.4) show that ammonium uptake rates (4-82 nmol N l^{-1} h^{-1}) were consistantly higher than nitrate uptake (0.3-17 nmol N l^{-1} h^{-1}) and nitrite uptake (0.3-10 nmol l^{-1} h^{-1}). When ammonium concentrations exceed 0.5 µM, nitrate utilization by phytoplankton is suppressed in favour of ammonium utilization (McCarthy *et al.*, 1977). Nitrite is not usually considered an important nitrogen source for phytoplankton compared to ammonium and nitrate (e.g. McCarthy *et al.*, 1984), due to its low availability. When nitrate and nitrite are both present, nitrate is generally taken up first (Eppley and Coatsworth, 1968; Lui and Roels, 1972; Kiefer, *et al.*, 1976; Harrison and Davies, 1977). However, Eppley and Rogers (1970) found that nitrite in the growth medium could be seen to be equivalent to nitrate. Harrison and Davies (1977) observed low rates of release and accumulation of nitrite in phytoplankton culture media until the nitrate concentration dropped below 1-2 µM. During cyclonic events, high

concentrations of ammonium become available to phytoplankton through release from the sediment and remineralization from organic nitrogen and would therefore suppress nitrate utilization. As a result, nitrate and nitrite derived from many sources would be conserved in the water column compared to ammonium.

c) Upwelling

Direct evidence of upwelling during cyclone "Winifred" was not found, however, there was a well-defined intrusion concided with the occurence of cyclone "Joy" (December, 1990) (Furnas *et al.*, 1993). Furnas *et al.* (1993) suggested that some intruded water and nutrients are probably mixed back off the shelf in the Eastern Australian Current without contributing any important fraction to the shelf production. According to the temperature record, the upwelling occuring during cyclone was not unduly large when compared to upwelling which occurs at other times. High levels of nitrate due to upwelling are largely measured in relatively small shelf areas compared to the high nitrate levels measured over the area > 5000 km^2 following the cyclonic event. Therefore, which upwelling contributes nitrate into shelf water column but could not be considered the main factor for abnormally high nitrate and nitrite in GBR waters following cyclone "Winifred".

Therefore, experimental results (Chapter 3) clearly suggested that the abnormally high nitrate and nitrite concentrations measured in the water column following a cyclonic event are mainly due to the local accumulation of nitrite and nitrate. Nitrate and nitrite are not totally taken up by phytoplankton when sufficient ammonium was available from porewater derived from suspended sediment and then further supplied by remineralization processes. As nitrogen uptake rates in this present study are higher than measured nitrification rates, nitrifying bacteria must compete with phytoplankton. However, the low light intensity in water column is favourable to enhanced nitrification processes as the uptake of inorganic nitrogen is stimulated by light (MacIsaac and Dudgale, 1972; MacIsaac, 1978; Nelson and Conway, 1979; Olson *et al.*, 1980; Garside, 1981). Measurements of nitrogen transformation in GBR coral reef sediment show that nitrification is responsible for much of the decreasing ammonium (Capone *et al.*, 1992) and major source of nitrite in most sediment habitats is presumably due to ammonium oxidation (Belser, 1979).

4.3.2 Calculated nitrite and nitrate production during cyclonic event

The rates of ammonium and nitrite oxidation obtained in the laboratory experiments can be used to calculate the amount of nitrate and nitrite which should be in the water after a sediment resuspension event for comparison with actual measured nitrate and nitrite levels following cyclone "Winifred". Nitrite and nitrate production were estimated from nitrite accumulation and nitrite oxidation rates measured in seawater with ^{15}N isotopes and suspended sediment.

The amount of sediment resuspended into water column during the cyclone's passage was calculated from the estimates of reworked sediment volume made by Gagan *et al.* (1990). Gagan *et al.* (1990) estimated that a sediment layer ranging between 5.1-6.9 cm in thickness was resuspended in the area affected by the eye of cyclone "Winifred". Integrating these thicknesses of sediment over a cross-shelf area 1 m in width and 57 km in length, the volume averaged maximum amount of suspended sediment dispersed into a water column (volume of approximately 2258 Ml) is 1.89 $cm^3\ l^{-1}$.

Laboratory estimation of the nitrite accumulation rates and nitrite oxidation rates in the seawater with frozen-thawed sediment added and freshly collected sediment added were normalized to the calculated maximum suspended sediment load (1.89 $cm^3\ l^{-1}$). The rates obtained in seawater with freshly collected sediment are considered to be more appropriate. The estimated nitrite and nitrate concentrations averaged throughout the water depth after four days ranged from 0.33 to 0.98 μM and from 0.02 to 0.11 μM, respectively (Table 4.5). Average nitrite concentrations actually measured (0.10-0.16 μM) are lower than the calculated nitrite using the nitrite accumulation rate. In contrast, average nitrate concentration measured in the water column (0.49-0.58 μM) are higher than calculated from those nitrite oxidation rates.

Nitrate production was also estimated from the indirect nitrification rates based on dark C uptake/N oxidation ratios. The estimated nitrate production extrapolated from NSDCBU rates (from ^{14}C method) using fresh seawater and sediment ranged from 0.08 to 0.71 μM and cover the measured nitrate range. Estimated nitrate production using nitrification rates based on Billen's (1976) and Owens' (1986) C/N conversion ratios are also presented. Higher production rates are obtained in both cases using their ratios (Table 4.6).

Table 4.5

Estimated nitrite and nitrate production after 4 days from nitrite accumulation rates and nitrite oxidation rates in seawater with sediment added, as compared to measured nitrite and nitrate concentrations measured after cyclone "Winifred". Sediment added (gram) in the seawater samples are normalized to volume (cm^3).

Sample	Rate nmol cm^{-3} h^{-1}	*Estimated productions for 4-day period µM	#Measured concentrations 4 days after the cyclone µM
Nitrite accumulation rate			
1. ^{15}N method			
Seawater with frozen-thawed sediment	0.3-3.3	0.05-0.60	Nitrite: 0.10-0.16
Seawater with freshly collected sediment	1.8-5.4	0.33-0.98	
Nitrite oxidation rate			
1. ^{15}N method			
Seawater with frozen-thawed sediment	0.2-4.9	0.03-0.39	Nitrate: 0.49-0.58
Seawater with freshly collected sediment	0.1-9.6	0.02-0.11	
2. ^{14}C method			
Seawater with freshly collected sediment converted by ratio of			
: this present study	0.45-3.90	0.08-0.71	
: Billen's (1976)	2.72-23.72	0.49-4.3	
: Owen's (1986)	1.92-16.75	0.3-3.04	

* The amount of sediment (1.89 cm^3 l^{-1}) mixed in the water column was calculated using the reworked sediment volume of Gagan *et al.*, (1990). The amount of sediment of 5.1-6.9 cm thickness in area of 1 metre width and 57 km length resuspended into 2258 Ml of water volume.

Concentration ranges of nitrite and nitrate measured 4 days after cyclone Winifred passed this station (35 m depth). Data from Stn 23 (Furnas and Mitchell, unpublished data).

Table 4.6

Estimated nitrification rates in central GBR seawater, calculated from dark bicarbonate uptake measurements with and without suspended sediment added. Calculations are based on C uptake /N oxidation ratios from the present study, Billen (1976) and Owens (1986).

Site	NSDBCU rate	Converted nitrification rate using C uptake/N oxidation ratio from		
		this present study tropical	Billen (1976) temperate	Owens (1986) temperate
	nmol C l^{-1} h^{-1}	nmol N l^{-1} h^{-1}	nmol N l^{-1} h^{-1}	nmol N l^{-1} h^{-1}
Seawater				
C uptake/N oxidation ratios		0.59	0.12	0.17
IS7	0.94	1.59	7.80	5.59
IS8	2.55	4.32	21.25	15.18
IS9	0.35	0.59	2.92	2.08
MS2	3.50	5.93	29.17	20.83
MS3	1.24	2.10	10.33	7.38
MS4	2.14	3.62	17.83	12.74
OS6	2.98	5.05	24.83	17.74
OS7	0.39	0.66	3.25	2.32
OS8	0.74	1.25	6.16	4.40
Range	**0.35-3.50**	**0.59-5.93**	**2.92-29.17**	**2.08-20.83**
	nmol C cm^3 (sediment) h^{-1}	nmol N cm^3 (sediment) h^{-1}	nmol N cm^3 (sediment) h^{-1}	nmol N cm^3 (sediment) h^{-1}
Seawater with suspended sediment				
C uptake/N oxidation ratios		0.73	0.12	0.17
IS7	2.85	3.90	23.72	16.75
IS8	0.35	0.48	2.94	2.08
IS9	0.95	1.30	7.94	5.61
MS2	0.60	0.82	4.97	3.51
MS3	0.78	1.07	6.50	4.59
MS4	0.74	1.01	6.14	4.33
OS6	0.66	0.90	5.47	3.86
OS7	2.29	3.14	19.06	13.45
OS8	0.33	0.45	2.72	1.92
Range	**0.33-2.85**	**0.45-3.90**	**2.72-23.72**	**1.92-16.75**

An explanation for the discrepancy between nitrate production and measured stocks of nitrate in the water column after the cyclonic event may be result of reduced nitrite availability in experimental seawater as compared to natural seawater following cyclonic events. Nitrite concentration in experimental seawater was controlled by the ammonium oxidation rate while nitrite in the *in situ* seawater were derived from other sources (e.g. river runoff). Experimental results showed that when concentrations of the substrate (nitrite) were high (0.5 μM for the $^{15}NO_2^-$ addition), nitrite oxidation rate were higher than that obtained from the $^{15}NH_4^+$ addition. A population of nitrifying bacteria will only increase as long as the rate of substrate supply is in excess of that needed to meet the maintenance energy requirements of that population (Belser, 1979). Following the cyclone, nitrite which may have also been derived from other sources (e.g. runoff, sediment porewater, rainfall), was available for nitrite oxidation in the water column and would be in addition to nitrite oxidized from ammonium.

4.3.3 Comparison of nitrogen transformation rates with other studies

Published measurements of potential ammonium oxidation and nitrite oxidation rates in seawater are summarized in Table 4.7. These ammonium oxidation and nitrite oxidation rates are of similar magnitude to the present measurements, though generally lower. High rates of ammonium oxidation were measured by Horrigan *et al.* (1990) in Chesapeake Bay following storm conditions (17-1378 nmol N l^{-1} h^{-1}) . Their data clearly confirm that storm-induced mixing can have a major, albeit transient, influence on the rate of inorganic nitrogen transformations, especially nitrification. With the exception of rates measured during a storm (Horrigan *et al.*, 1990), in oxygen-deficient water (Lipschultz *et al.*, 1990) and in the chlorophyll maximum in the Gulf of Mexico (French *et al.*, 1983), ammonium oxidation and nitrite oxidation rates measured in the seawater mixed with suspended sediment were higher when compared to rates in other studies measured in seawater without sediment.

4.3.4 Chlorophyll level following cyclonic event

Following the cyclonic event, chlorophyll levels measured in water column were also elevated (Figures 3.39). Furnas (1989) observed that a pronounced phytoplankton bloom occurred within days following the cyclonic disturbance. The availability of additional dissolved inorganic nutrients from runoff, rainfall and sediment resuspension enhanced rates of nitrogen ultilization in the water column (e.g. Dugdale and Goering, 1967; MacIsaac and Dugdale, 1969; Hattori and Wada, 1972; Olson,

Table 4.7

Estimates of ammonium oxidation rates in seawater from temperate and tropical regions.

Location	Method	Rate nmol N l^{-1} h^{-1}	Referrences
Temperate regions			
North Pacific	Chemical assay	2.8	Hattori and Wada, 1971
North Pacific	Chemical assay: 5 °C	0.38-0.67	Wada and Hattori, 1971
Sagami Bay, Japan	^{15}N assay; 5,10 µM NH_4^+	0.65-1.14	Miyazaki *et al.*, 1973
Chesapeake Bay	^{15}N assay; 0.05-5 µM NH_4^+	3.0-10	McCarthy *et al.*, 1984
Chesapeake Bay	^{15}N assay; 0.05 µM NH_4^+	17-1378*	Horrigan *et al.*, 1990
Southern California	^{15}N assay ;0-21 µM NH_4^+	1.9-2.5	Olson, 1981a
Southern California	^{15}N assay	0.8	Ward *et al.*, 1982
Southern California Bight	^{15}N assay	0-2	Ward, 1985
Caracao Trench	^{15}N assay; 0.1-10 µM NH_4^+	0.1-0.6	Hashimoto *et al.*, 1983
Skau Bay, Alaska	^{15}N assay; 10 µM NH_4^+	0.5-1.96	Hattori *et al.*, 1978
Narragansett Bay	increase in NO_2^- and NO_3^-	< 20	Berounsky and Nixon, 1985
Baltic Sea	^{14}C/N-serve converted by 8.3	1-280	Enoksson, 1986
Tropical regions			
East China Sea	^{15}N assay; 10 µM NH_4^+	0.16-0.26	Miyazaki *et al.*, 1975
Philippines Sea	^{15}N assay; 10 µM NH_4^+	0.21-0.30	Miyazaki *et al.*, 1975
West Pacific	^{15}N assay; 10 µM NH_4^+	0.37-1.17	Miyazaki *et al.*, 1975
Gulf of Mexico	increase in NO_2^- and NO_3^-	20-90	French *et al.*, 1983
Southern tropical Pacific	^{15}N assay	0-12.5	Lipschultz *et al.*, 1990
Carribean	^{15}N assay, 5 µM NH_4^+	0.01-0.09	Hashimoto, 1981
GBR, Australia	^{15}N assay, 0.2-5 µM NH_4^+:		**this study**
	-Seawater	0.6-3.9	
	-Seawater with sediment added	0.9-6.0	
	^{14}C/N-serve method converted by C uptake/N oxidation ratio		
	-Seawater	0.6-5.9	
	-Seawater with sediment added	0.5-3.9	

Estimates of nitrite oxidation rates in seawater.

Location	Method	Rate nmol N l^{-1} h^{-1}	Referrence
Chesapeake Bay	^{15}N assay; 0.05 µM NH_4^+	15-1453*	Horrigan *et al.*, 1990
Southern Pacific Ocean	^{15}N assay	0-8.75	Lipschultz *et al.*, 1990
Southern Pacific Ocean	^{15}N assay	0-3.3	Ward, 1987
Southern California	^{15}N assay: dark	0.16-0.96	Olson, 1981a
Southern California	^{15}N assay: surface water	0.01-0.22	Olson, 1981a
Southern Carifornia	^{15}N assay	0.6	Ward, *et al.*, 1982
GBR, Australia	^{15}N assay, 0.2-5 µM NH_4^+		**this study**
	-Seawater	0.2-1.2	
	-Sewater with sediment added	0.1-2.1	

* rates include measurement following a storm

1981a). The observed higher rates of ammonium, nitrite and nitrate uptake in seawater with suspended sediment support this observation (Table 4.4). Enhanced remineralization of organic nitrogen associated with resuspended sediment may be considered to be a source for contributing primary production in GBR waters following the cyclone. Remineralization rates in reef water are known to be higher when extra organic matter is contributed from benthic substratum (Hopkinson *et al.*, 1987). It is estimated that ammonium regeneration in the water column of Davies Reef supplied almost 3 times more inorganic N to the water column than sediment regeneration in lagoonal portions of the reef (Hopkinson *et al.*, 1987).

Dissolved inorganic nitrogen uptake rates in sediment amended seawater cannot be readily compared with uptake rates measured in seawater elsewhere as the conditions are quite different. Even at the very low light intensities used herein, the measured nitrogen uptake rates are high compared with rates at similar light levels (e.g. Ward, 1985). In most cases, however, the major factor affecting nitrogen uptake rates is likely the concentration of the limiting nutrient in the environment as ammonium uptake is not strongly controlled by both ammonium concentration and light intensity (e.g. MacIsaac and Dugdale, 1972; Ward, 1985).

Experimental results showed that dark bicarbonate uptake rates increased directly with the amount of ammonium added (Figure 4.3) suggesting nitrogen is limiting (Morris *et al.*, 1971a&b). Phytoplankton biomass in GBR waters is regarded as being nitrogen limited (Furnas and Mitchell, 1986b). Plankton blooms were observed within days after cyclone "Winifred" (Furnas, 1989) and other cyclones (Furnas *et al.*, 1993) in GBR waters. Calculated DIN:DIP ratio in the water column following the cyclone "Winifred" showed that N:P ratio was 5.5 compared to the N:P ratio of 2 during normal summer conditions. (Table 3.6 and Figure 3.39). The low N:P ratio (< 16) showed that the pelagic biomass in GBR water is nitrogen limited. However, the higher N:P ratio was relatively higher during cyclonic event. Although nitrogen still appears to be limiting in the GBR waters following the cyclones, these episodic events of plankton bloom after the injection of nutrients showed that nutrients especially nitrogen can be supplied into the waters and reducing the the constraints of nitrogen-limited status in this water.

4.3.5 Constraints of nitrogen transformation measurements

Measurement of nitrogen transformation rates using either dark ^{14}C and ^{15}N tracer

methods are subject to a number of difficulties and potential errors. In the case of the dark ^{14}C uptake method, the efficiency of the nitrification inhibitor is the most critical factor in the estimation of the nitrification rate. As nitrification rate is estimated from the difference between the amount of dark ^{14}C uptake in samples with and without inhibitors. Effects of bottle confinement and seawater transfer on phytoplankton cannot be avoided when dealing with experimental measurements. A major limitation to the interpretation of rates directly measured with ^{15}N tracer methods is that the measured rates are often potential rates since the ambient substrate is usually increased by the addition of isotope to the samples.

Whatever the limits of the ^{14}C and ^{15}N isotope techniques, the direct comparison herein of nitrification rates estimated by these two methods has been the first in the tropics and should provide useful information regarding nitrogen dynamics in tropical waters. The problems and difficulties encountered in applying tracer methodologies have provided fundamental information to guide further investigations of nitrogen dynamics in the GBR. Practical limitations to measuring specific nitrogen transformation rates in GBR waters are discussed in detail as follows.

a) Nitrification inhibitors

Differences in the performance of inhibitor have been reported in a number of other studies. ATU was not effective in blocking dark bicarbonate uptake in seawater samples with GBR sediments added, even though ATU has been reported to be effective for complete inhibition of ammonium oxidation in freshwater sediment at a concentration of 5 μM (Hofman and Lees, 1953; Lees, 1955; Hall, 1984). In direct comparison, Hall (1984) reported that the apparent nitrification rates in lake sediments were higher using ATU than N-serve. Reason for these differences were not resolved.

Direct effects of ethanol, the organic N-serve carrier, on dark bicarbonate uptake rates are not consistent between experimental systems. In common with other studies (Hauck, 1980; Hall, 1984), I found that the organic carbon (ethanol or acetone) affected dark bicarbonate uptake rates while in a few cases no such effect was observed (Christofi, Ph.D. thesis, 1978 cited in Hall, 1982). It may be that different species of ammonia producing micro-organisms in individual systems may exhibit different degrees of sensitivity towards particular solvents (Hall, 1984). In order to minimize the effect of the ethanol carrier on estimates of dark uptake rate, the results

herein suggest that Hach2533 can be substituted N-serve for nitrification experiments in natural seawater without high sediment loaded.

Many micro-organisms present in the natural environment are known to assimilate bicarbonate, usually phototrophically but also through anaplerotic (dark) pathways (Somville, 1978). Lack of efficient nitrification blocking in high ammonium seawater with sediment added may occur because other non-nitrifing organisms can take up bicarbonate and incorporate it at high ammonium concentrations (Somville, 1978). The various range of N-serve concentrations required in various studies (eg. Billen, 1976; Somville, 1978; Hall, 1984) to efficiently block nitrification are vary probably due to the different environments or strains of ammonium-oxidizers involved (Belser and Schmidt, 1981).

A particular problem with the use of nitrification inhibitors is that no single chemical is known which immediately and completely prevents nitrification while allowing all other processes to continue unaffected. N-serve is known to inhibit other organisms such as heterotrophic bacteria, some fungi and actinomycetes which are capable of oxidizing ammonium (Alexander, 1965; Painter, 1970; Jones and Hood, 1980; Campbell and Lees, 1967; Verstraete, 1975; Verstraete and Alexander, 1972, 1973; Eylar and Schmidt, 1959; Hirsch *et al.*, 1961). At the concentrations required to prevent nitrification, N-serve inhibits the activity of methane-oxidizers, sulfate-reducers (Somville, 1978) and methane-producers (Salvas and Taylor, 1980). Therefore, at the high concentrations required in the present study to block nitrification in the presence of suspended sediment, N-serve may likely affect the estimated dark uptake rate.

b) Dark inorganic C uptake/N oxidation ratio

The range of dark inorganic C uptake/N oxidation ratios determined in this study (0.59-0.73) are higher than estimated in previous studies (Table 4.8). It is known that dark C fixation/N oxidation ratios can vary from 0.025 during exponential growth of marine nitrifiers to 0.25 in the stationary phase (Kaplan, 1983) and the physiological state of nitrifying organisms *in situ* varies continuously with time.

In the present study, the dark C uptake/N oxidation ratios were measured using natural populations in seawater, whereas most published estimates (Table 4.8) were determined using enrichment cultures of nitrifying organisms in which population

Table 4.8

Measured ratios of dark inorganic carbon incorporated to nitrogen oxidation for autotrophic nitrifying bacteria.

Organisms	C/N ratio	Method used	References
Ammonium oxidizing bacteria			
Nitrocystis oceanus	0.13-0.07	Ratio of oxygen consumption to nitrite production in culture of ammonium oxidizing bacteria	Gundersen *et al.*, 1966
Nitrocystis oceanus	0.14	Ratio of oxygen consumption to nitrite production in culture of ammonium oxidizing bacteria	Gundersen and Mountain, 1973
Nitrosomonas sp.	0.09	Ratio of oxygen consumption to ammonium oxidized in culture	Wezernak and Gannon, 1968
Nitrocystis oceanus	0.1-0.06	N-serve sensitive dark ^{14}C-bicarbonate incorporation and nitrite production in culture of ammonium oxidizing bacteria	Carlucci and Strickland, 1968
Enrichment culture ammonium oxidizer	0.088	N-serve sensitive dark ^{14}C-bicarbonate incorporation and nitrite production in culture of ammonium oxidizing bacteria	Billen, 1976
Nitrosomonas ammonium oxidizer	0.033	Bacterial carbon yield and the concentration of growth limiting substrate in culture	Helder and de Vries, 1983
	0.168	N-serve sensitive dark 14C-bicarbonate incorporation and nitrite production in culture of ammonium oxidizing bacteria	Owens, 1986
ammonum oxidizer	0.59-0.73	Ratio of N-serve sensitive dark ^{14}C bicarbonate incorporate and ammonium oxidation rate measured by ^{15}N tracer techniques	**This study**
Nitrite oxidizing bacteria			
Nitrobacter sp.	0.04	Ratio of oxygen consumption to nitrite production in culture of ammonium oxidizing bacteria	Gundersen and Mountain, 1973
Nitrobacter sp.	0.01	Ratio of oxygen consumption to ammonium oxidized in culture	Wezernak and Gannon, 1968
Nitrobacter sp.	0.01	N-serve sensitive dark ^{14}C-bicarbonate incorporation and nitrite production in culture of nitrite oxidizing bacteria	Billen, 1976
Nitrobacter culture	0.02	Bacterial carbon yield and the concentration of growth limiting substrate in culture	Helder and de Vries, 1983

numbers, nutrient concentrations, and rates of activity are different than would be found in natural environments. The extrapolation of values from culture studies could lead to an overestimation of the apparent rate of nitrification process in other studies. It has not been demonstrated to what extent the genera/species used to derive C uptake/N oxidation ratios in laboratory cultures are responsible for the nitrification occurring in the ocean (Hashimoto, 1981). In culture media, concentrations of ammonium are often three or four orders of magnitude greater than ambient concentrations in the ocean. Such conditions produce cells with greatly altered metabolic states relative to those in ammonium-depleted natural conditions. This metabolic state is not easily measured or compared, as it is difficult to measure or define the metabolic state of nitrifying bacterial cells widely dispersed in seawater. The ratios obtained in previous studies were mainly measured in sediments while in the present study they were measured in seawater. It is interesting to note that the comparatively high ratio (0.168) obtained by Owens (1986) was measured using a culture of nitrifying bacteria from turbid estuarine water (Table 4.8).

The high dark C uptake/N oxidation ratio found in this study may also be due to differences between nitrifying organisms in tropical and temperate environments. Most other comparisons were carried out in temperate regions, or in eutrophic water where nitrogen availability is far greater than in tropical regions. The dark C uptake/N oxidation ratio, when used as a measure of the growth yield of these organisms, is known to change with conditions in the environment (temperature, nutrients, etc.) as well as with biomass of the organisms (Belser and Schmidt, 1980).

Variation in the ratio of the C uptake/N oxidation directly affect the estimation of the nitrification from the dark ^{14}C-bicarbonate uptake rates. The ratio determined in the present study can be best compared to ratios determined in two other studies. Billen (1976) measured the C uptake/N oxidation ratio in an enrichment culture of nitrifying bacteria taken from marine sediment. Owens (1986) made similar measurements using a culture of nitrifying bacteria isolated from turbid estuarine water. When the ratios from these two published studies and the ratio from the present study are used to estimate nitrification rate, different values result (Table 4.6). The nitrification rates estimated in this study are lower (0.6 to 5.9 nmol N l^{-1} h^{-1} in plain seawater and 0.5 to 3.9 nmol N cm^{-3} h^{-1} in seawater with suspended sediment added) compared to rates determined using either of the other two C uptake/N oxidation ratios (Billen: 2.9-29.2 nmol N l^{-1} h^{-1} in plain seawater and 2.7 to 23.7 nmol N cm^{-3} h^{-1} in seawater with suspended sediment; Owens: 2.1-20.8 nmol N l^{-1} h^{-1} in seawater and 1.9 to 16.8

nmol N cm^{-3} h^{-1} in seawater with suspended sediment). The difference is almost an order of magnitude which raises questions about the reliability of using published estimates in other work. Thus, it is important to calculate one's own ratio and not rely on estimates from other studies. This may be important, when as in the present case, one has moved from the temperate environment of previous studies to the tropics. The estimated nitrification rate based on the C uptake/N oxidation ratio in this study are of the same order as previous studies measured in tropical regions (Table 4.7). Therefore, to reliably estimate nitrification rates in any system by the dark ^{14}C method, a local calibration of the C uptake/N oxidation ratio for that system is required.

c) ^{15}N tracer experiments and nitrification rate calculations

The absolute magnitude of ammonium oxidation, nitrite oxidation and nitrogen uptake rates measured using ^{15}N tracer techniques are dependent upon the assumptions involved in the rate calculations once the isotope ratios are determined (Caperon *et al.*, 1979; Glibert *et al.*, 1982, 1985; Garside and Glibert, 1984; Garside, 1984; Laws, 1984). Changes in the isotopic composition of the ammonium pool over time were measured in trials N.1 and N.4, but not in N.2 and N.3. Rates of ammonium or nitrite oxidation and nitrogen uptake obtained from trials N.1 and N.4 were calculated by using atom % enrichment measured in the medium at each sampling point (modified from Glibert *et al.*, 1982; the mean atom % enrichment of the substrate pool is measured at each time point and is used as the divisor in the equation to calculate the rate over the following time interval; see Appendix V: Table V-3). Rates from trials N.2 and N.3 were calculated by using the equation of Dugdale and Goering (1967) (Equation 6; the isotopic content of the substrate pool is considered to be constant with time and the initial ratio is used as the divisor in the equation). The potential for error and underestimation of rates arising from the use of Dugdale and Goering's equation has been discussed elsewhere (see above references). Calculation based on the atom % enrichment measured in the medium produced higher results, the difference being a factor of 1.7 (S.D. = 0.4) as compared to calculated atom % enrichment (Dugdale and Goering, 1967) from trial N.1 data. Thus the rates (trials N.2 and N.3) obtained by using the initial atom % enrichment, should be considered as underestimates (Glibert *et al.*, 1982a) by a factor of 1.7 ($\pm$ 0.4 SD).

d) Potential rates

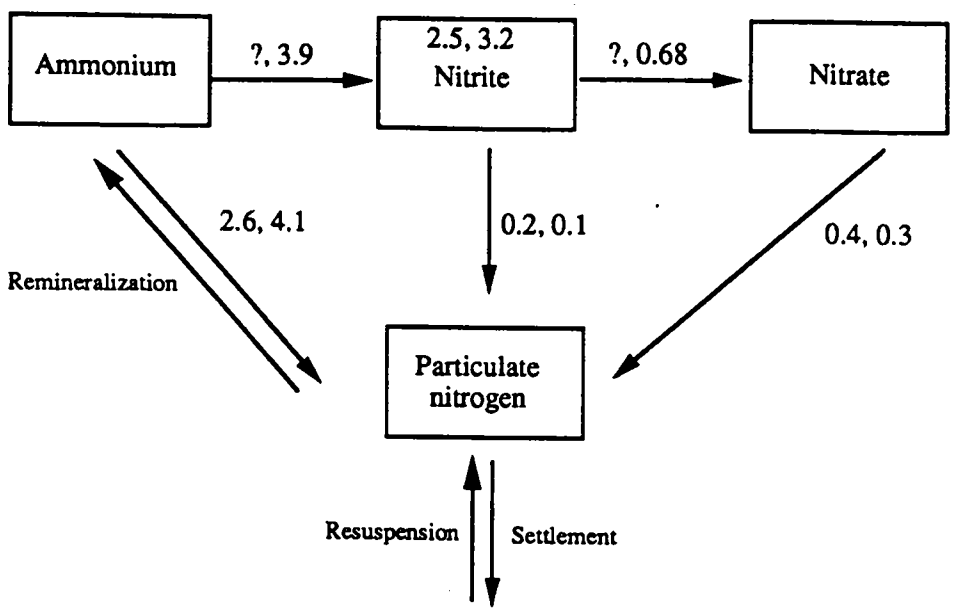
As spiking samples with high concentrations of isotopes in the ^{15}N transformation experiment cannot avoid enhancing the substrate concentrations by a significant amount, the nitrogen transformation rates in at least some cases (e.g. in control seawater) presented herein must be considered to be potential rates (e.g. Eppley *et al.*, 1973, 1977; Harrison, 1983a; Ward, 1985). It is difficult to measure nitrogen transformation rates precisely when dealing with water such as those found in GBR waters which contain natually low dissolved inorganic nitrogen concentrations. However, because of natural enhancements following resuspension rates of ammonium oxidation, nitrite oxidation and ammonium uptake measured in the seawater with suspended sediment added (spiked with 0.5 μM $^{15}NH_4^+$) should be considered to be close to actual rates. This is because water column ammonium concentrations following the cyclone were approximate 0.2-0.5 μM (Furnas, 1988) which were similar to amount of ammonium spiked in the experimental seawater (0.5 μM $^{15}NH_4^+$). In other cases, nitrogen transformation rates measured in this study should be considered as potential rates.

Ammonium uptake has been shown to be rapid during short-term incubations (Conway, 1974; Conway and Harrison, 1977; Glibert and Goldman, 1981; Wheeler *et al.*, 1982; Harrison,1983b). McCarthy (1982) found that twenty percent of the added ammonium is consumed during the first minute of incubation, increasing to 30 % consumption after 5 minutes. In trial N.1, approximately 2 nmol N l^{-1} ^{15}N-PN was detected in the water samples (immediate sampling after isotope addition- time 0). This may be considered to result from the rapid uptake process as the adsorption onto the particulate nitrogen can not account for this higher amount of PN.

e) Measurement of nitrogen transformation rates in the experimental and *in situ* conditions

Nitrogen transformation rates measured in the laboratory can be different from the rates measured *in situ* in the water column. Computations of mass balances were not attempted because the sum of measured rates was never sufficient to result in complete consumption of the added tracer (Ward, 1987). The ranges of measured transformation rates in seawater with and without added sediment are summarized in Figures 4.16 - 4.20. As mentioned above, ammonium oxidation, nitrite oxidation and ammonium uptake rates in the seawater with suspended sediment added and spiked

A. Control (natural) seawater



B. Seawater with suspended sediment (frozen-thawed)

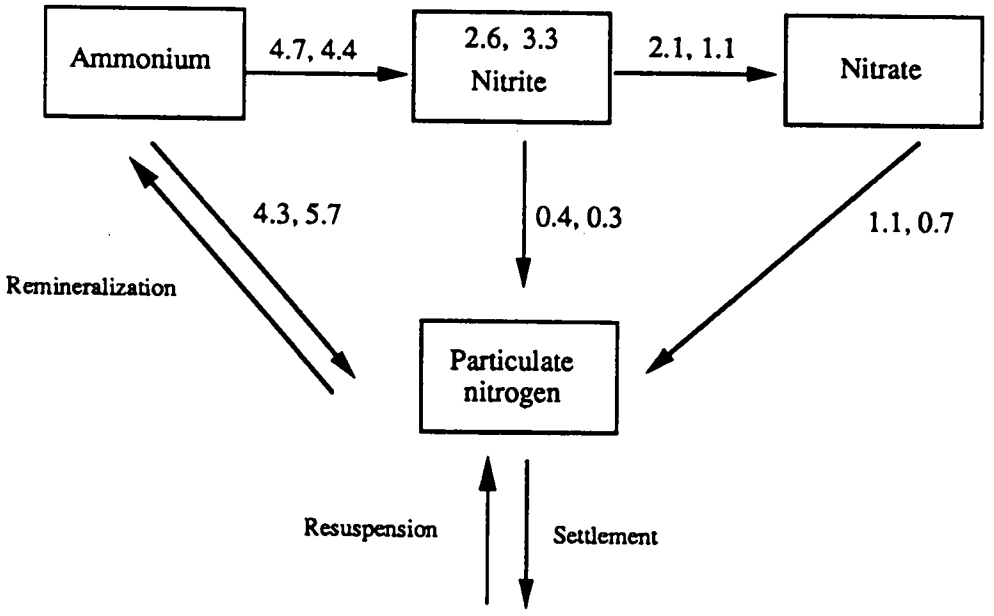
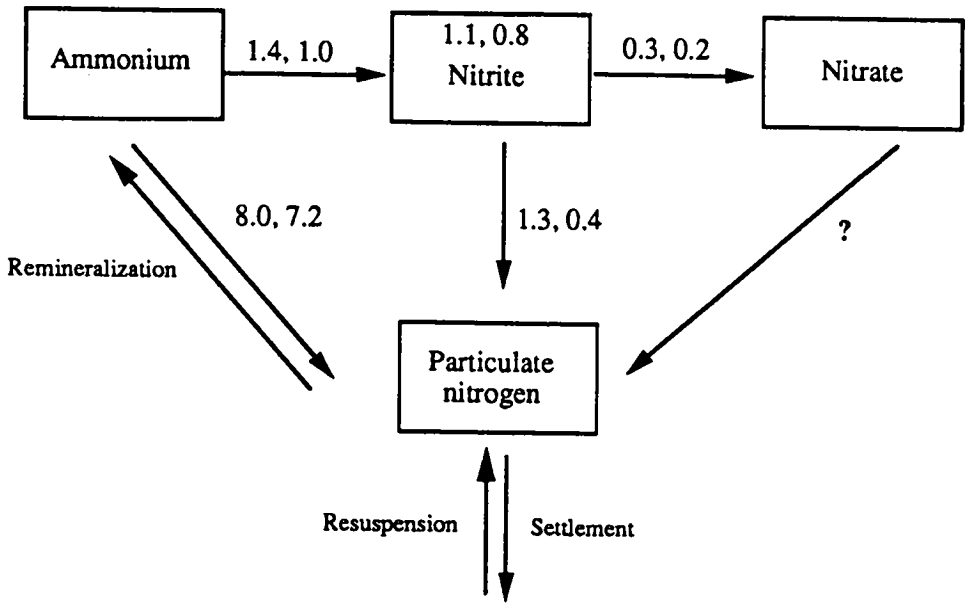


Figure 4.16 Nitrogen transformation rates (nmol N l^{-1} h^{-1}) in control seawater (A) and seawater with frozen-thawed sediment added (B) from trial N.1 with 5 μM isotope additions. The left of values shows average rate over the 0-4 h period while the right shows the average rate over the 0-6 h period. Values within boxes refer nitrite accumulation rates. Symbol "?" means rates were not available.

A. Control (natural) seawater



B. Seawater with suspended sediment (frozen-thawed)

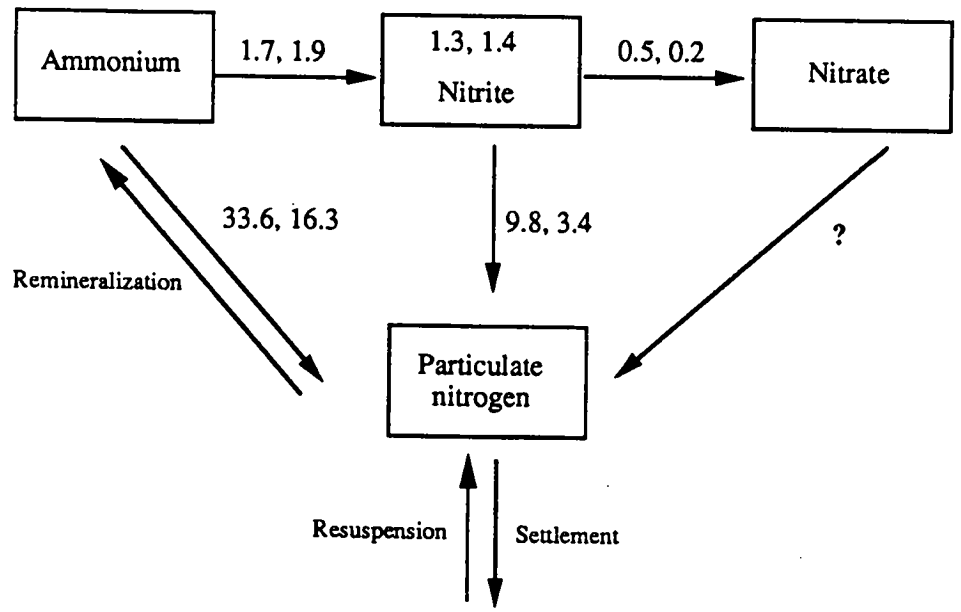
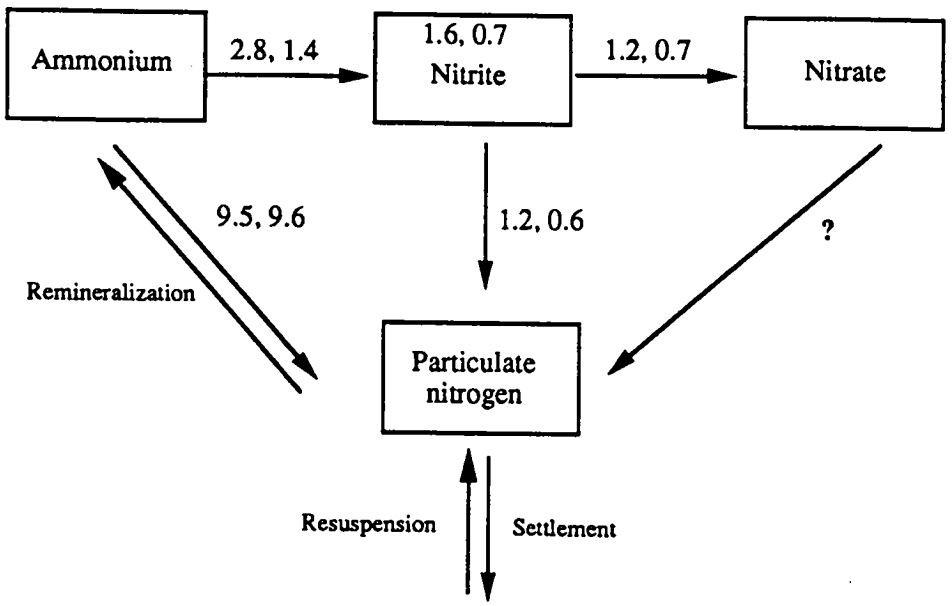


Figure 4.17 Nitrogen transformation rates (nmol N l^{-1} hr^{-1}) in control seawater (A) and seawater with frozen-thawed sediment added (B) from trial N.2 with 2 μM isotope additions. The left value shows average rate over the 0-3 h period while the right value shows average rate over the 0-6 h period. Values within boxes refer nitrite accumulation rates. Symbol "?" means rates are not available.

A. Control (natural) seawater



B. Seawater with suspended sediment (frozen-thawed)

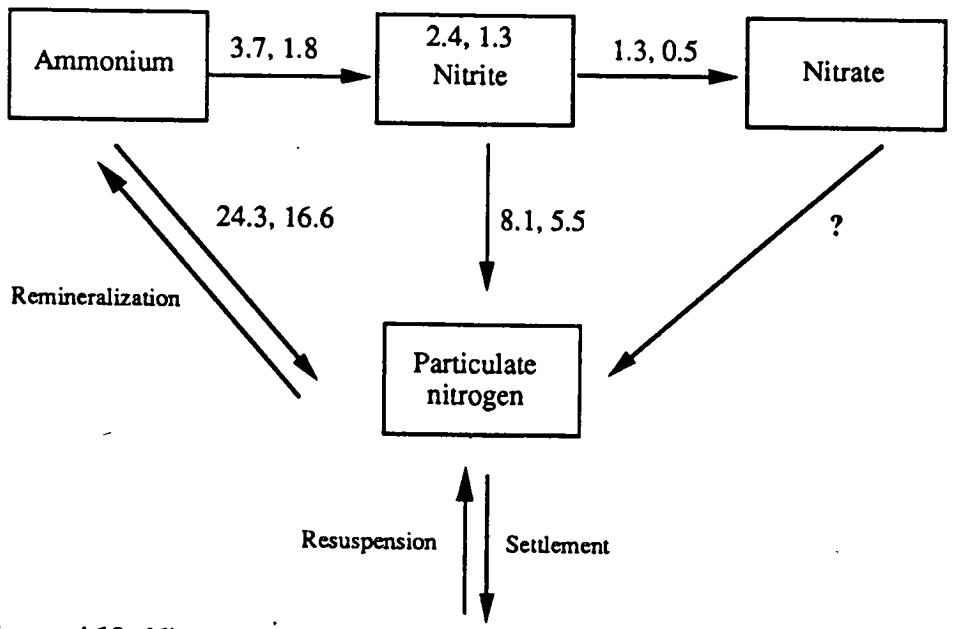


Figure 4.18 Nitrogen transformation rates (nmol N l^{-1} hr^{-1}) in control seawater (A) and seawater with frozen-thawed sediment added (B) from trial N.2 with 0.5 μM isotope additions. The left value shows average rate over the 0-3 h period while the right value shows average rate over the 0-6 h period. Values within boxes refer nitrite accumulation rates. Symbol "?" means rates are not available.

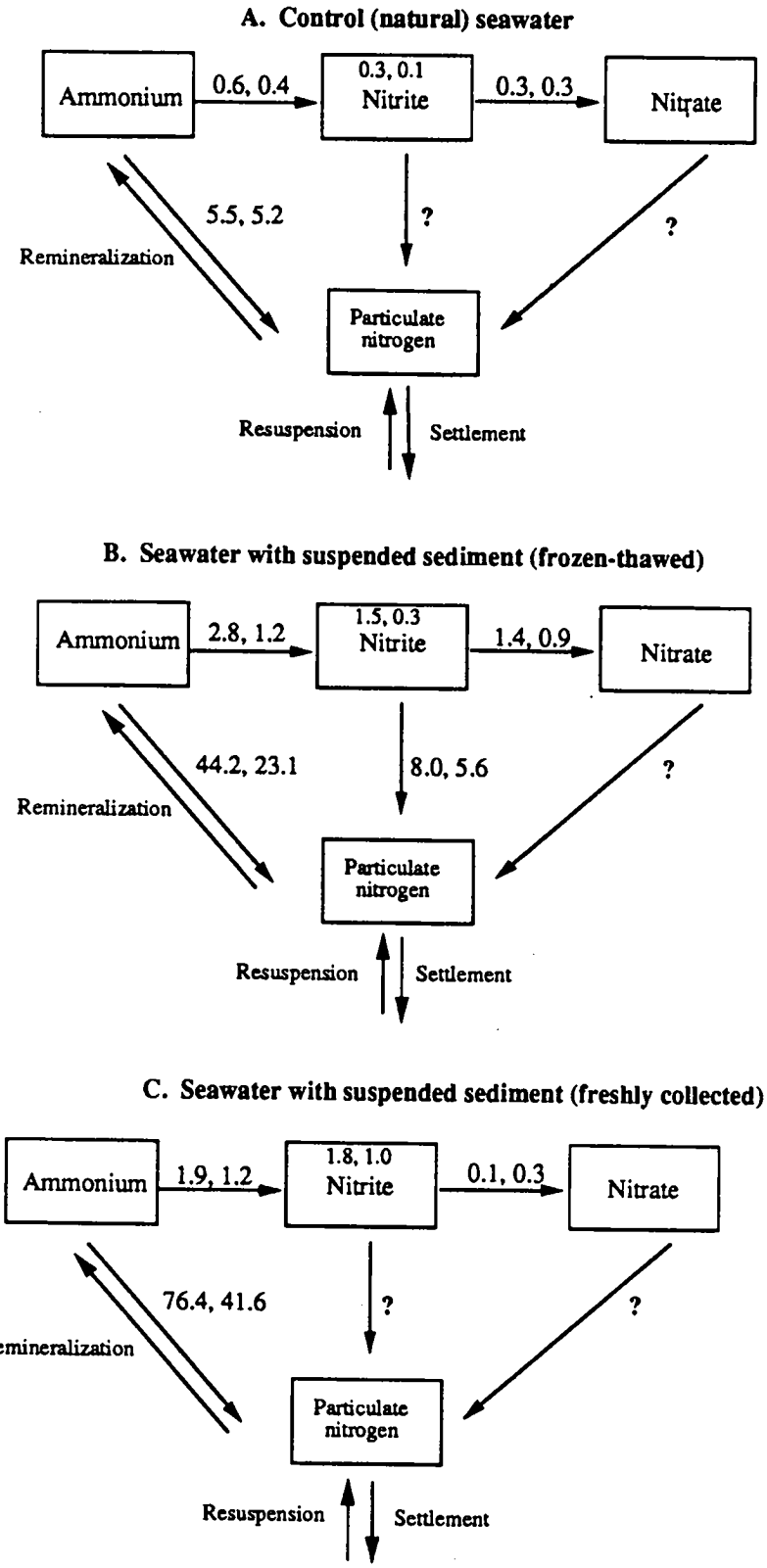


Figure 4.19 Nitrogen transformation rates (nmol $N\,l^{-1}h^{-1}$) in control seawater (A), seawater with frozen-thawed sediment (B) and with freshly collected sediment (C) added from trial N.3 with 0.5μM isotope additions. The left value shows average rate over the 0-3 h period while the right value shows average rate over the 0-6 h period. Values within boxes refer to nitrite accumulation rates. Symbol "?" means rates are not available.

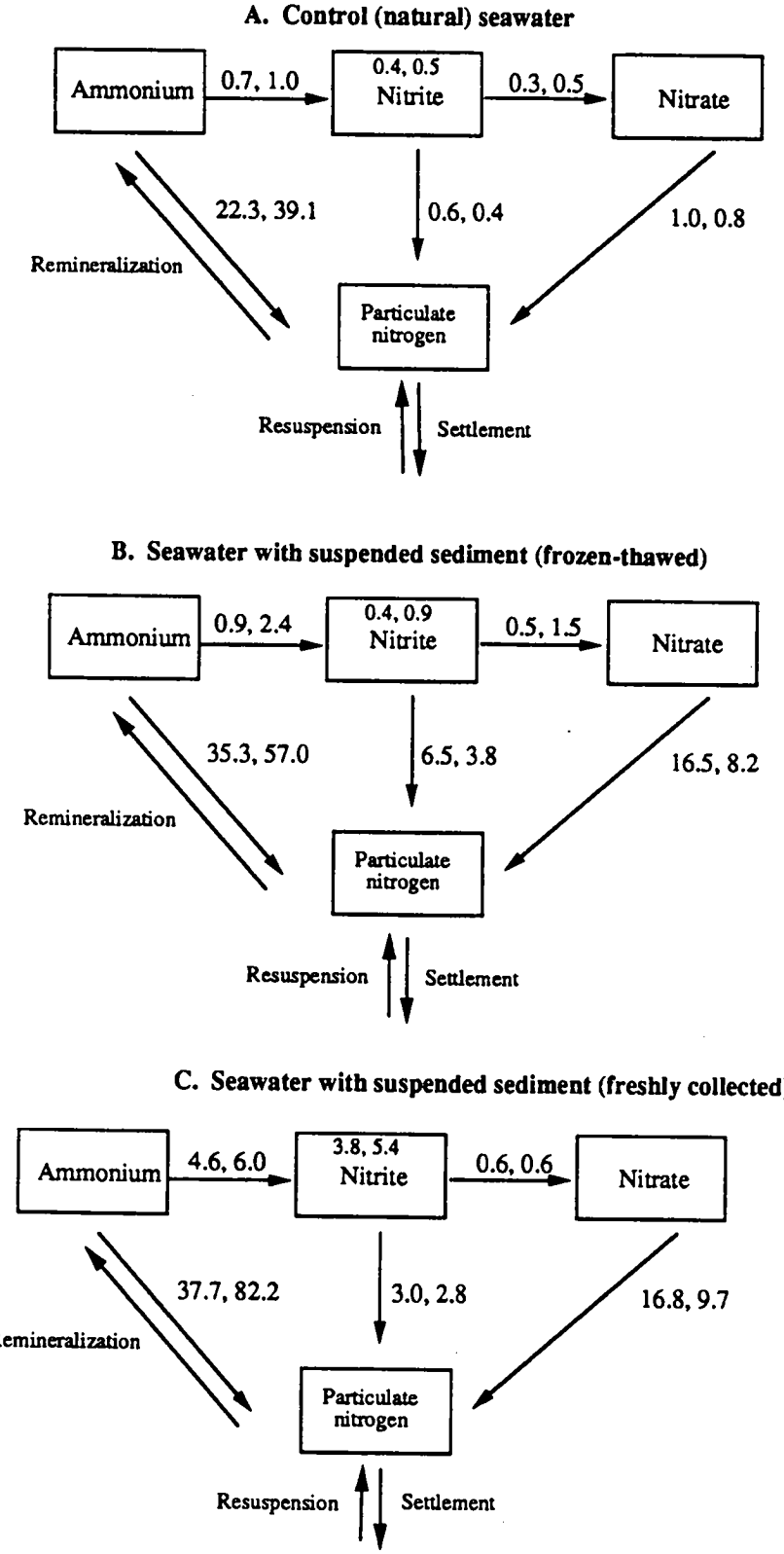


Figure 4.20 Nitrogen transformation rates (nmol N l^{-1} h^{-1}) in control seawater (A), seawater with frozen-thawed sediment (B) and with freshly collected sediment (C) added from trial N.4 with 0.5 µM. The left value shows average rate over the 0-3 h period while the right value shows average rate the over 0-6 h period. Values within boxes refer nitrite accumulation rate.

with 0.5 μM $^{15}NH_4^+$ should be closest to *in situ* rates since the concentration of ammonium substrate was closer to the ambient ammonium concentrations measured following a cyclone (N transformation rates in trials N.2 [with 0.5 μM $^{15}NH_4^+$; Figure 4.18B], N.3 [Figure 4.19B & C] and N.4 [Figure 4.20B & C]). The remaining transformation rates should be considered more as being closer to potential rates.

In most cases, experiments showed that the rates of individual N species consumption were higher than rates of N production, especially in seawater with sediment added. The measured consumption of nitrite (nitrite oxidation and nitrite uptake) consistantly exceeds the nitrite production (Figure 4.17B, 4.18B, 4.19B, 4.20B &C). It seems unlikely that conditions in the experimental seawater were unlike conditions either under normal state in the shelf or following a cyclonic event when nitrite concentration were readily detected. If nitrite consumption rates are greater than nitrite production rates, nitrite should not be detectable. The lack of balance between rates of nitrite transformation obtained in the experiments are most likely due to the experimental procedure adopted here, which involved separate measurements of each process and the use of much higher levels of tracer additions than the ambient nitrite concentrations normally found in GBR seawater.

The nitrite production rates (from ammonium oxidation and nitrite accumulation) were measured in one carboy spiked by $^{15}NH_4^+$ isotope, while nitrite uptake rates were measured in the other carboy spiked by $^{15}NO_2^-$ isotope. This resulted in the different proportion of ammonium, nitrate and nitrite levels in the samples. When 0.5-5 μM $^{15}NO_2^-$ was added in the water samples containing naturally low ambient ammonium and nitrate concentrations, nitrite concentrations in such conditions (> 0.5-5 μM) were very high in comparison to ammonium and nitrate levels. Measured high nitrite uptake rates therefore reflect the unavailability of both ammonium and nitrate to phytoplankton. In the natural seawater either during normal conditions or following resuspension event of sediment, ammonium or nitrate concentrations are always higher than nitrite. To solve this problem the addition of the same amount of $^{14}NO_3^-$ and $^{14}NH_4^+$ are suggested to be added in the samples with $^{15}NO_2^-$ addition.

An alternate explanation of high nitrite uptake rates observed in the carboy containing $^{15}NO_2^-$ relates to the preferential use of ammonium over nitrate and nitrite by marine phytoplankton(e.g. Eppley and Rogers, 1970; Harvey and Caperon, 1976; McCarthy *et al.*, 1977; Glibert *et al.*, 1982). The high nitrite uptake rates obtained in the

laboratory should not occur under *in situ* conditions in GBR waters because ammonium and nitrate concentrations are always higher than nitrite. Thus, nitrite uptake rates in natural GBR water, are likely to be lower than uptake rates measured by isotope additions. To correct for the unbalanced rates in the nitrite transformation pathways, the total concentrations of nitrite and ammonium in both carboys must be adjusted to the same level.

The global ranges and means of transformation rates from all trials are summarized in Figure 4.21. Overall, N transformation rates clearly indicate the effect of sediment resuspension on the microbial nitrogen transformation process. The study of nitrogen transformations provides an understanding of nitrogen dynamics in GBR water under both the normal and cyclonic conditions. Microbial transformations of nitrogen are an important source, if only episodically, of oxidized nitrogen species (nitrate and nitrite) in GBR water. Cyclonic disturbances give the chance to quantify the water column nitrification process as a source of N substrates (either direct ammonium from sediment or remineralized from particulate nitrogen mixed into the water column). The abnormally high levels of oxidized nitrogen species are shown to be derived from nitrification processes and their accumulation is suggested to be due to the preference of phytoplankton for ammonium as compared to these oxidized nitrogen species (nitrate and nitrite). With the further refinement of dark C uptake/N oxidation ratios and improvement of ^{15}N techniques, the field measurements of nitrogen transformation processes in the water column subsequent to the cyclone passage would provide further insights into *in situ* nutrient transformation processes.

4.6 CONCLUSIONS

1. N-serve was found to be the most efficient inhibitor for blocking ammonium oxidation in seawater with and without suspended sediment.

2. Dark carbon uptake to nitrogen oxidation ratios obtained in this study (0.59-0.73) are higher than ratios determined in other studies (0.06-0.17). This is due to a combination of (i) the differences between environments (temperate vs tropical), (ii) differences resulting from the use of cultured bacteria and bacteria occurring in the natural system, (iii) the differing concentrations of N-serve or other inhibitors used. To measure nitrification rates in seawater (especially with suspended sediment) by ^{14}C method, a locally calibrated C uptake/N oxidation ratio is required in each system to convert dark uptake rate to

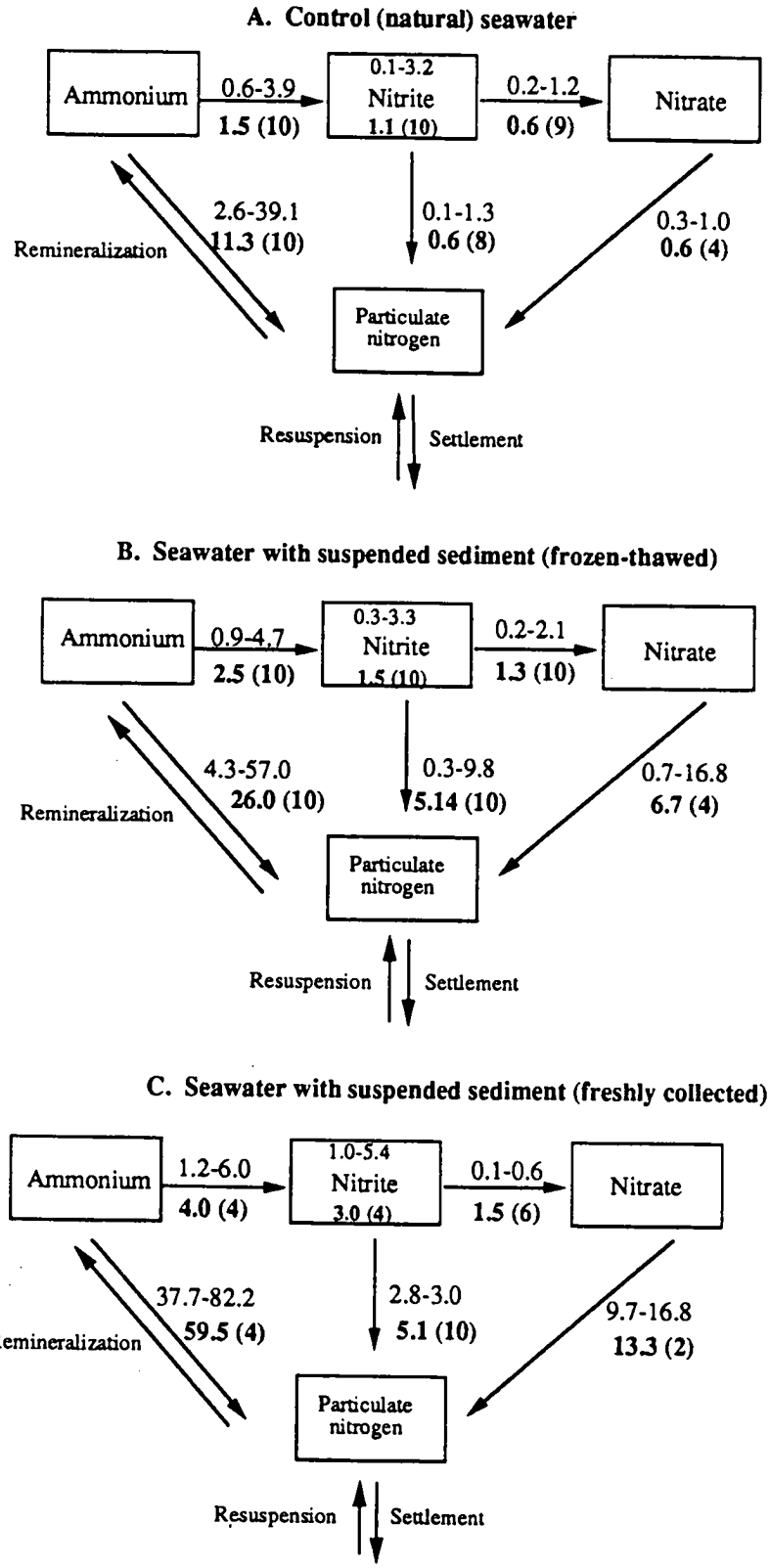


Figure 4.21 Nitrogen transformation rates (nmol N $l^{-1}h^{-1}$) in control seawater (A), seawater with frozen-thawed sediment (B) and with freshly collected sediment (C) added from all trials. Top values show ranges of rates and bottom values (in bold) show the mean rate with number of replicates in parenthesis. Values within boxes refer to nitrite accumulation rates.

- nitrification rate.

3. Nitrification rates (obtained using either dark ^{14}C-bicarbonate incorporation or ^{15}N technique), nitrite oxidation rates, and uptake rates of ammonium, nitrite and nitrate in water with suspended sediment were consistently higher than rates in seawater without sediment. This appears to be the result of the enhanced substrate supply derived from resuspended sediments and availabilty of nitrifying bacteria associated with sediment.

4. Elevated nitrite and nitrate concentrations measured a few days after the cyclonic event are most likely from an accumulation of nitrate and nitrite due to the ammonium preference of phytoplankton utilization and nitrification processes in the water column.

CHAPTER 5

GENERAL DISCUSSION, CONCLUSIONS AND FURTHER RESEARCH

5.1 GENERAL DISCUSSION

5.1.1 Nutrient release and nitrogen transformation following cyclone "Winifred"

Surface waters of tropical oceans are characterized by low dissolved nutrient concentrations and plankton biomass levels (e.g. Eppley *et al.*, 1973; Furnas and Smayda, 1984; Legendre *et al.*, 1988; Furnas *et al.*, 1990). Nutrients within marine water may be derived from either external or internal sources, however, it has been shown that internal nutrient recycling processes usually provide most of the nutrients required to sustain primary production (e.g. McCarthy *et al.*, 1977; Harrison, 1978; Glibert, 1982; Smith, 1984). In shallow waters, sediments constitute an important reservoir of nutrients (reviewed by Val Klump and Martens, 1983). Benthic nitrogen regeneration contributes 26-101% of the phytoplankton demand in coastal areas (summarized by Billen and Lancelot, 1988). Nutrients from the benthos may be returned to the pelagic zone by several different mechanisms which occur both within the sediments and at the sediment-water interface. These processes may operate at a slow, regular rate or respond quickly to punctuated, sporadic events.

Like most tropical shelf systems, waters on the GBR shelf also contain low concentrations of dissolved nutrients and low plankton biomass levels (e.g. Furnas and Mitchell, 1986b; Furnas *et al.*, 1990). During calm conditions, steady state benthic nutrient regeneration appears to contribute only a small proportion (13%) of the nutrient demand of phytoplankton (Alongi, 1989c). Therefore, there must be substantial alternative sources of nutrients to maintain ongoing primary production rates. These sources include inputs from runoff, upwelling, rainfall, remineralization and resuspension events. However, most of the required nutrients are regenerated *in situ* (Smith, 1984). Water column regeneration is the most important process contributing nutrient inputs to the nutrient cycle in the tropical shallow continental

shelf waters. Nutrient released from sediments are also considered to represent regenerated nutrients. Resuspension by cyclonic event have a much potential to transfer a much higher proportion of the nutrient pool to the pelagic system. With the nutrient release into water column, remineralization would supply most of the short-term nutrient demands to maintain pelagic primary production.

Previous studies have suggested that sediment resuspension may be one of the mechanisms which enhance nutrient inputs into or recycling within tropical, coastal and shelf waters (e.g. Walker and O'Donnell, 1981; Fanning, *et al.*, 1982; Ullman and Sandstrom, 1987; Simon, 1989). Given the variety of mechanisms which are capable resuspending sediment: the action of currents, wind induced waves etc; a corresponding range of temporal, spatial and intensity levels occur (Table 5.1). The most massive disruptions, cyclones, occur twice a year on average in the GBR region (Lourensz, 1981) and generate intensive turbulent mixing of the benthos (Chang and Anthes, 1979; Gagan *et al.*, 1990). Cyclones generally disturb and resuspend sediments over the full width of the shelf (Gagan, 1990), but are extremely episodic phenomena if specific locations are considered (Lourensz, 1981). For example, cyclone "Winifred" (1986) resuspended sediment over an area of the GBR of at least 1,200 km^2 (Gagan *et al.*, 1988). This is in contrast to resuspension by the action of currents, wind induced waves, etc. which may be assumed to occur with a higher perhaps daily frequency, yet are confined to localized areas such as shallow waters. Such areas are however only a small fraction of the total GBR shelf (Hopley *et al.*, 1989). Despite the potential importance of this resuspension processes, no quantification of the amounts of nutrients released from sediments in the open GBR shelf into the water column by large events such as a cyclone have previously been made.

In this study I have attempted to quantify the amounts of nutrients which would be released into the water column during a cyclonic disturbance of GBR shelf sediments. Simulations of resuspension events using sediment from inner, mid- and outer shelf areas were carried out to estimate resulting nutrient changes in the water column. The potential magnitude of cross-shelf differences in quantification of nutrient released from inner and outer shelf areas were also assessed .

The experiments carried out in this study show that cyclonic resuspensions of sediment can be an episodically important mechanism for increasing the concentrations of nutrients and chlorophyll in the water column. Results from experimental

Table 5.1

Resuspension of sediment on the GBR shelf - mechanisms, periods and spatial scales

Resuspension mechanism	period	Area of effect
Tidal currents	average 12-24 hours	All areas, e.g., nearshore, reef lagoons
Tidal currents, spring tides	2 weeks	All zones up to top of continental slope
Wind, average 5-10 knots	daily	Shallow areas (e.g. < 3 m depth)
Wind, SE Trades > 20 knots	seasonal	Shallow to deeper areas, e.g. < 20 m depth
Wind, cyclones > 100 knots	episodic	Regional, but wide disturbance to about 80 m depth

simulations of resuspension events show that concentrations of a number of nutrient species (PN, PP, NH_4^+, PO_4^{3-}, $Si(OH)_4$, chlorophyll *a*, phaeophytin) increased in significant amounts as a result of sediment resuspension. Changes in concentrations of other nutrients (NO_3^-, NO_2^-, DON, DOP) as a result of sediment resuspension were comparatively small. Relatively, high analytical variability, low concentrations of some species (NO_3^-, NO_2^-) in sediments or high background concentrations (DOP, DON) in shelf waters, made estimates about their behaviour difficult to quantify.

Both the absolute amount of nutrients and chlorophyll, and the form in which the nutrients are released from resuspended sediments are determined by the concentration of these substances in the porewater and the solid-phase sediment fractions (Wainright, 1990). During normal conditions, nutrient fluxes have been shown to depend on sediment type and grain size (Aller and Benniger, 1981; Fisher *et al.*, 1982a; Alongi, 1989c). However, nutrient releases from sediments by cyclones would not be as dependent on the local sediment type and grain size since massive amounts of sediment are disturbed over a large spatial scales. Experiments carried out to compare the amount and speciation of nutrients released from the two major shelf sediment types showed that with the exception of the amounts of total phosphorus and silicate, volume or mass-specific release of most nutrient forms did not differ significantly between terrigenous inner shelf sediments and calcareous outer shelf sediment. The greater release of total phosphorus from outer shelf sediments was likely due to a higher potential for phosphorus desorption (e.g. Stumm and Leckie, 1971; de Kanel and Morse, 1978).

In contrast, silicate releases were higher in seawater mixed with inner shelf sediment. The higher silicate releases resulted, in large part, from higher porewater silicate concentrations (Alongi, 1989c). Inner shelf sediments are affected by river runoff, and contain more silica than the outer shelf sediment (Brodie and Mitchell, 1992). In the experiments where temporal changes in post-release nutrient concentrations were followed, silicate concentrations tended to gradually decrease in all treatments but were higher in seawater containing inner shelf sediment (Figures 3.12-14). The decreasing silicate concentration likely resulted from diatom utilization. Post-cyclone phytoplankton blooms are known to be dominated by diatom assemblages with high potential growth rates (2 day^{-1}, Furnas, 1989). Such blooms would require increases in the availability of silicate either by sediment resuspension (Chapter 3) or from river runoff (Brodie and Mitchell, 1992).

The quantities of individual nutrient species released in the resuspension experiments were found to be linearly proportional to the amount of sediment resuspended. For most nutrient species (except suspended solids, PO_4^{3-}, phaeophytin, total pigments), similar amounts of nutrients were released per unit weight of inner and outer shelf sediment added. However, variability in the amount of porewater nutrients within the sediment sampling sites and the patchiness of nutrient concentrations, along with nutrient depth profiles in sediments (Ullman and Sandstrom, 1987; Alongi, 1989c) made it difficult to detect a relationship between sediment mass and the release of NH_4^+, NO_3^- or NO_2^-. The very low concentrations of NO_3^- and NO_2^- in the sediment due to the denitrification process in anaerobic sediment made it difficult to measure their release into water column and thus to detect such a relationship.

The measurement of water column nutrient concentrations immediately following the passage of a cyclone presents obvious logistic difficulties. It is therefore desirable to know whether significant changes in nutrient concentration occur over several days follow in the passage of a cyclone. Experimental investigation of daily changes in nutrient concentration and speciation over periods of 8-15 days indicated that within the time frame of these experiments, relatively small changes which were dependent on nutrient species, were observed during the first few days after the initial increases in nutrient concentration caused by the mixing of sediments. This suggests that water sampling carried out within a period between 1-4 days following a cyclonic disturbance event should still give a reasonable view of immediate cyclone-induced nutrient changes in the water column. Although average daily changes were small, both nutrient concentrations and speciations fluctuated erratically on a daily basis which precludes the use of point samples taken (9, in this study) days apart to describe the overall pattern of temporal changes.

The amount of nutrients potentially released by resuspension processes during cyclone "Winifred" can be estimated from the volume of sediment reworked into the water column. Nutrient releases as a result of the cyclone passage were estimated from the thickness of reworked sediment which ranged between 5.1 and 6.9 cm across the shelf), as estimated by Gagan *et al.* (1990). Nutrient concentrations estimated to result from sediment resuspension in this study are compared with nutrient concentrations (M. Furnas and A. Mitchell unpubl. data) measured during a normal period (one year after the cyclone) and concentrations measured approximately one week following cyclone "Winifred" (called post-cyclone). These are shown in Figure 5.1.

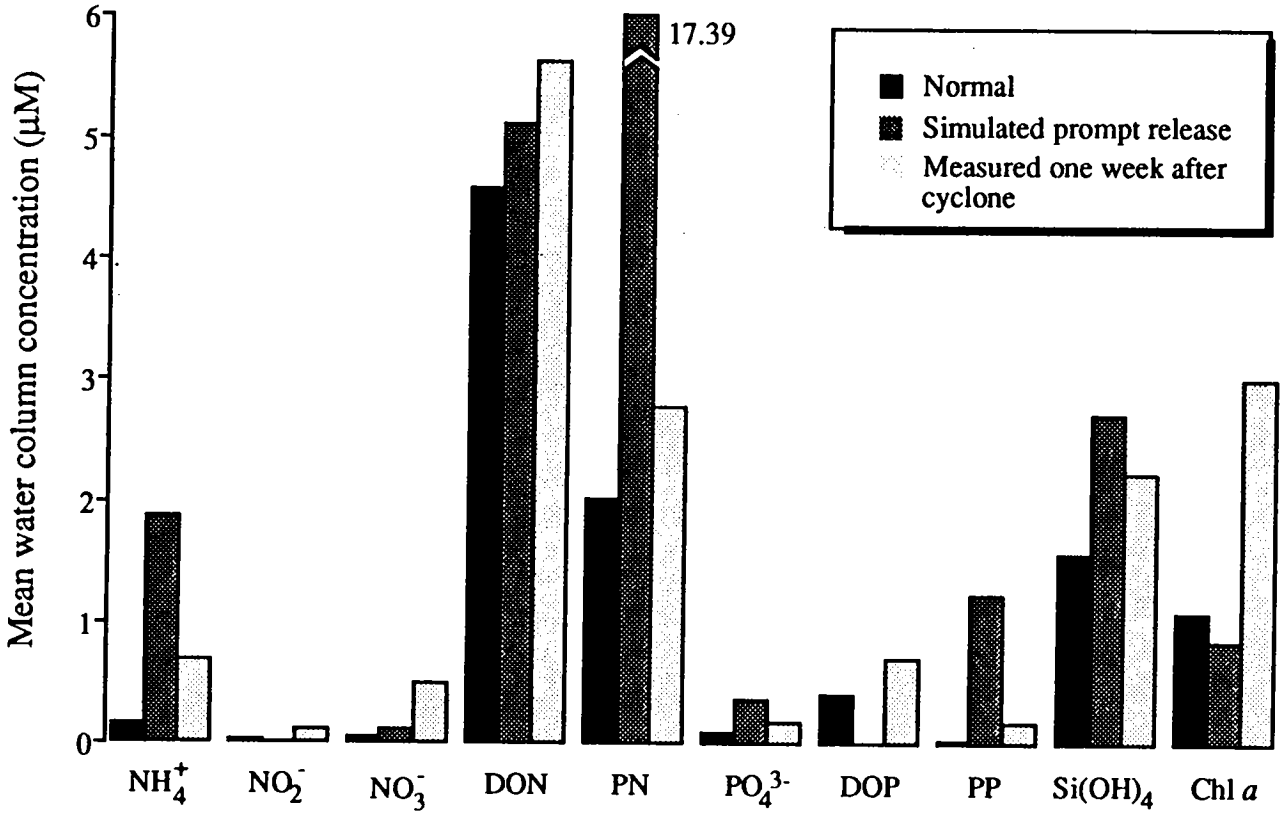


Figure 5.1 A comparison between depth-weight mean water column concentrations of nutrients from a cross-shelf transect (Stations 38-42) under normal summer conditions, mean concentrations measured on the same transect (Stations 21-26) measured one week after cyclone "Winifred" (February, 1986) and estimated concentrations as a result of resuspension from shelf sediments as simulated in experiments herein. Note that PN and PP concentrations were averaged from the concentrations measured following cyclone "Aivu" (1989) as data after cyclone "Winifred" were not available.

The comparison shows that resuspension events have a clear effect on nutrient concentrations, with higher concentrations observed following real and simulated resuspension. A large portion of the measured nutrient release was in the particulate form (PN and PP) though the PN and PP concentrations were derived from measurements following cyclone "Aivu" (1989) made by Furnas (1991b). Estimated PN from sediment resuspension was much higher (about 9-fold), compared to post-cyclone levels of PN.

Concentrations of PN and PP measured one week after cyclone "Winifred" were higher than those measured under normal conditions but lower than concentrations immediately after the cyclones as estimated from experimental sediment resuspensions. This is probably due to the rapid settling of particulate matter to the bottom and to a lesser extent, from the remineralization of PN and PP (Taft *et al.*, 1975; Nixon, 1981; Furnas, 1989; Horrigan *et al.*, 1990). Similar pattern were found in NH_4^+ and PO_4^{3-} concentrations. Increases in NH_4^+ and PO_4^{3-} concentrations were released directly from porewater during sediment resuspension. Decreases in NH_4^+ and PO_4^{3-} concentrations as measured one week after the cyclone are likely due to utilization by phytoplankton and bacteria.

Measured post-cyclonic levels of DOP and DON were higher than concentrations of DOP and DON estimated from the simulated resuspension event and those measured under normal conditions. The measured high levels of DOP and DON were derived directly from porewater and excretion of microorganisms in the water column following the sediment resuspension events. Measured post-cyclone $Si(OH)_4$ concentrations were similar to the concentration of $Si(OH)_4$ estimated from resuspension experiments and were higher than non-cyclonic levels. The higher $Si(OH)_4$ post-cyclone concentrations occur because $Si(OH)_4$ is also supplied from river runoff (Brodie and Mitchell, 1992) following cyclonic events but some is subsequently utilized by diatoms (Furnas, 1989).

Increases in chlorophyll concentration were also measured in the water column over the area of several 1000's of km^2 a short time after cyclone "Winifred" (Furnas, 1987, 1989). This was the result of increases in phytoplankton substrates (N, P and Si species). Sediment resuspension processes alone (Figure 5.1) could not account for the higher chl *a* measured a week following cyclone "Winifred" (Furnas, 1989). The obvious explanation is that nutrients released by cyclonic resuspension were taken up by phytoplankton to permit rapid population growth (Furnas, 1989).

Increased concentration of individual nutrient species in the water column following a cyclone result from river runoff, rainfall, transformation by micro-organisms or resuspension releases from the benthos. The simulated resuspension experiments showed that only a small amount of the nitrite and nitrate measured after a cyclone event can be attributed to immediate release from the sediment via resuspension. Similarly, the anticipated contributions of nitrite and nitrate from rainfall are quite small (Paerl *et al.*, 1990; Furnas *et al.*, 1993) while inputs from river runoff are restricted to the inner shelf waters (e.g. Brodie and Mitchell, 1992). Nitrate and nitrite may be provided from Coral Sea upwelling even though at present there is little evidence as to the intensity of upwelling. Recent information from Cyclone "Joy" (1990) showed a cyclone associated intrusion event did occur (Furnas *et al.*, 1993); however the upwelling which coincided with the cyclone was similar in magnitude to that which occured at other times. It can be anticipated that the net nitrate contribution from Coral Sea upwelling would not be large compared to other upwelling which occurs at other time. However, the external nitrate and nitrite sources gives above cannot fully account for the increase in dissolved inorganic nitrogen measured in the water column following cyclone "Winifred" (Furnas, 1989). It can be hypothesized that the missing portion is produced by nitrification and mineralization processes.

Profiles of ammonium, nitrate, nitrite, chl *a* and light intensity in the water column (Figure 5.2) at a cyclone affected station (M. Furnas unpubl. data) illustrate the probable occurrence of nitrogen transformation processes. Nutrients were first sampled at this station four days after the cyclone (Figure 5.2a). Abnormally high nitrate and nitrite concentrations were found throughout the 35-m depth of the water column, as compared to the concentrations measured seven days following the cyclone passage (Figure 5.2b).

Seven days after cyclone "Winifred", ammonium, nitrate, nitrite, chlorophyll and light intensity were again measured at this station and profiles of these factors are shown in Figure 5.2b. Nitrate and nitrite in the surface water had decreased toward the lower levels normally found in GBR shelf waters. Ammonium, nitrite and nitrate were probably taken up by phytoplankton when light was available. Significant denitrification is unlikely causes as it does not occur to any extent in oxygenated water column. High concentrations of nitrate, nitrite and ammonium remain in the deeper water columns below the euphotic zone[8]. High concentrations of dissolved inorganic

[8]Where the net rate of photosynthesis is positive.

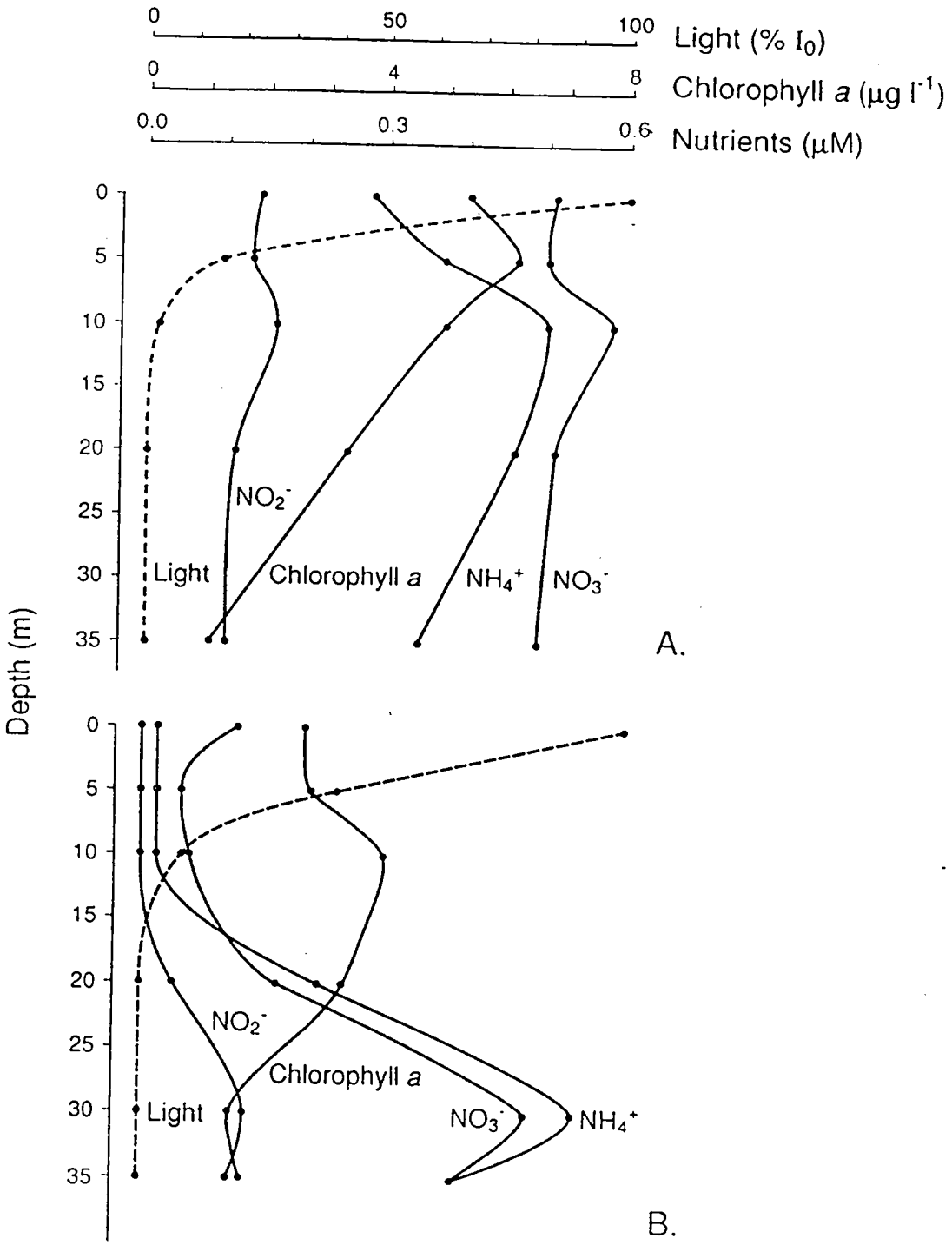


Figure 5.2 Depth profiles of sub-surface light intensity, ammonium, nitrite, nitrate and chlorophyll *a* concentrations at a station 4 days (A) and 7 days (B) following passage of cyclone "Winifred" (M. Furnas and A. Mitchell, pers. comm.). The location of the station was directly under the cyclone's path.

nitrogen at deeper depth also occurred at other stations in the area (Unpublished data by M. Furnas and A. Mitchell). The high levels of nitrate and nitrite in the deeper water column were probably due to the lack of demand for nitrite and nitrate when adequate ammonium, a preferred nitrogen source compared to nitrate and nitrite, is available to phytoplankton (e.g. McCarthy *et al.*, 1984). The other potential source of nitrate and nitrite is nitrification. It is well known that rates of ammonium oxidation are reduced by exposure to light (e.g. Horrigan *et al.*, 1981; Olson, 1981b; Ward, *et al.*, 1984; Lipschultz *et al.*, 1985; Ward, 1985). The availability of ammonium substrate and the low-light environment at the deeper water column created ideal conditions for nitrification to occur. Studies on the depth distribution of nitrification (Wada and Hattori, 1971; Olson, 1981a; Ward *et al.*, 1984; Ward, 1987) show that nitrification can be a significant nitrogen source within the euphotic zone at the depth of 5 or 10% surface light if sufficient substrates are available. However, there was no information at the time of sampling whether nitrification process had occurred since *in situ* nitrification measurement in the water column were not conducted at that time. High levels of ammonium were directly released from porewater during sediment resuspension and also would be remineralized from particulate nitrogen.

Nitrogen transformation processes in the water column were investigated in more detail using isotopic ^{15}N tracer techniques. Overall, higher rates of ammonium and nitrite oxidation were measured in seawater samples with resuspended sediment (0.9-6.0 and 0.1-2.1 nmol N l^{-1} h^{-1}, respectively) than in water without sediment (0.6-3.9 and 0.2-1.2 nmol N l^{-1} h^{-1}, respectively). It is therefore likely that the cyclone associated increase in ammonium concentration resulted in an increase in the rate of nitrite and nitrate production (Wada and Hattori, 1971; Olson, 1980). The observed increase in ammonium and nitrite oxidation rates result from a combination of the greater availability of ammonium substrate as a result of the resuspension event and optimal conditions for bacterially-mediated nitrogen oxidation reactions. These conditions include the low *in situ* light intensity, high water temperature and innocula of nitrifying bacteria with the sediment (either attached to sediment particles or released directly into the water column from porewater).

Nitrification processes involve a complex sequence of microbial events with rate-limiting steps controlled by the availability of both the substrate and the essential nitrifying organisms. Rates of nitrification increase directly with increase in substrate concentration (e.g. Olson, 1981a; Berounsky and Nixon, 1985, Ward, 1985). Release of organic matter from the sediment will also enhance the nitrification rate by

providing carbon and ammonium substrates through the process of remineralization (e.g. Mevel and Chamroux, 1981; Owens, 1986). Particulate N released from sediment can be remineralized to organic and dissolved inorganic nitrogen by microorganisms (e.g. Nixon, 1981). This process would subsequently provide a significant amount of ammonium for nitrifying organisms as a large amount of PN was released (17 μM) .

The concentrations of nitrifying bacteria in the water column would also affect the potential nitrification rate. Sediments are known to contain concentrated populations of nitrifying organisms (e.g. Webb and Wiebe, 1975; Matulewich and Finstein, 1978). The highest rates of nitrification are inevitably found in the upper few centimetres of sediment (Billen, 1976). During a cyclonic resuspension events, nitrifying organisms within the sediment will be injected into the water column along with increased substrate. Experimental data clearly showed that nitrification rates in seawater with freshly collected sediment (1.2-6.0 nmol N l^{-1} h^{-1}) were higher than rates measured concurrently in water with frozen-thawed (normally abiotic) sediment (0.9-2.8 nmol N l^{-1} h^{-1}) due to the addition of viable bacteria to the system (Rheinheimer, 1991).

The physical conditions occurring in GBR shelf waters following cyclonic disturbance are highly favourable for enhanced nitrification. First, light penetration through the water column was greatly reduced by the turbidity produced by resuspended sediment. Such low light conditions favour oxidizing bacteria, whose activities are normally inhibited by light (e.g. Müller-Neuglück and Engel, 1961; Olson, 1981b; Horrigan *et al.*, 1981; Ward, 1985; Vanzella *et al.*, 1989). Increased circulation around the resuspended particles provide conditions that are more oxic, than those that would normally be available within the sediment. Furthermore, since nitrification rates are positively correlated with temperature (Berounsky and Nixon, 1990), increasing with temperatures up to 25°-35° C (e.g. Carlucci and Strickland, 1968; Jones and Hood, 1980; Helder and de Vries, 1983), nitrification is aided by the high summer temperatures (average 27° C) which prevail during the cyclone season.

An alternative source of the NO_2^- in post cyclone waters is that directly released by phytoplankton which grow on NO_3^- (Vaccaro and Ryther, 1960; Carlucci *et al.*, 1970; Kiefer *et al.*, 1976). Vaccaro and Ryther (1960) and Kiefer *et al.* (1976) demonstrated that phytoplankton release nitrite at rapid rates when grown with excess nitrate. This process preferentially occurs at low light levels (McCarthy *et al.*, 1984)

and may account for at least some of the increased nitrite in the water column following a cyclonic event when the *in situ* light intensity was low (Furnas, 1989). Denitrification rates in oxygenated water are considered too slow to account for the production of nitrite (Hattori and Wada, 1971).

The high nitrification rates occurring in response to increased concentrations substrate and nitrifying organisms, low light intensity and high water temperature following simulated resuspension of sediment do not fully account for the high levels of nitrate which remained in the water column for some time after the cyclone (Table 4.5). The most likely explanation for the accumulation of nitrate in the seawater following a cyclonic resuspension event is the preferential use of ammonium over nitrate and nitrite by phytoplankton. It has long been known that nitrite and nitrate are only taken up by phytoplankton to a small degree when adequate amounts of ammonium are present (Eppley and Rogers, 1970; McCarthy and Eppley, 1972; Harvey and Caperon, 1976; Eppley *et al.*, 1977; McCarthy *et al.*, 1977; Glibert *et al.*, 1982). Nitrite is generally not considered to be an important nitrogen source for phytoplankton as compared to ammonium and nitrate (McCarthy *et. al.*, 1984). The large amount of ammonium produced by resuspension during a cyclonic event will far exceed the normal requirements of existing phytoplankton at least in a short term. This preference for ammonium as a substrate by phytoplankton is reflected in the higher uptake rates measured for ammonium (37.7-82.2 nmol N l^{-1} h^{-1}), as compared to nitrate (9.7-16.8 nmol N l^{-1} h^{-1}) and nitrite (2.8-3.0 nmol N l^{-1} h^{-1}). It is therefore likely that nitrate and nitrite which are derived from many sources, but most likely water column nitrification process, will accumulate in the water. The availability of ammonium from sediment resuspension and especially that continuously mineralized from particulate nitrogen are sufficient to maintain the phytoplankton N requirement for some time. When ammonium concentrations decrease to a level which is too low to sustain the demand of phytoplankton, then nitrate and eventually nitrite would be taken up (McCarthy *et al.*, 1984) as well.

The higher rates of nitrogen transformation measured in seawater with suspended sediment indicate that sediment resuspension events can have a significant, if transient, effect on the nitrogen dynamics of pelagic systems. The rates of a number of microbial-mediated processes are known to be greatly enhanced by storm-induced mixing of the water column (e.g. Horrigan *et al.* , 1990). Horrigan *et al.* (1990) found ammonium oxidation rates in Chesapeake Bay increased from 135 nmol N l^{-1} h^{-1} before a storm to 1380 nmol N l^{-1} h^{-1} and 2480 nmol N l^{-1} h^{-1} one day and four

days after the storm, respectively. Concurrent nitrite oxidation increased from 112 nmol N l^{-1} h^{-1} to 726 and 834 nmol N l^{-1} h^{-1}, respectively. Ammonium remineralization rates were also affected. Rates before the storm were low (0-900 nmol N l^{-1} h^{-1}) increasing to 500-6000 nmol N l^{-1} h^{-1} after the storm.

Because of higher water temperature (22-30° C), lower *in situ* light intensity and rapid rates of nutrient transformations within the water column (e.g. Furnas *et al.*, 1986; Furnas, 1987, 1988) following a cyclone, phytoplankton population can take up nitrogen equivalent to the standing crop within hours (Furnas, 1988). The time course of ammonium uptake measured in this study confirmed estimate of rapid turnover of water column ammonium pools (Furnas, 1988). In GBR inter-reefal waters, phytoplankton biomass is N-limited (Furnas and Mitchell, 1986b). Increased concentrations of nitrogen from resuspension of sediments contributed nitrogen stocks up to 11 times greater than water column nutrient concentrations measured during normal condition (see Table 3.6).

Not only do cyclones resuspend sediments over a wide area, the energy involved in cyclonic resuspension events also liberates nutrients from the sediments at deeper waters (e.g. down to 80 m) and from deeper in the sediment profiles (e.g. to 14.4 cm, Gagan *et al.*, 1990) than normal current and wind-wave shelf resuspension processes (Walker and O'Donnell, 1981). Under non-cyclonic conditions, wave driven resuspension can stir sediment to a maximum water depth of 15 m (E. Wolanski, pers. comm.), though such events recur with high frequency (e.g. hourly, daily). The nutrients stored within deep water sediments have likely not been recycled into the water column since they were deposited with the sediment. This would also be true of nutrients buried deep within sediment profiles. Hence, the more extensive mobilization of nutrients from the deeper sources by cyclonic resuspension events is, in a manner, analogous to processes such as riverine inputs or upwelling which import external nutrients to the shelf system. Using this analogy, nutrients liberated by cyclonic resuspension may be considered as "new" additions to the pelagic stocks over the wide area on the basis of a long-term (yearly) interval of disturbance. This process may be considered to be an important mechanism to recycle "new" nutrient in the large scale into GBR water. The contribution of "new" nutrient stocks by cyclonic events is probably important to maintain the ongoing primary production in oligotrophic water such as in the GBR. Primary production rates measured following the sediment resuspension event were higher (approximately 8-folds) than the production rates during normal conditions (Furnas and Mitchell, 1984).

Phytoplankton blooms and high rates of primary production in the wide areas are evidence to illustrate the importance of nutrient inputs associated with cyclonic phenomena.

Tropical shelf systems such as the GBR are affected by a variety of episodic, seasonal or intermittent fluctuations such as river runoff (e.g. Mitchell, *et al.*, 1990), upwelling (e.g. Andrews and Gentien, 1982; Furnas *et al.*, 1993) and physical disturbance such as cyclones and other energetic storms (e.g. Furnas, 1989). These processes are associated with the input, release, mineralization and uptake of substantial stocks of "new" nutrients from the land, sediment, atmosphere and deeper waters. Even though these events are usually of short duration and adjacent result in equally short-term fluctuations in water column nutrient levels, they often affect wide areas. Due to the frequency of occurrence of cyclones in this area, and the subsequent wide spatial scale disturbance and great magnitude of nutrient enhancement, cyclones can be considered as important mechanisms for the contribution of the "new" nutrients. These large episodic events must be considered to be important regional contributors to the nutrient dynamics of tropical shelf ecosystems.

5.1.2 Constraints in measurements of nitrogen transformation rates using ^{14}C and ^{15}N methods.

i) Potential vs *in situ* rates

Significant additions of nitrogen tracers relative to ambient stocks are sometimes needed for reliable isotopic measurements. Such high substrate levels result in perturbations of the experimental systems, particularly in the case of the natural low concentration in the control seawater (e.g. Dugdale, 1967; Dugdale and Goering, 1967; Mevel and Chamroux, 1981; Wada and Hattori, 1971; Ward, 1985). In trials where spike concentrations are high relative to natural levels, nitrogen transformation rates measured should be considered as potential rates particularly in the control treatment seawater (without sediment addition) (Eppley *et al.*, 1973, 1977; Harrison, 1983). In experimental treatments with suspended sediment added, which emulate conditions following cyclonic resuspension events, elevated concentrations of ammonium (0.28-0.50 μM) and nitrite (0.10-0.16 μM) were measured (M. Furnas and A. Mitchell, unpubl. data). In these treatments, the addition of moderate amounts of substrate can therefore be considered to be closer to the prevailing post-cyclonic concentrations, and the resulting ammonium oxidation and ammonium uptake rates

therefore should be closer to actual *in situ* rates.

In most experiments undertaken within this study, nitrite oxidation and nitrite uptake rates exceeded nitrite production (ammonium oxidation rates and nitrite accumulation rates) (e.g. Figure 4.17b). This does probably not occur under natural conditions, either during normal conditions or following cyclonic resuspension events since nitrite is detectable, though in very low concentrations, even during normal conditions. The lack of balance between nitrite transformation rates observed herein is therefore most likely due to the experimental procedures adopted here in which separate measurement of oxidation and uptake process were made, and tracer additions were set at higher than the concentrations normally found in seawater. Additions of 0.5-5 μM $^{15}NO_2^-$ to water samples are very high in comparison to the nitrite levels normally available for phytoplankton in the natural seawater. Accordingly all nitrite uptake rates presented herein should be considered as potential rates.

In trials N.2 (Figures 4.17 & 4.18) and N.3 (Figure 4.19) nitrogen transformation rates were likely underestimated by the factor of 1.7 (± 0.4) when the rates were calculated using the Dugdale and Goering's (1967) equation. The factors causing underestimated uptake rates have been discussed in some studies (Caperon *et al.*, 1979; Glibert *et al.*, 1982, 1985; Garside and Glibert, 1984; Laws, 1984). One factor of the underestimated uptake rates was a result of progressive dilution through remineralization of nitrogen taken up (e.g. Garside, 1984). Using calculations based on the Glibert *et al.*'s (1982) equation, rates from trials N.2 and N.3 should be higher than those reported here.

ii) Nitrification inhibitors

Estimations of nitrification rates based upon the ^{14}C dark uptake method are technically simple to carry out. However, the results depend on an efficient and selective nitrification inhibitor. At present there is no chemical known which immediately and completely inhibits the nitrification process while allowing all other processes to continue unaffected.

Among the three nitrification inhibitors tested in this study, nitrapyrin (N-serve) was shown to be the most efficient in blocking dark bicarbonate uptake. In seawater with resuspended sediment, however, higher concentrations of N-serve were required for efficient blocking of the nitrification process as compared to concentrations used in

other published studies. This may be due to different environment conditions resulting in different strain of ammonium-oxidizers being present (Belser and Schmidt, 1981). Sediment particles in samples with suspended sediments may also affect the dark uptake rate because N-serve is partially inactivated by absorption to sediment (Briggs, 1975; Henriksen, 1980).

Hach2533, a water soluble derivative of N-serve can be recommended as a replacement for N-serve to minimize the effect of solvent carrier (e.g. ethanol), but only in the experiments where suspended sediment concentration are low. Even though carrier solvents have been shown to not affect the dark uptake in some studies (Hauck, 1980; Hall, 1984), ethanol was shown to inhibit dark uptake in this study. Different systems with different assemblages of ammonia producing micro-organisms, therefore appear to exhibit different sensitivities towards solvent (Hall, 1984).

Allylthiourea (ATU) was found to be less effective in blocking dark bicarbonate uptake even though previous studies reported it to be efficient in freshwater systems (Hall, 1984). As long as an inhibitor is not completely efficient in blocking nitrification, the ^{14}C method should therefore be used with caution and local calibration.

iii) Dark C uptake/N oxidation ratio

To accurately estimate nitrification rates from ^{14}C dark uptake rates, accurate estimates of the dark C uptake/ N oxidization ratio are needed. ^{14}C uptake/^{15}N oxidation ratios obtained in this study (0.59-0.73) were higher than those obtained in previous studies. ^{14}C uptake/N oxidation ratios in other studies were derived using a range of different methods. ^{15}N tracer methods were used to directly measure the nitrification processes herein and the present study represents the first report to obtain a direct quantification of the ^{14}C uptake/^{15}N oxidation ratio in a tropical system (Table 4.6). The use of ^{15}N methods to measure ammonium oxidation in parallel with the ^{14}C uptake has the advantage that both methods can be readily carried out in natural seawater.

The considerable difference between ^{14}C uptake/^{15}N oxidation ratios estimated in this study and those obtained in previous studies may arise for several reasons. In the present study the ratios were measured using natural population in natural seawater, whereas in other studies they were largely determined using enrichment cultures. Differences in nitrifier population numbers (Hashimoto, 1981; Ward, 1987), nutrient

concentrations (e.g. Olson, 1981a), and rates of activity between natural and enriched cultured bacteria (Belser, 1979) could easily result in differences in dark uptake and ammonium oxidation. The ratios derived in other studies were obtained in temperate regions (e.g. Billen, 1976; Schell, 1978; Hall, 1984; Owens, 1986). It is unresolved whether assemblages of nitrifying organism differ significantly between tropical and temperate environments, as nitrogen availability in temperate zones is known to be greater than found in tropical regions. The ratio almost certainly changes with environmental conditions (temperature, nutrients, etc.) as well as bacterial biomass (Belser and Schmidt, 1980). In addition, measurement of dark uptake in this present study was carried over a short term (24 h) while in some other studies, the experiments (e.g. Billen, 1976) for estimating the ratio took a 15-day period. The physiological state of nitrifying organisms may differ between short-term and long-term experiments.

Differences between the composition of marine bacteria assemblages in the sediment and the water column may lead to differences either in the carbon uptake or ammonium oxidation. The C uptake/N oxidation ratios obtained in previous studies were mainly derived from nitrate and nitrite production in cultures of nitrifying bacteria isolated from sediment (e.g. Billen, 1976). It is noteworthy that a higher ratio (0.168) was reported by Owens (1986), when the ratio was measured using cultured nitrifying bacteria from turbid estuarine water.

N-serve at high concentration (50 mg l^{-1}) is known to inhibit the activity of other microorganisms. The concentration of N-serve at 5 mg l^{-1} was used to block the nitrification process in other studies (e.g. Billen, 1976). There are some suggestions that at the low concentrations of N-serve used in other studies, ammonium-oxidizing bacteria but not nitrite-oxidizing bacteria are preferentially inhibited (Campbell and Aleem, 1965; Hall and Murphy, 1980). More extensive measurements of dark C uptake/N oxidation ratio should be made to resolve whether the differences in ecological systems result in different ratios.

iv) Bottle confinement

Some problems may arise from the physical limitations of a laboratory study. Most obviously, the transfer of samples into experimental bottle may grossly affect nitrifying cells and may cause their growth and activity to deviate from the behaviour

normally exhibited in their natural habitat. Venrick *et al.* (1977) reported that small-volume and short-period containment had discernible effects on natural plankton and their productivity. Venrick *et al.* (1977) also found that increasing heterogeneity of the phytoplankton during incubation resulted in an increase in the variability of replicate samples and changes in the composition of the micro-organisms in the container. The larger amounts of water (20 litres) and short-period incubations (6 h) used in the ^{15}N experiments herein are expected to minimize these effects.

5.2 CONCLUSIONS

The potential impact arising from enhanced terrestrial sediment and nutrient runoff into the shelf ecosystems of the GBR region is currently a major management concern. Measurement of nutrient levels following cyclonic events in the GBR region provide information relating to natural patterns of nutrient enrichment which occur in the GBR. An understanding of the variability in the concentration and forms of nutrients occurring in GBR shelf waters during normal conditions and following cyclonic events is necessary to assess the relative extent to which human activities alter nutrient levels in GBR waters. Any attempt to explore the question of eutrophication of GBR waters must take the variability in concentration and forms of nutrients arising from natural, but episodic events into account.

Similarly with the process of sedimentation, a better understanding of natural sedimentation patterns under both normal and cyclonic conditions will enhance identification and isolation of man-induced sedimentation problems for effective management of the impact of man-induced problem in the GBR coastal region. Monitoring of transformation rates in seawater following cyclones provides an improved understanding of the GBR nutrient status and nitrogen dynamics in tropical shelf systems.

The experiments carried out in this present study demonstrated that:

1. Resuspension of shelf sediments can deliver significant amounts of particulate (PN, PP) and dissolved nutrients (NH_4^+, NO_3^- plus NO_2^-, PO_4^{3-}, $Si(OH)_4$) into the GBR water column and stimulated the growth of phytoplankton as shown by plant pigments (chlorophyll *a*, phaeophytin).

2. With the exception of total phosphorus, volume specific amounts of individual

nutrient species released from inner and outer shelf sediments did not differ significantly in simulated resuspension events. The greater release of total phosphorus from outer shelf sediment may be inferred to reflect a high rate of phosphorus desorption. After nine days of sediment resuspension, silicate concentrations in seawater containing inner shelf sediment increased.

3. Relationships between the mass of inner and outer shelf sediments resuspended and the amount of nutrient released varied between individual nutrient species. For most nutrient species, a linear relationship between the mass of sediment resuspended and the amount of nutrient released was found.

4. Concentrations of dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), nitrate (NO_3^-) and nitrite (NO_2^-) were not found to be significantly increased in the water column as a result of sediment resuspension processes. This is in part due to noise limitations inherent in the chemical analysis of these nutrient species. The very low natural concentrations of NO_3^- and NO_2^- within sediments and very high background concentration of DON and DOP in the water column made it difficult to detect small changes of these nutrient species caused by sediment resuspension. The variation of nutrient concentrations in the different levels of water subsampling, sediment site and sediment subsample also contributed to difficulty in detecting the changes of nutrient concentration. Depth variations in NH_4^+, NO_3^- and NO_2^- concentrations within surficial sediments are likely responsible for the lack of a linear relationship between sediment mass and nutrient release.

5. Short-term (daily) temporal changes in nutrient and chlorophyll concentrations following simulated resuspension events differed between individual experiments and between control and experimental seawater. In most cases, DON and DOP concentrations were similar in water with, and without suspended sediment, and were stable over time. Concentrations of PN and PP were generally also relatively constant through time. Concentrations of ammonium, nitrate and nitrite fluctuated erratically, without clear temporal trends. Phosphate and silicate concentrations decreased. Concentration of phaeophytin were stable, while chlorophyll *a* increased a few days following the prompt release of nutrients which was the result of increasing phytoplankton biomass.

6. After the initial increase in nutrient concentration following the resuspension of sediment, nutrient concentration were relatively stable over the following 1-4 days. Measurements of nutrient concentrations in water sampled 1-4 days after cyclones should therefore still reasonably represent the water characteristics after that event in terms of nutrient concentration and speciation in the water column.

7. Estimated nitrification rates (obtained from either dark ^{14}C-bicarbonate incorporation or ^{15}N technique), nitrite oxidation, and uptake rates of ammonium, nitrite and nitrate in water with suspended sediment were higher than rates in seawater without sediment.

8. N-serve (Nitrapyrine) was found to be the most efficient inhibitor for blocking ammonium oxidation in seawater (both with and without suspended sediment) as compared to ATU (Allylthiourea) and Hach2533. When compared to earlier studies, a higher concentration of N-serve (50 mg l^{-1}), was required for efficient blocking of the ammonium oxidation process especially in seawater with suspended sediment. Sediment particles hinder the counting of radioisotopes and N-serve may be adsorbed by sediment. The high concentration of N-serve required for efficient blocking may affect the nitrification process, as N-serve is also known to block the activity of other organisms. This blocking effect may result in a higher apparent nitrification rate.

9. The measured ratios of dark ^{14}C-bicarbonate uptake to ^{15}N-nitrogen oxidation obtained in this study (0.59-0.73) are considerably higher than ratios measured in other studies (0.06-0.17). This difference may be the result of differences between environmental conditions (temperate vs tropical populations), variation between rates mediately cultured bacteria and natural populations, the concentration of N-serve used or specific artefacts associated with the ^{15}N technique being used in natural systems .

10. Measurements of net nitrification rates by observation of changes in ammonium consumption or nitrate and nitrite production with and without nitrification inhibitors was not successful as the changes involved were too small to detect.

11. The elevated nitrification rates observed in seawater with suspended sediment are likely the result of a combination of higher levels of ammonium substrate and optimal conditions for oxidation reactions. These conditions include low light intensity, high water temperatures and the presence of nitrifying bacteria mixed into the water column with the sediment particles and the preferential uptake of ammonium by phytoplankton. The significant releases of inorganic nutrients and rapid uptake of ammonium, nitrate and nitrite in seawater with suspended sediment is suggested to be responsible for the phytoplankton blooms observed 2-3 days after a cyclone.

13. Higher rates of nitrogen transformation were measured in seawater with freshly collected sediment added, as compared to seawater mixed with frozen-thawed sediment. This indicates that live nitrifying organisms in resuspended sediment elevated nitrification rates in the water column.

14. Concentrations of PN, NH_4^+, PP, PO_4^{3-} measured one week after cyclone "Winifred" were higher than those measured under normal conditions but lower than concentrations immediately after the cyclones as estimated from experimental sediment resuspensions. This is probably due to the rapid settling of particulate matter to the bottom and to a lesser extent, from the remineralization of PN and PP. Decreases in NH_4^+ and PO_4^{3-} concentrations are likely due to utilization by phytoplankton and bacteria.

5.3 SUGGESTED FURTHER RESEARCH

1. Further *in situ* measurements of nutrient transformation processes in the water column immediately following a cyclone are suggested. These would provide improved estimates of rates in the actual environment and minimize any perturbations caused by experimental artefacts.

2. To improve estimates of nitrification rates in seawater by the ^{14}C method (especially particle-loaded seawater), further calibration of the dark C uptake/ N oxidation ratio is required to resolve whether the differences in the ratio result from the difference between ecosystems. To better measure nitrification, both ^{14}C and ^{15}N methods should be employed so that the disadvantages of the individual techniques can be offset against each other.

3. Measurement of the amount of suspended solids related to "normal" currents, waves and wind-induced turbulence in the GBR areas is suggested since this mechanism involves a continual resuspension of sediment and recycling of nutrients into the water column. Such measurements will provide information as to the chronic nutrient inputs from resuspended sediment during normal (non-cyclonic) conditions and for the long term sustainment of primary production.

APPENDICES

APPENDIX I

I-1

Analysis of variance or covariance was performed by a Statistix 3.5 program (Analytical software, 1991). Sources of variation are treated as follows:

Site = inner shelf site, outer shelf site and control = fixed factor
Day = day 1 and day 9 of the experimental period = fixed factor
Sediment subsample (Sedsub) = two sediment subsamples within each sites = random factor
Water subsample = two water subsamples within each sediment subsamples = random factor

In the table of ANOVA or AOCV, factor "day" tested against (shown by *) "site" = site*day ,
"sediment subsample" nested in "site" and "site * day" = site (sediment subsample), site *day (sediment subsample) and
" water subsample" are nested in "sediment subsample" = sediment subsample (water subsample).

The Covariate in the AOCV is the amount of sediment weight in terms of wet weight, dry weight and estimated porewater volume.

Cochran's C test = largest variance / sum of variance from each group of replicates.

Table I-1

Results of the analysis of variance and covariance for individual nutrients in experiment 3: Variability of measured nutrient releases related to sediment and water subsampling.

Source of variation	Degree of freedom	Total N			PN			TDN		
		Mean square	F value	Probability	Mean square	F value	Probability	Mean square	F value	Probability
Site	2	74.913	20.880	**0.017**	103.500	31.720	**0.010**	9.280	1.630	0.332
Sediment subsample (site)	3	3.587			3.263			5.707		
Day	1	7.313	9.760	0.052	1.213	0.630	0.485	6.528	4.740	0.118
Day * site	2	7.930	10.590	**0.044**	12.543	6.520	0.081	0.353	0.260	0.789
Sediment subsample (Day * Site)	3	0.749			1.924			1.378		
Sediment subsample	6	2.168	0.946	0.498	2.593	1.853	0.171	3.543	2.719	0.066
Water subsample (Sedsub (Day * Site))	12	2.291	1.752	0.117	1.400	1.694	0.132	1.303	2.922	**0.004**
Residual (Total N = 24, PON =24, TDN = 48)		1.307			0.827			0.446		

Source of variation	Degree of freedom	DON			DIN			NH4		
		Mean square	F value	Probability	Mean square	F value	Probability	Mean square	F value	Probability
Site	2	7.810	1.900	0.293	0.053	0.720	0.556	0.012	0.100	0.904
Sediment subsample (site)	3	4.105			0.074			0.120		
Day	1	1.919	1.960	0.257	0.044	0.460	0.546	0.110	3.090	0.177
Day * site	2	0.515	0.520	0.638	0.551	5.810	0.093	0.268	7.520	0.068
Sediment subsample (Day * Site)	3	0.982			0.095			0.360		
Sediment subsample	6	2.544	1.314	0.323	0.085	0.377	0.879	0.240	3.038	**0.048**
Water subsample (Sedsub (Day * Site))	12	1.936	3.445	**0.001**	0.224	3.556	**0.001**	0.079	39.500	**<0.001**
Residual (DON = 48, DIN = 41, NH4 = 39)		0.562			0.063			0.002		

Table I-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 3: Variability of measured nutrient releases related to sediment and water subsampling.

		NO3 + NO2			NO3			NO2				
Source of variation	Degree of freedom	Mean square	F value	Probability	Mean square	F value	Probability	SV	DF	Mean square	F value	Probability
Site	2	0.00015	0.450	0.675	0.00000	0.010	0.992	Site	2	0.00560	458.2	**<0.001**
Sediment subsample (site)	3	0.00034			0.00036			Sedsub	3	0.00001		
Day	1	0.00000	0.000	1.000	0.00233	28.750	**0.013**	Day	1	0.00028	98.2	**0.001**
Day * site	2	0.00047	14.120	**0.030**	0.00064	7.940	0.063	Day * Site	2	0.00032	72.9	**0.001**
Sediment subsample (Day * Site)	3	0.00003			0.00008			Covariate	1		51.6	**0.019**
Sediment subsample	6	0.00019	1.563	0.240	0.00022	1.725	0.198	Residual	2	0.00000		
Water subsample (Sedsub (Day * Site))	12	0.00012	1.239	0.285	0.00013	1.356	0.205					
Residual *	48	0.00010			0.00009							

		Total P			PP			TDP			
Source of variation	Degree of freedom	Mean square	F value	Probability	Mean square	F value	Probability	Degree of freedom	Mean square	F value	Probability
Site	2	0.098	0.500	0.652	0.109	6.500	0.081	2	0.0109	1.970	0.284
Sediment subsample (site)	3	0.031			0.017			3	0.0055		
Day	1	0.023	0.390	0.577	0.016	10.230	**0.049**	1	0.0000	0.000	0.950
Day * site	2	0.004	14.130	**0.030**	0.001	4.090	0.139	2	0.0294	4.270	0.133
Sediment subsample (Day * Site)	3	0.008			0.002			3	0.0069		
Sediment subsample	6	0.019	2.182	0.118	0.009	0.937	0.504	6	0.0062	0.585	0.736
Water subsample (Sedsub (Day * Site))	18	0.009	1.416	0.245	0.010	2.512	**0.038**	12	0.0106	3.574	**<0.001**
Residual (Total P = 41, POP = 41)		0.006			0.004			48	0.0030		

Table I-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 3: Variability of measured nutrient releases related to sediment and water subsampling.

		DOP			PO4			Si(OH)4		
Source of variation	Degree of freedom	Mean square	F value	Probability	Mean square	F value	Probability	Mean square	F value	Probability
Site	2	0.081	10.760	**0.043**	0.045	10.410	**0.045**	2.578	9.270	0.052
Sediment subsample (site)	3	0.008			0.004			0.278		
Day	1	0.064	3.340	0.165	0.061	4.300	0.130	16.175	54.680	**0.005**
Day * site	2	0.103	5.430	0.101	0.037	2.630	0.219	1.109	3.750	0.153
Sediment subsample (Day * Site)	3	0.019			0.014			0.296		
Sediment subsample	6	0.014	0.794	0.592	0.009	4.093	**0.018**	0.287	47.833	**<0.001**
Water subsample (Sedsub (Day * Site))	12	0.017	2.429	**0.015**	0.002	0.702	0.742	0.006	1.000	0.463
Residual	48	0.007			0.003			0.006		

		Chl a + Phaeo			Phaeophytin			Chlorophyll a		
Source of variation	Degree of freedom	Mean square	F value	Probability	Mean square	F value	Probability	Mean square	F value	Probability
Site	2	5.305	44.320	**0.006**	2.437	31.160	**0.009**	0.835	103.130	**0.002**
Sediment subsample (site)	3	0.119			0.078			0.008		
Day	1	22.475	1594.280	**<0.001**	6.066	1273.520	**<0.001**	5.188	703.450	**<0.001**
Day * site	2	1.948	138.170	**0.001**	0.949	199.250	**<0.001**	0.358	48.580	**0.005**
Sediment subsample (Day * Site)	3	0.014						0.007		
Sediment subsample	6	0.067	3.167	**0.042**	0.005	0.500	0.797	0.008	0.750	0.655
Water subsample (Sedsub (Day * Site))	12	0.021	2.100	0.059	0.010	1.000	0.477	0.010	5.000	**<0.001**
Residual	24	0.010			0.010			0.002		

Table I-2

Summary of analysis of covariance between nutrient and chlorophyll concentrations and sediment weight (Covariance = wet weight) from experiment 3. Degree of freedom (df) = 1, 2 (see detail in analysis of covariance table). Significance at $\underline{P} < 0.05$ (number in bold); Not significance at $\underline{P} > 0.05$.

Variables	Covariate Wet weight F value	Probablility
Total N	3.34	0.2091
PN	0.47	0.5638
TDN	0.87	0.4497
DON	0.88	0.4472
DIN	0.23	0.6788
NH_4^+	0.23	0.6788
$NO_3^- + NO_2^-$	0.63	0.5106
NO_3^-	8.25	0.1029
NO_2^-	51.63	**0.0188**
TOTAL P	0.19	0.7055
PP	1.72	0.32
TDP	0	1
DOP	1.47	0.3491
PO_4^{3-}	2.56	0.2507
$Si(OH)_4$	0.08	0.8039
Chlorophyll *a*	0	1
Phaeophytin	3.04	0.2234
Chl *a* + Phaeo	0.47	0.5638

Table I-3

Summary of analysis of variance comparing nutrient and chlorophyll release in experimental and control containers during experiment 3. Mean concentration in experimental containers (E), mean concentration in control (C), One standard error in parentheses, Significance level ($P < 0.05$; number in bold), N = number of replicates.

No. of replicates		Control n = 12 n = 8#	Experimental n = 24 n = 16 #	E-C
Variable	Day	Mean (SE)	Mean (SE)	
Total N	1	6.77 (0.79)	9.23 (0.31)	**2.46**
	9	6.68 (1.23)	10.66 (0.60)	**3.97**
PN #	1	1.94 (0,79)	5.26 (0.06)	**3.32**
	9	0.98 (0.14)	6.22 (0.09)	**5.24**
TDN *	1	4.83 (0.98)	3.97 (0.04)	-0.86
	9	5.70 (1.08)	4.44 (0.04)	-1.27
DON *	1	4.67 (0.93)	3.65 (0.04)	-1.02
	9	4.86 (1.14)	4.05 (0.04)	-0.81
DIN *	1	0.16 (0.02)	0.32 (0.01)	0.16
	9	0.85 (0.69)	0.20 (0.03)	-0.65
NH_4^+ *	1	0.11 (0.08)	0.26 (0.01)	0.25
	9	0.79 (0.68)	0.69 (0.01)	-0.10
$NO_3^- + NO_2^-$ *	1	0.05 (<0.01)	0.06 (<0.01)	0.01
	9	0.06 (0.02)	0.05 (<0.01)	-0.01
NO_3^-* *	1	0.05 (<0.01)	0.04 (<0.01)	-0.01
	9	0.03 (<0.01)	0.03 (<0.01)	0.00
NO_2^-*	1	<0.01 (<0.01)	0.02 (<0.01)	0.01
	9	0.04 (<0.01)	0.02 (<0.01)	-0.02
TOTAL P#	1	0.45 (0.03)	0.42 (0.02)	-0.03
	9	0.36 (0.05)	0.48 (0.03)	0.12
PP#	1	0.13 (0.01)	0.16 (0.02)	0.03
	9	0.08 (0.01)	0.21 (0.02)	0.13
TDP *	1	0.32 (0.11)	0.26 (0.01)	-0.06
	9	0.28 (0.07)	0.28 (0.01)	0.00
DOP *	1	0.14 (0.13)	0.05 (0.21)	-0.09
	9	0.07 (0.13)	0.21 (0.02)	0.14
PO_4^{3-}	1	0.19 (0.03)	0.21 (<0.01)	0.02
	9	0.21 (0.08)	0.29 (0.01)	0.08
$Si(OH)_4$	1	1.38 (0.18)	1.52 (0.02)	0.14
	9	1.84 (0.42)	2.72 (0.03)	0.88
Chlorophyll *a*#	1	0.05 (0.09)	0.96 (0.03)	**0.92**
	9	0.06 (<0.01)	0.19 (0.02)	0.13
Phaeophytin#	1	0.30 (0.05)	1.40 (0.03)	**1.07**
	9	0.15 (0.08)	0.41 (0.02)	0.26
Chl *a* + Phaeo#	1	0.80 (0.10)	2.35 (0.03)	**2.32**
	9	0.21 (0.01)	0.59 (0.02)	0.38

number of replicates in indicated variables.

* concentrations were higher in the control containers than in the experimental containers.

Table I-4

Summary of mean concentrations of nutrients and chlorophyll in experimental bottles with resuspended inner and outer shelf sediments during experiment 3. Data were presented for both day 1 and day 9 samplings.
I = O : no difference between means ($P > 0.05$)
I > O : means of inner shelf bottles greater ($P < 0.05$)
I < O : mean of outer shelf bottles greater ($P < 0.05$)

Sites Sediment added (wet wt.) No. of replicates		Inner shelf IS1 0.69-0.70 gm. n = 12	Outer shelf OS1 0.89-0.91 gm. n = 12	Results
Variable	Day	Mean (SE)	Mean (SE)	
Total N	1	9.37 (0.30)	9.19 (0.32)	I = O
	9	12.01 (0.21)	9.30 (0.18)	I > O
PN	1	5.17 (0.28)	5.36 (0.44)	I = O
	9	7.51 (0.04)	4.93 (0.07)	I > O
TDN	1	4.10 (0.32)	3.83 (0.12)	I = O
	9	4.50 (0.29)	4.37 (0.25)	I = O
DON	1	3.73 (0.32)	3.57 (0.10)	I = O
	9	4.40 (0.29)	3.70 (0.35)	I = O
DIN	1	0.37 (0.01)	0.27 (0.03)	I = O
	9	0.11 (0.01)	0.14 (0.02)	I = O
NH_4^+	1	0.32 (0.01)	0.21 (0.03)	I = O
	9	0.06 (0.01)	0.09 (0.02)	I = O
$NO_3^- + NO_2^-$	1	0.06 (<0.01)	0.06 (<0.01)	I = O
	9	0.05 (<0.01)	0.06 (<0.01)	I = O
NO_3^-	1	0.03 (<0.01)	0.04 (0.04)	I = O
	9	0.04 (<0.01)	0.03 (<0.01)	I = O
NO_2^-	1	0.02 (<0.01)	0.02 (<0.01)	I = O
	9	0.02 (<0.01)	0.03 (<0.01)	I = O
TOTAL P	1	0.46 (0.03)	0.38 (0.05)	I = O
	9	0.43 (0.03)	0.54 (0.02)	I = O
PP	1	0.18 (0.03)	0.15 (0.07)	I = O
	9	0.18 (0.04)	0.23 (0.02)	I = O
TDP	1	0.29 (0.01)	0.26 (0.02)	I = O
	9	0.25 (0.02)	0.31 (0.02)	I = O
DOP *	1	0.08 (0.02)	0.01 (0.02)	?
	9	- 0.11 (0.03)	0.09 (0.02)	?
PO_4^{3-}	1	0.21 (<0.01)	0.21 (<0.01)	I = O
	9	0.36 (0.03)	0.22 (0.02)	I > O
$Si(OH)_4$	1	1.64 (0.04)	1.41 (0.03)	I = O
	9	2.89 (0.06)	2.55 (0.13)	I = O
Chl *a* + Phaeo	1	2.57 (0.06)	2.14 (0.08)	I > O
	9	0.64 (0.04)	0.55 (0.07)	I = O
Chlorophyll *a*	1	1.22 (0.05)	0.69 (0.01)	I > O
	9	0.23 (0.02)	0.15 (0.02)	I = O
Phaeophytin	1	1.35 (0.04)	1.45 (0.08)	I = O
	9	0.42 (0.03)	0.40 (0.05)	I = O

* Some of DOP data were negative in value due to error either from TDP or PO4 so that their ANOVA result was inconclusive.

APPENDIX II

II-1

Analysis of variance or covariance was performed by a Genstat program. Sources of variation are treated as follows:

Treatment = control and experimental bottles = fixed factor
Inner-outer = inner or outer shelf sediments = fixed factor
Site = three sites in each inner and outer shelf = random factor
Day = day 1 and day 9 of the experimental period = fixed factor
Sediment subsample = two sediment subsamples within each sites = random factor

In the table of ANOVA or AOCV,
factor "tratment" tested against "inner-outer" = "treatment*inner-outer"
factor "day" tested against "treatment" and "inner-outer" = "day*treatment*inner-outer"
factor "site" nested in "day" = day (site),
factor "sediment subsample" nested in "site" which nested in "day" = "day (site sedsub)),
factor "replicate" nested in "sediment subsampled" which nested in "site" and nested in "day" = day (site (sedsub (rep))).

The Covariate in the AOCV is the amount of sediment weight expressed as wet weight, water-free weight and estimated porewater volume.

Cochran's C test = largest variance / sum of variance from each group of replicates.

Table II-1

Results of the analysis of variance and covariance for individual nutrients in experiment 4: A comparison of the amount of nutrients released from inner and outer shelf sediments.

		Total N			PN		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	55004.7	45.340	**0.007**	4326.96	66.410	**0.004**
treatment*inner-outer	1	226.75	1.870	0.265	161.38	2.477	0.214
Covariates	1	0.57	0.005	0.948	3.80	0.058	0.825
Residual	3	121.41	10.220		65.16	6.152	
Total	6	1016.0	85.520		781.27	73.766	
Day (site) Stratum							
day	1	198.51	2.800	0.193	667.31	6.315	0.087
day*treatment	1	88.33	1.250	0.345	198.27	1.876	0.264
day.*treatment*inner-outer	1	43.00	0.610	0.534	34.65	0.328	0.607
Covariates	1	14.81	0.209	0.678	28.08	0.266	0.642
Residual	3	70.81	5.960		105.66	9.977	
Total	7	79.59	6.699		177.90	16.797	
Day (site (sedsub)) Stratum							
Covariates	1	212.33	4.884	**0.044**	141.42	4.629	**0.048**
Residual	15	43.48	3.660		30.55	2.885	
Total	16	54.03	4.548		37.48	3.539	
Day (site (sedsub (rep))) Stratum	90	11.88			10.59		
Grand Total	119						

		TDN			DON		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	70.798	4.718	0.096	50.502	3.527	0.134
treatment*inner-outer	1	0.179	0.012	0.918	0.117	0.008	0.933
Residual	4	15.007	6.380		14.320	5.627	
Total	6	21.834	9.283		17.980	7.066	
Day (site) Stratum							
day	1	135.875	30.157	**0.005**	54.784	11.479	**0.028**
day*treatment	1	21.307	4.729	0.095	8.290	1.737	0.258
day.*treatment*inner-outer	1	2.163	0.480	0.527	2.229	0.467	0.532
Residual	4	4.506	1.916		4.773	1.875	
Total	7	25.338	10.773		12.056	4.737	
Day (site (sedsub)) Stratum	16	8.147	3.464		8.173	3.211	
Day (site (sedsub (rep))) Stratum	90	2.352			2.545		
Grand Total	119						

Table II-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 4: A comparison of the amount of nutrients released from inner and outer shelf sediments.

		DIN			NH4		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	1.710	81.370	**0.001**	1.799	112.374	**<0.001**
treatment*inner-outer	1	0.007	0.311	0.607	0.011	0.717	0.445
Residual	4	0.021	0.402		0.016	0.303	
Total	6	0.300	5.743		0.312	5.922	
Day (site) Stratum							
day	1	18.10	1434.27	**<0.001**	17.218	1503.40	**<0.001**
day*treatment	1	3.016	2238.96	**<0.001**	2.546	222.27	**<0.001**
day.*treatment*inner-outer	1	0.001	0.040	0.851	0.004	0.366	0.578
Residual	4	0.013	0.242		0.011	0.217	
Total	7	3.024	57.879		2.831	53.643	
Day (site (sedsub)) Stratum	16	0.122	2.331		0.114	2.162	
Day (site (sedsub (rep))) Stratum	90	0.052			0.053		
Grand Total	119						

		NO2 + NO3			NO3		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	0.00110	2.221	0.210	0.00069	0.769	0.430
treatment*inner-outer	1	0.00067	1.315	0.315	0.00003	0.034	0.863
Residual	4	0.00051	1.684		0.00089	1.578	
Total	6	0.00065	2.115		0.00072	1.263	
Day (site) Stratum							
day	1	0.01104	20.091	**0.011**	0.07747	146.35	**<0.001**
day*treatment	1	0.19900	36.223	**0.004**	0.01867	35.278	**0.004**
day.*treatment*inner-outer	1	0.00176	3.202	0.148	0.00520	4.763	0.095
Residual	4	0.00055	1.797		0.00053	0.929	
Total	7	0.00499	16.305		0.01439	25.277	
Day (site (sedsub)) Stratum	16	0.00113	3.726		0.00139	2.436	
Day (site (sedsub (rep))) Stratum	90	0.00031			0.00057		
Grand Total	119						

Table II-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 4: A comparison of the amount of nutrients released from inner and outer shelf sediments.

		NO2			Total P		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	0.00005	0.099	0.769	57.020	78.838	**0.001**
treatment*inner-outer	1	0.00045	0.855	0.408	7.479	10.340	**0.032**
Residual	4	0.00005	2.627		0.723	2.146	
Total	6	0.00044	2.206		11.232	33.320	
Day (site) Stratum							
day	1	0.02980	81.367	**0.001**	11.678	19.534	**0.012**
day*treatment	1	0.00002	0.062	0.816	2.695	4.508	0.101
day.*treatment*inner-outer	1	0.00006	0.156	0.713	3.314	5.544	0.078
Residual	4	0.00037	1.857		0.598	1.773	
Total	7	0.00448	22.708		2.868	8.509	
Day (site (sedsub)) Stratum	16	0.00022	1.092		0.581	1.722	
Day (site (sedsub (rep))) Stratum	90	0.00020			0.337		
Grand Total	119						

		PP			DOP		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	46.980	77.697	**0.001**	0.212	1.488	0.290
treatment*inner-outer	1	4.780	7.905	**0.048**	0.320	2.244	0.193
Residual	4	0.605	1.781		0.142	14.878	
Total	6	9.030	26.591		0.184	19.172	
Day (site) Stratum							
day	1	9.968	19.941	**0.011**	0.022	0.181	0.692
day*treatment	1	2.248	4.498	0.101	0.098	0.791	0.424
day.*treatment*inner-outer	1	3.391	6.784	0.060	0.043	0.347	0.588
Residual	4	0.500	1.472		0.124	12.917	
Total	7	2.515	7.407		0.094	9.814	
Day (site (sedsub)) Stratum	16	0.608	1.791		0.048	4.993	
Day (site (sedsub (rep))) Stratum	90	0.340			0.010		
Grand Total	119						

Table II-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 4: A comparison of the amount of nutrients released from inner and outer shelf sediments.

		TDP			Si(OH)4		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	0.486	2.848	0.190	29.670	33.000	**0.011**
treatment*inner-outer	1	0.129	0.756	0.449	49.990	55.590	**0.005**
Covariates	1	0.000	0.001	0.977	12.210	13.610	**0.035**
Residual	3	0.171	27.170		0.899	4.610	
Total	6	0.188	29.915		15.760	80.838	
Day (site) Stratum							
day	1	0.042	3.107	0.176	6.222	2.960	0.184
day*treatment	1	0.013	0.977	0.396	6.550	3.119	0.176
day.*treatment*inner-outer	1	0.069	5.159	0.437	7.412	3.529	0.157
Covariates	1	0.302	22.430	**0.018**	3.616	1.722	
Residual	3	0.013	2.144		2.100	10.766	
Total	7	0.067	10.620		4.300	22.044	
Day (site (sedsub)) Stratum							
Covariates	1	0.029	0.734	0.405	7.087	7.397	**0.016**
Residual	15	0.040	6.352		0.958	4.911	
Total	16	0.039	6.246		1.341	6.875	
Day (site (sedsub (rep))) Stratum	90	0.006			0.195		
Grand Total	119	2.786			163.720		

		PO4			Chl a + Phaeophytin		
Source of variation	D.F.	Mean square	F value	Probablility	Mean square	F value	Probablility
Site Stratum							
treatment	1	0.055	1.093	0.385	110.360	21.715	**0.010**
treatment*inner-outer	1	0.000	0.006	0.942	12.417	2.443	0.193
Residual	4	0.051	12.702		5.083	34.599	
Total	6	0.043	10.796		23.852	162.370	
Day (site) Stratum							
day	1	0.168	13.401	**0.022**	10.976	1.078	0.358
day*treatment	1	0.029	2.337	0.201	1.012	0.099	0.769
day.*treatment*inner-outer	1	0.035	2.770	0.171	5.095	0.501	0.518
Residual	4	0.013	3.127		10.179	69.293	
Total	7	0.040	10.055		8.257	56.211	
Day (site (sedsub)) Stratum	16	0.006	1.492		0.510		
Day (site (sedsub (rep))) Stratum	90	0.004			0.147		
Grand Total	119						

Table II-1 (cont.)

Results of the analysis of variance and covariance for individual nutrients in experiment 4: A comparison of the amount of nutrients released from inner and outer shelf sediments.

Chlorophyll a

Source of variation	D.F.	Mean square	F value	Probablility
Site Stratum				
treatment	1	17.479	96.822	**0.002**
treatment*inner-outer	1	1.006	5.573	0.099
Covariates	1	2.469	13.678	0.034
Residual	3	0.181	3.425	
Total	6	3.582	67.969	
Day (site) Stratum				
day	1	3.238	3.590	0.154
day*treatment	1	2.525	2.800	0.193
day.*treatment*inner-outer	1	0.563	0.624	0.487
Covariates	1	0.051	0.057	0.827
Residual	3	0.902	17.110	
Total	7	1.298	24.620	
Day (site (sedsub)) Stratum				
Covariates	1	0.164	1.054	0.321
Residual	15	0.156	2.951	
Total	16	0.156	2.961	
Day (site (sedsub (rep))) Stratum	90	0.053	12.810	
Grand Total	119	37.821		

Phaeophytin

Source of variation	D.F.	Mean square	F value	Probablility
Site Stratum				
treatment	1	40.003	7.087	**0.047**
treatment*inner-outer	1	14.847	2.630	0.180
Residual	4	5.644	37.072	
Total	6	12.905	84.755	
Day (site) Stratum				
day	1	26.464	4.683	0.097
day*treatment	1	6.808	1.205	0.334
day.*treatment*inner-outer	1	2.351	0.416	0.554
Residual	4	5.651	37.112	
Total	7	8.318	54.629	
Day (site (sedsub)) Stratum	16	0.216	1.420	
Day (site (sedsub (rep))) Stratum	90	0.152		
Grand Total	119			

Table II-2

Summary of analysis of covariance between nutrient and chlorophyll concentrations and sediment weight (Covariance = wet weight) from experiment 4. Significant level at $P < 0.05$ (number in bold), Not significant at 0.05.

Variables	Error term Wet weight	Degree of freedom	F value	Probability
Total N	site	1,3	0.005	0.9481
	day(site)	1,3	0.209	0.6786
	day(site(sedss))	1,15	4.884	**0.0439**
PN	site	1,3	0.058	0.8252
	day(site)	1,3	0.266	0.6069
	day(site(sedss))	1,15	4.629	**0.0481**
TDN	site	1,3	0.416	0.5649
	day(site)	1,3	0.397	0.5734
	day(site(sedss))	1,15	0.874	0.3647
DON	site	1,3	0.406	0.5693
	day(site)	1,3	0.389	0.5771
	day(site(sedss))	1,15	1.013	0.3102
DIN	site	1,3	0.318	0.6122
	day(site)	1,3	0.049	0.8390
	day(site(sedss))	1,15	0.304	0.5893
NH_4^+	site	1,3	0.335	0.5938
	day(site)	1,3	0.003	0.9589
	day(site(sedss))	1,15	0.353	0.5613
$NO_3^- + NO_2^-$	site	1,3	0.143	0.7305
	day(site)	1,3	0.824	0.4309
	day(site(sedss))	1,15	0.053	0.8210
NO_3^-	site	1,3	0.658	0.4766
	day(site)	1,3	0.167	0.7102
	day(site(sedss))	1,15	0.008	0.9299
NO_2^-	site	1,3	0.448	0.5512
	day(site)	1,3	1.86	0.2659
	day(site(sedss))	1,15	0.587	0.4555
TOTAL P	site	1,3	0.005	0.9481
	day(site)	1,3	1.282	0.3400
	day(site(sedss))	1,15	0	0.9999
PP	site	1,3	0.0004	0.9535
	day(site)	1,3	0.08	0.7957
	day(site(sedss))	1,15	0.037	0.8500
TDP	site	1,3	0.001	0.9768
	day(site)	1,3	22.43	**0.0178**
	day(site(sedss))	1,15	0.734	0.4051
DOP	site	1,3	0.638	0.4828
	day(site)	1,3	9.656	0.0530
	day(site(sedss))	1,15	1.554	0.2317
PO_4^{3-}	site	1,3	2.471	0.2148
	day(site)	1,3	0.285	0.6305
	day(site(sedss))	1,15	1.649	0.2186
$Si(OH)_4$	site	1,3	13.616	**0.0345**
	day(site)	1,3	1.722	0.2808
	day(site(sedss))	1,15	7.397	**0.0158**
Chlorophyll *a*	site	1,3	0.073	0.8045
	day(site)	1,3	0.08	0.7959
	day(site(sedss))	1,15	1.436	0.2494
Phaeophytin	site	1,3	13.678	**0.0343**
	day(site)	1,3	0.14	0.8267
	day(site(sedss))	1,15	1.054	0.3209
Chl *a* + Phaeo	site	1,3	0.105	0.7622
	day(site)	1,3	0.088	0.7861
	day(site(sedss))	1,15	0.884	0.3620

Table II-3

Summary of ANOVA analyses comparing differences between concentrations in control (C) and experimental bottles (with suspended sediment) in experiment 4. Data were presented in day 1 and day 9. Values given are the mean concentrations (one standard error). Significant level at $\underline{P} < 0.05$ (number in bold), n = number of replicates. Positive values: mean of experimental bottles greater ($\underline{P} < 0.05$), negative values: mean of control grater ($\underline{P} < 0.05$).

No. of replicates		Control n = 12	Experimental n = 48	E-C
Variable	Day	Mean (SE)	Mean (SE)	
Total N	1	8.97 (0.37)	23.8 (0.65)	**14.83**
	9	8.12 (0.80)	27.15 (0.79)	**19.03**
PN	1	1.96 (0.15)	13.81 (0.68)	**11.85**
	9	1.55 (0.10)	19.72 (0.76)	**18.17**
TDN	1	7.01 (0.35)	9.99 (0.26)	2.98
	9	6.57 (0.84)	7.44 (0.27)	0.87
DON	1	7.10 (0.34)	8.72 (0.27)	1.62
	9	6.14 (0.83)	6.44 (0.27)	0.30
DIN	1	0.57 (0.03)	1.27 (0.05)	**0.70**
	9	0.43 (0.02)	0.33 (0.01)	-0.10
NH_4^+	1	0.54 (0.03)	1.22 (0.05)	**0.68**
	9	0.37 (0.01)	0.31 (0.01)	-0.06
$NO_3^- + NO_2^-$	1	0.03 (0.01)	0.06 (<0.01)	**0.03**
	9	0.06 (0.01)	0.04 (<0.01)	**-0.02**
NO_3^-	1	0.02 (<0.01)	0.05 (<0.01)	0.03
	9	0.02 (<0.01)	0.00 (<0.01)	-0.02
NO_2^-	1	0.01 (<0.01)	0.01 (<0.01)	0.00
	9	0.04 (<0.01)	0.04 (<0.01)	0.00
TOTAL P	1	0.16 (0.03)	1.51 (0.10)	**1.35**
	9	0.19 (0.01)	2.73 (0.08)	**2.54**
PP	1	0.02 (0.01)	1.24 (0.11)	**1.22**
	9	0.05 (0.01)	1.96 (0.08)	**1.91**
TDP	1	0.14 (0.03)	0.27 (0.03)	0.13
	9	0.14 (0.01)	0.33 (0.01)	0.19
DOP	1	0.06 (0.02)	0.09 (0.03)	0.03
	9	0.00 (0.02)	0.09 (0.02)	0.09
PO_4^{3-}	1	0.08 (0.01)	0.18 (0.01)	0.10
	9	0.22 (0.01)	0.24 (0.02)	0.02
$Si(OH)_4$	1	0.25 (0.22)	1.81 (0.05)	**1.56**
	9	0.65 (0.05)	2.46 (0.15)	**1.81**
Chl *a* + Phaeo	1	0.45 (0.01)	3.08 (0.16)	**2.63**
	9	0.21 (0.02)	2.38 (0.08)	**2.17**
Chlorophyll *a*	1	0.38 (0.01)	0.97 (0.04)	**0.59**
	9	0.13 (0.02)	1.45 (0.06)	**1.32**
Phaeophytin	1	0.07 (0.01)	2.11 (0.14)	**2.04**
	9	0.09 (0.01)	0.93 (0.07)	**0.84**

Table II-4

Summary of mean concentrations of nutrients and chlorophyll measured after release from inner and outer shelf sediments during experiment 4. Data from day 1 and day 9 samplings are presented.
I = O : no difference between means ($P > 0.05$)
I > O : mean of inner shelf bottles greater ($P < 0.05$)
I < O : mean of outer shelf bottles greater ($P < 0.05$)

Sites Sediment added (wet wt.) No. of replicates		Inner shelf IS2, IS3, IS4 1.933-2.426 gm. n = 24	Outer shelf OS2, OS3, OS4 2.204-2.952 gm. n = 24	Results
Variable	Day	Mean (SE)	Mean (SE)	
Total N	1	22.03 (0.94)	25.57 (0.93)	I = O
	9	24.28 (0.82)	30.03 (1.41)	I = O
PN	1	11.93(0.78)	15.69 (0.88)	I = O
	9	17.04 (0.88)	22.40 (1.28)	I = O
TDN	1	10.09 (0.37)	9.88 (0.36)	I = O
	9	7.24 (0.42)	7.63 (0.36)	I = O
DON	1	8.84 (0.38)	8.60 (0.40)	I = O
	9	6.92 (0.42)	7.29 (0.36)	I = O
DIN	1	1.26 (0.07)	1.28 (0.09)	I = O
	9	0.33 (0.01)	0.34 (0.01)	I = O
NH_4^+	1	1.2 (0.07)	1.23 (0.09)	I = O
	9	0.31 (0.01)	0.32 (0.01)	I = O
NO_3^-+ NO_2^-	1	0.06 (<0.01)	0.05 (<0.01)	I = O
	9	0.02 (<0.01)	0.02 (0.01)	I = O
NO_3^-	1	0.05 (<0.01)	0.04 (0.01)	I = O
	9	0.02 (0.01)	0.02 (0.01)	I = O
NO_2^-	1	<0.01 (<0.01)	<0.01 (<0.01)	I = O
	9	0.04 (<0.01)	0.04 (<0.01)	I = O
TOTAL P	1	1.42 (0.07)	1.60 (0.23)	**I < O**
	9	1.82 (0.10)	2.75 (0.12)	**I < O**
PP	1	1.21 (0.07)	1.28 (0.23)	I = O
	9	1.55 (0.10)	2.37 (0.12)	**I < O**
TDP	1	0.21 (0.03)	0.33 (0.04)	I = O
	9	0.27 (0.01)	0.38 (0.03)	I = O
DOP	1	0.01 (0.04)	0.16 (0.04)	I = O
	9	0.06 (0.03)	0.13 (0.03)	I = O
PO_4^{3-}	1	0.20 (0.01)	0.16 (0.01)	I = O
	9	0.22 (0.08)	0.25 (0.07)	I = O
$Si(OH)_4$	1	2.61 (0.08)	0.97 (0.07)	I = O
	9	3.93 (0.30)	1.04 (0.12)	**I > O**
Chl *a* + Phaeo	1	2.49 (0.15)	3.67 (0.08)	I = O
	9	2.24 (0.08)	2.51 (0.12)	I = O
Chlorophyll *a*	1	0.93 (0.06)	1.01 (0.06)	I = O
	9	1.55 (0.07)	1.34 (0.11)	I = O
Phaeophytin	1	1.56 (0.11)	2.66 (0.28)	I = O
	9	0.70 (0.06)	1.17 (0.14)	I = O

APPENDIX III

Table III-1

Relationships between nutrient release (μM) and pigments (μg l^{-1}) and added sediment weight for sites from inner and outer shelf areas. "r" showes correlation coefficient.

Variables	Sediment shelf	Site	Intercept	Slope	r
Total N	Inner	IS2	8.003	4.146	0.940
		IS3	6.651	3.016	0.952
		IS4	7.174	4.674	0.924
	Outer	OS2	8.107	4.876	0.976
		OS3	9.158	2.202	0.818
		OS4	5.384	6.584	0.998
PN	Inner	IS2	3.278	3.584	0.943
		IS3	2.694	2.302	0.919
		IS4	2.411	4.011	0.901
	Outer	OS2	2.919	4.532	0.980
		OS3	4.350	1.741	0.748
		OS4	0.579	5.947	0.995
TDN	Inner	IS2	4.725	0.562	0.789
		IS3	3.957	0.715	0.930
		IS4	4.763	0.663	0.734
	Outer	OS2	5.189	0.344	0.511
		OS3	4.809	0.461	0.927
		OS4	4.804	0.637	0.961
DON	Inner	IS2	3.249	0.571	0.892
		IS3	2.898	0.699	0.938
		IS4	3.799	0.629	0.711
	Outer	OS2	4.424	0.245	0.397
		OS3	4.028	0.416	0.949
		OS4	3.903	0.644	0.953
DIN	Inner	IS2	1.475	-0.009	0.055
		IS3	1.058	0.015	0.145
		IS4	0.964	0.034	0.900
	Outer	OS2	0.765	0.099	0.901
		OS3	0.781	0.022	0.491
		OS4	0.901	-0.007	0.114
NH_4^+	Inner	IS2	1.383	-0.014	0.089
		IS3	1.024	-0.005	0.055
		IS4	0.928	0.018	0.678
	Outer	OS2	0.739	0.086	0.875
		OS3	0.730	0.041	0.466
		OS4	0.848	-0.015	0.249
NO_3^-	Inner	IS2	0.090	0.004	0.148
		IS3	0.026	0.011	0.636
		IS4	0.017	0.017	0.926
	Outer	OS2	0.007	0.012	0.915
		OS3	0.089	-0.008	0.606
		OS4	0.034	0.010	0.758
NO_2^-	Inner	IS2	0.003	0.000	0.371
		IS3	0.009	-0.001	0.575
		IS4	0.019	-0.001	0.118
	Outer	OS2	0.019	0.001	0.689
		OS3	0.020	0.000	undefined
		OS4	0.018	-0.001	0.387

Table III-1 (cont.)

Variable	Sediment shelf	Site	Intercept	Slope	r
Total P	Inner	IS2	0.990	0.133	0.587
		IS3	0.617	0.202	0.943
		IS4	0.802	0.102	0.609
	Outer	OS2	0.604	0.161	0.548
		OS3	0.635	0.279	0.934
		OS4	0.724	0.267	0.858
PP	Inner	IS2	0.666	0.098	0.489
		IS3	0.382	0.175	0.891
		IS4	0.476	0.104	0.646
	Outer	OS2	0.401	0.111	0.440
		OS3	0.410	0.257	0.900
		OS4	0.552	0.275	0.874
TDP	Inner	IS2	0.324	0.034	0.956
		IS3	0.236	0.027	0.734
		IS4	0.326	-0.002	0.138
	Outer	OS2	0.202	0.049	0.842
		OS3	0.225	0.022	0.713
		OS4	0.172	-0.008	0.348
DOP	Inner	IS2	0.227	0.012	0.860
		IS3	0.188	-0.006	0.330
		IS4	0.208	-0.020	0.577
	Outer	OS2	0.111	0.010	0.308
		OS3	0.161	-0.022	0.847
		OS4	0.077	-0.014	0.577
PO_4^{3-}	Inner	IS2	0.097	0.022	0.308
		IS3	0.047	0.034	0.847
		IS4	0.118	0.018	0.669
	Outer	OS2	0.091	0.039	0.987
		OS3	0.065	0.043	0.935
		OS4	0.065	0.032	0.997
$Si(OH)_4$	Inner	IS2	2.836	0.063	0.152
		IS3	1.511	0.226	0.819
		IS4	1.499	0.251	0.706
	Outer	OS2	1.304	0.136	0.899
		OS3	1.747	0.034	0.230
		OS4	1.338	0.143	0.909
Chl *a* + Phaeo	Inner	IS2	2.077	0.338	0.415
		IS3	0.628	0.430	0.936
		IS4	1.758	0.287	0.521
	Outer	OS2	0.802	1.437	0.894
		OS3	0.625	0.713	0.876
		OS4	0.882	0.956	0.826
Chlorophyll *a*	Inner	IS2	1.043	0.056	0.158
		IS3	0.265	0.094	0.920
		IS4	0.605	0.019	0.145
	Outer	OS2	0.222	0.133	0.884
		OS3	0.266	0.146	0.699
		OS4	0.388	0.240	0.620
Phaeophytin	Inner	IS2	1.034	0.282	0.581
		IS3	0.363	0.336	0.938
		IS4	1.154	0.268	0.602
	Outer	OS2	0.580	1.304	0.894
		OS3	0.359	0.567	0.919
		OS4	0.495	0.716	0.889

APPENDIX IV

Table IV-1

The effect of nitrification inhibitors on temporal changes in NH_4^+ and NO_3^-+ NO_2^- concentrations (±SD) in seawater and seawater with suspended sediment added (70 mg l^{-1}), n=3.

Final concentration of solutions	NH_4^+ (µM) Time (hrs)				NO_3^-+ NO_2^- (µM) Time (hrs)			
	0	3	6	24	0	3	6	24
Control seawater	1.42 (.03)	1.44 (.08)	1.35 (.08)	0.9 (.4)	0.36 (.02)	0.30 (.04)	0.27 (.01)	0.28 (.01)
+Ethanol (392 µg ml^{-1})	1.61 (.12)	1.80 (.29)	1.54 (.73)	1.03 (.15)	0.34 (.02)	0.36 (.06)	0.28 (.001)	0.26 (.01)
+N-Serve (50 µg ml^{-1})	1.54 (.09)	1.79 (.07)	2.16 (.24)	0.95 (.10)	0.46 (.16)	0.37 (.04)	0.26 (.03)	0.27 (.001)
+ATU (50 µg ml^{-1})	2.75 (.16)	2.64 (.02)	3.07 (.27)	2.81 (.46)	0.28 (.04)	0.23 (.03)	0.31 (.09)	0.23 (.03)
+Hach2533 (500 µg ml^{-1})	1.51 (.16)	1.61 (.27)	1.12 (.05)	1.70 (.70)	0.38 (.07)	0.32 (.11)	0.33 (.15)	0.32 (.05)
Seawater with sediment	1.70 (.14)	1.76 (.40)	1.47 (.13)	0.53 (.41)	0.35 (.02)	0.30 (.03)	0.27 (.01)	0.26 (.02)
+Ethanol (392 µg ml^{-1})	1.88 (.12)	1.70 (.29)	1.88 (.91)	0.94 (.15)	0.34 (.04)	0.27 (.001)	0.37 (.13)	0.25 (.001)
+N-Serve (50 µg ml^{-1})	1.92 (.11)	1.90 (.07)	2.25 (.12)	1.20 (.17)	0.36 (.03)	0.29 (.02)	0.31 (.03)	0.28 (.001)
+ATU (50 µg ml^{-1})	3.62 (.62)	2.89 (.01)	3.28 (.62)	2.81 (.09)	0.3 (.03)	0.21 (.005)	0.24 (.02)	0.23 (.02)
+Hach2533 (500 µg ml^{-1})	1.84 (.50)	1.14 (.34)	1.58 (.24)	2.60 (.69)	0.34 (.18)	0.37 (.10)	0.31 (.02)	0.31 (.02)

Table IV-2

Effect of ethanol and nitrification inhibitors on the measurement of NH_4^+, NO_3^- and NO_2^- in standard solutions.

Standard solution with nitrification inhibitors or carrier (final concentration)	% recovery of standard solutions			
	NH_4^+	NO_3^-+ NO_2^-	NO_3^-	NO_2^-
Ethanol (392 µg ml^{-1})	93	94	101	93
N-Serve (50 µg ml^{-1})	92	97	71	101
ATU (50 µg ml^{-1})	81	95	262	72
Hach2533 (500 µg ml^{-1})	108	101	131	98

APPENDIX V

Table V-1

EXPERIMENTAL TRIAL N.1 : November 1990

Nitrite accumulation by using 5 μM $^{15}NH_4^+$ (99 % atom).

Frozen-thawed sediment from IS3 site and mid-shelf water from SW6: AS = seawater with suspended sediment (frozen-thawed), C = control seawater.

* Atom % enrichment (dilution factor) of the medium was measured directly.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation SD	Average $[^{14}NO_2^- + ^{15}NO_2^-]$ μM	N carrier μmol	Extracted seawater volume ml	Average $[NO_2^-]$ yield nM	SD	Nitrite accumulation rate at each time interval (nM h^{-1})	SD
C-NO_2^-	5 μM $^{15}NH_4^+$	0	4	0.00465	0.00027	0.01	0.538	200	6.72	0.69		
C-NO_2^-	5 μM $^{15}NH_4^+$	4	4	0.00520	0.00057	0.01	0.538	200	9.90	5.53	**2.47**	1.38
C-NO_2^-	5 μM $^{15}NH_4^+$	6	4	0.00563	0.00049	0.01	0.538	200	19.25	8.63	**3.21**	1.44
AS-NO_2^-	5 μM $^{15}NH_4^+$	0	4	0.00425	0.00032	0.01	0.538	200	5.12	2.78		
AS-NO_2^-	5 μM $^{15}NH_4^+$	4	4	0.00484	0.00048	0.01	0.538	200	10.31	4.21	**2.58**	1.05
AS-NO_2^-	5 μM $^{15}NH_4^+$	6	4	0.00594	0.00040	0.01	0.538	200	19.99	6.49	**3.33**	1.08

Table V-1 (cont.)

EXPERIMENTAL TRIAL N.2 : July 1991

Nitrite accumulation by using 2 and 0.5 μM $^{15}NH_4^+$ (99 % atom).

Frozen-thawed sediment from IS3 site and mid-shelf water from SW7: AS = seawater with suspended sediment (frozen-thawed), C = control seawater.

* Atom % enrichment (dilution factor) was calculated from the ^{15}N addition.

Water sample	Isotope addition	Icubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average $[^{14}NO_2^- + ^{15}NO_2^-]$ μM	N carrier μmol	Extracted seawater volume ml	Average $[NO_2^-]$ yield nM	SD	**Nitrite accumulation rate at each time Interval (nM h^{-1})**	SD
C-NO_2^-	2 μM $^{15}NH_4^+$	3	3	0.00426	0.00047	0.00	0.400	200	3.23	2.53	**1.08**	0.84
C-NO_2^-	2 μM $^{15}NH_4^+$	6	3	0.00458	0.00076	0.00	0.400	200	4.93	4.08	**0.82**	0.68
AS-NO_2^-	2 μM $^{15}NH_4^+$	3	3	0.00427	0.00006	0.00	0.400	200	3.74	0.34	**1.25**	0.11
AS-NO_2^-	2 μM $^{15}NH_4^+$	6	3	0.00502	0.00020	0.00	0.400	200	8.32	1.21	**1.39**	0.20
C-NO_2^-	0.5 μM $^{15}NH_4^+$	3	3	0.00425	0.00024	0.00	0.400	200	4.93	2.03	**1.64**	0.68
C-NO_2^-	0.5 μM $^{15}NH_4^+$	6	3	0.00434	0.00184	0.00	0.400	200	4.24	3.39	**0.71**	0.56
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	3	3	0.00434	0.00023	0.00	0.400	200	7.22	2.47	**2.41**	0.82
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	6	3	0.00523	0.00058	0.00	0.400	200	7.86	4.68	**1.31**	0.78

Table V-1 (cont.)

EXPERIMENTAL TRIAL N.3 : September 1991

Nitrite accumulation by using 0.5 μM $^{15}NH_4^+$ (99 % atom).

Sediment used from IS5 site and mid-shelf water from SW8.

C + control (natural seawater); FS = seawater with suspended sediment (freshly collected); AS = seawater with suspended sediment (frozen-thawed).

NO_2^- = ^{15}N enrichment was measured in the form of nitrite.

* Atom % enrichment (dilution factor) was calculated from the ^{15}N addition.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation SD	Average [$^{14}NO_2^-$ + $^{15}NO_2^-$] μM	N carrier μmol	Extracted seawater volume ml	Average [NO_2^-] yield nM	SD	Nitrite accumulation rate at each time interval (nM h^{-1})	SD
C-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.00414	0.00019	0.018	0.15	400	0.88	0.35	**0.29**	0.12
C-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.00398	0.00020	0.031	0.15	400	0.61	0.39	**0.10**	0.06
FS-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.00583	0.00060	0.102	0.15	400	5.25	1.48	**1.75**	0.49
FS-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.00605	0.00007	0.096	0.15	400	5.72	0.08	**0.95**	0.01
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.00582	0.00141	0.035	0.15	400	4.37	2.83	**1.46**	0.94
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.00464	0.00033	0.038	0.15	400	2.00	0.70	**0.33**	0.12

Table V-1 (cont.)

EXPERIMENTAL TRIAL N.4 : November 1991

Nitrite accumulation by using 0.5 μM $^{15}NH_4^+$ (99 % atom).

Sediment used from IS6 site and mid-shelf water from SW9.

C = control seawater; FS = seawater with suspended sediment (freshly collected); AS = seawater with suspended sediment (frozen-thawed).

NO_2^- = ^{15}N enrichment was measured in the form of nitrite.

* Atom % enrichment (dilution factor) of the medium was measured directly.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average [$^{14}NO_2^-$ + $^{15}NO_2^-$] μM	N carrier μmol	Extracted seawater volume ml	Average [NO_2^-] yield nM	SD	**Nitrite accumulation rate at each time Interval (nM h^{-1})**	SD
C-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.00457	0.00057	0.00	0.20	800	1.18	0.74	**0.39**	0.25
C-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.00483	0.00004	0.00	0.20	800	3.13	0.10	**0.52**	0.02
FS-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.01045	0.00020	0.00	0.20	800	11.27	0.33	**3.76**	0.11
FS-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.01573	0.00527	0.00	0.20	800	32.65	14.28	**5.44**	2.38
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	3	2	0.00460	0.00008	0.00	0.20	800	1.21	0.11	**0.40**	0.04
AS-NO_2^-	0.5 μM $^{15}NH_4^+$	6	2	0.00548	0.00050	0.00	0.20	800	5.65	1.57	**0.94**	0.26

Table V-2

EXPERIMENTAL TRIAL N.1 : November 1990

Nitrite oxidation by using 5 µM $^{15}NH_4^+$ (99 % atom).

Frozen-thawed sediment from IS3 site and mid-shelf water from SW6.

C = control seawater; AS = seawater with suspended sediment (frozen-thawed).

* Atom % enrichment (dilution factor) of the medium was measured directly.

Water Sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average [$^{14}NO_2^-$ + $^{15}NO_2^-$] µM	N carrier µmol	Extracted seawater volume (ml)	Average [NO_3^- + NO_2^-] yield nM	SD	Average [NO_2^-] yield nM	SD	Avergae [NO_3^-] yield nM	SD	**Nitrite oxidation rate at each time interval (nM h^{-1})**	SD
C-NO_3^-	5 µM $^{15}NH_4^+$	0	4	0.00519	0.00108	0.01	0.538	200	6.17	1.00	6.72	0.69	-0.54	0.62		
C-NO_3^-	5 µM $^{15}NH_4^+$	4	4	0.00411	0.00036	0.01	0.538	200	6.95	1.51	9.90	5.53	-2.95	2.45	**-0.74**	0.61
C-NO_3^-	5 µM $^{15}NH_4^+$	6	4	0.00514	0.00063	0.01	0.538	200	23.33	9.91	19.25	8.63	4.08	4.23	**0.68**	0.71
AS-NO_3^-	5 µM $^{15}NH_4^+$	0	4	0.00442	0.00084	0.01	0.538	200	10.56	1.71	5.12	2.78	5.43	2.11		
AS-NO_3^-	5 µM $^{15}NH_4^+$	4	4	0.00497	0.00039	0.01	0.538	200	18.76	5.55	10.31	4.21	8.44	4.52	**2.11**	1.13
AS-NO_3^-	5 µM $^{15}NH_4^+$	6	4	0.00552	0.00018	0.01	0.538	200	26.46	2.55	19.99	6.49	6.47	3.25	**1.08**	0.54

Table V-2 (cont.)

EXPERIMENTAL TRIAL N.2 : July 1991

Nitrite oxidation by using 0.5 and 2 μM $^{15}NH_4^+$ (99 % atom).

Frozen-thawed sediment from IS3 site and mid-shelf water from SW7.

C = control seawater; AS = seawater with suspended sediment (frozen-thawed).

* Atom % enrichment (dilution factor) was calculated from ^{15}N addition.

Water Sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average [$^{14}NO_2^-$ + $^{15}NO_2^-$] μM	N carrier μmol	Extracted seawater volume ml	Average [NO_3^- + NO_2^-] yield nM	SD	Average [NO_2^-] yield nM	SD	Average [NO_3^-] yield nM	SD	Nitrite oxidation rate at each time interval (nM/h)	SD
C-NO_3^-	2 μM $^{15}NH_4^+$	3	3	0.00434	0.00047	0.01	0.400	200	4.08	2.71	3.23	2.53	0.85	0.44	**0.28**	0.15
C-NO_3^-	2 μM $^{15}NH_4^+$	6	3	0.00421	0.00033	0.01	0.400	200	5.97	2.50	4.93	4.08	1.04	0.43	**0.17**	0.07
AS-NO_3^-	2 μM $^{15}NH_4^+$	3	3	0.00443	0.00025	0.00	0.400	200	5.15	1.73	3.74	0.34	1.41	0.91	**0.47**	0.30
AS-NO_3^-	2 μM $^{15}NH_4^+$	6	1	0.00422	-	0.00	0.400	200	9.66	-	8.32	1.21	1.34	-	**0.22**	-
C-NO_3^-	0.5 μM $^{15}NH_4^+$	3	3	0.00458	0.00024	0.00	0.400	200	8.43	1.88	4.93	2.03	3.50	1.81	**1.17**	0.60
C-NO_3^-	0.5 μM $^{15}NH_4^+$	6	3	0.00454	0.00190	0.00	0.400	200	8.49	2.00	4.24	3.39	4.25	2.72	**0.71**	0.45
AS-NO_3^-	0.5 μM $^{15}NH_4^+$	3	3	0.00454	0.00020	0.00	0.400	200	11.08	2.61	7.22	2.47	3.85	1.58	**1.28**	0.53
AS-NO_3^-	0.5 μM $^{15}NH_4^+$	6	2	0.00394	0.00047	0.00	0.400	200	10.66	2.36	7.86	4.68	2.80	1.44	**0.47**	0.24

Table V-2 (cont.)

EXPERIMENTAL TRIAL N.3 : September 1991

Nitrite oxidation by using 0.5 µM $^{15}NH_4^+$ (99 % atom).

Sediment used from IS5 site and mid-shelf water from SW8.

C + control (natural seawater); FS = seawater with suspended sediment (freshly collected); AS = seawater with suspended sediment (frozen-thawed).

NO_{32}^- = NO_3^- + NO_2^- = ^{15}N enrichment was measured in the form of nitrite and nitrate.

* Atom % enrichment (dilution factor) was calculated from the ^{15}N addition.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average [$^{14}NO_{32}^-$ + $^{15}NO_{32}^-$] µM	N carrier µmol	Extracted seawater volume ml	Average [NO_{32}^-] yield nM	SD	Average [NO_2^-] yield nM	Average [NO_3^-] yield nM	SD	**Nitrite oxidation rate at each time interval (nM h^{-1})**	SD
C-NO_2^-	0.5 µM $^{15}NH_4^+$	3	2	0.00450	0.00041	0.061	0.15	400	1.76	0.36	0.88	0.88	0.35	**0.29**	0.12
C-NO_2^-	0.5 µM $^{15}NH_4^+$	6	2	0.00468	0.00016	0.016	0.20	400	2.52	2.17	0.61	1.92	1.26	**0.32**	0.21
FS-NO_2^-	0.5 µM $^{15}NH_4^+$	3	2	0.00596	0.00021	0.104	0.15	400	5.63	0.26	5.25	0.38	0.20	**0.13**	0.07
FS-NO_2^-	0.5 µM $^{15}NH_4^+$	6	2	0.00611	0.00007	0.092	0.20	400	7.40	2.42	5.72	1.68	1.56	**0.28**	0.26
AS-NO_2^-	0.5 µM $^{15}NH_4^+$	3	2	0.00559	0.00021	0.093	0.15	400	4.50	0.16	0.44	4.06	0.09	**1.35**	0.03
AS-NO_2^-	0.5 µM $^{15}NH_4^+$	6	2	0.00633	0.00288	0.037	0.20	400	7.14	2.52	2.00	5.14	1.60	**0.86**	0.27

Table V-2 (cont.)

EXPERIMENTAL TRIAL N.4 : November 1991

Nitrite oxidation by using 0.5 μM $^{15}NH_4^+$ (99 % atom).
Sediment used from IS6 site and mid-shelf water from SW9.
C = control seawater; FS = seawater with suspended sediment (freshly collected); AS = seawater with suspended sediment (frozen-thawed).
NO_3^- = ^{15}N enrichment was measured in the form of nitrite.
* Atom % enrichment (dilution factor) was calculated from the ^{15}N addition.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % abundance	Standard deviation	Average [$^{14}NO_3^-$ + $^{15}NO_3^-$] μM	N carrier μmol	Extracted seawater volume ml	Average [NO_3^-] yield nM	SD	Nitrite oxidation rate at each time interval (nM/h)	SD
C-NO_3^-	0.5 μM $^{15}NH_4^+$	3	2	0.00434	0.00023	0.000	0.20	800	0.87	0.30	**0.29**	0.10
C-NO_3^-	0.5 μM $^{15}NH_4^+$	6	2	0.00470	0.00000	0.000	0.20	800	2.79	0.00	**0.46**	0.00
FS-NO_3^-	0.5 μM $^{15}NH_4^+$	3	2	0.00473	0.00004	0.000	0.20	800	1.75	0.06	**0.58**	0.02
FS-NO_3^-	0.5 μM $^{15}NH_4^+$	6	2	0.00491	0.00006	0.000	0.20	800	3.40	0.18	**0.57**	0.03
AS-NO_3^-	0.5 μM $^{15}NH_4^+$	3	2	0.00479	0.00012	0.014	0.20	800	1.53	0.16	**0.51**	0.05
AS-NO_3^-	0.5 μM $^{15}NH_4^+$	6	2	0.00617	0.00225	0.036	0.20	800	8.79	7.72	**1.46**	1.29
C-NO_3^-	0.5 μM $^{15}NO_2^-$	3	2	0.00742	0.00043	0.048	0.20	800	2.27	0.22	**0.76**	0.07
C-NO_3^-	0.5 μM $^{15}NO_2^-$	6	2	0.00905	0.00007	0.030	0.20	800	3.06	0.04	**0.51**	0.01
FS-NO_3^-	0.5 μM $^{15}NO_2^-$	3	2	0.02887	0.00050	0.030	0.20	800	14.58	0.11	**4.86**	0.04
FS-NO3	0.5 μM $^{15}NO_2^-$	6	2	0.02871	0.00292	0.035	0.20	800	14.47	0.29	**2.41**	0.05
AS-NO_3^-	0.5 μM $^{15}NO_2^-$	3	2	0.01789	0.00307	0.014	0.20	800	7.64	1.65	**2.55**	0.55
AS-NO3	0.5 μM $^{15}NO_2^-$	6	2	0.01255	0.00027	0.024	0.20	800	4.95	0.15	**0.83**	0.02

Table V-3

Calculated starting ("Time 0") atom % enrichment (or isotope dilution, R) by the equation of Dugdale and Goering (1967) and measured following Glibert *et al.* (1982).

Trial	* Calculated atom % enrichment									** Measured atom % enrichment								
	$^{15}NH_4^+$			$^{15}NO_2^-$			$^{15}NO_3^-$			$^{15}NH_4^+$			$^{15}NO_2^-$			$^{15}NO_3^-$		
	C	AS	FS	C	AS	FS	C	AS	FS	C	AS	FS	C	AS	FS	C	AS	FS
N.1																		
Initial	.847	.861	-	.99	.99	-	.63	.67	-									
Time 0	-	-	-	-	-	-	-	-	-	.547	.627	-	.901	.526	-	.306	.452	-
Time 4	-	-	-	-	-	-	-	-	-	.616	.679	-	.752	.567	-	.288	.476	-
Time 6	-	-	-	-	-	-	-	-	-	.674	.702	-	.901	.632	-	.407	.479	
N.2 (2 µM)																		
Initial	.752	.661	-	.99	.99	-	-	-	-	-	-	-	-	-	-	-	-	-
N.2 (0.5 µM)																		
Initial	.479	.378	-	.99	.99	-	-	-	-	-	-	-	-	-	-	-	-	-
N.3																		
Initial	.420	.404	.395	.99	.90	.91	-	-	-	-	-	-	-	-	-	-	-	-
N.4																		
Initial	.386	.308	.303	.99	.99	.99	.569	.623	.635	-	-	-	-	-	-	-	-	-
Time 0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Time 3	-	-	-	-	-	-	-	-	-	.186	.161	.180	-	-	-	-	-	-
Time 6	-	-	-	-	-	-	-	-	-	.162	.155	.165	-	-	-	-	-	-

* To use "R" from Dugdale and Goering (1967), the "R" was calculated from initial enrichment of isotope added in the medium (Equation 6 in text).
** The "R" was obtained by measuring atom % enrichment in the medium at each time point.
To use this "R" to calculate transformation rate, "R" at time point t+1 was used to calculate the rate at time t. This modified the equation from Glibert *et al.* (1982).
C = the control, AS = seawater with frozen-thawed sediment added and FS = seawater with freshly collected sediment added.

Table V-4

EXPERIMENTAL TRIAL N.1 : November 1990

Uptake of ammonium, nitrite and nitrate by using 5 µM $^{15}NH_4^+$ (99 % atom), $^{15}NO_2^-$ (99 % atom) and $^{15}NO_3^-$ (95 % atom).
Frozen-thawed sediment from IS3 site and mid-shelf water from SW6: AS = seawater with suspended sediment (frozen-thawed), C = control seawater.
PN = ^{15}N enrichment was measured in the form of particulate nitrogen.
* Atom % enrichment (dilution factor) of the medium was measured directly.

Water sample	Isotope addition	incubation time interval (h)	No. of replicates	Average atom % excess	Standard Deviation (1SD)	Averge [$^{15}N + ^{14}N$ PN] µM	Average [PN] yield nM	SD	Uptake rate at each time interval nM/h	SD
C-PN	5 µM $^{15}NH_4^+$	0	4	0.01482	0.00307	1.74	2.03	0.42		
C-PN	5 µM $^{15}NH_4^+$	4	4	0.07341	0.00787	1.77	10.23	1.10	**2.56**	0.27
C-PN	5 µM $^{15}NH_4^+$	6	4	0.11454	0.00378	1.78	24.41	0.81	**4.07**	0.13
AS-PN	5 µM $^{15}NH_4^+$	0	4	0.00478	0.00083	5.18	2.63	0.46		
AS-PN	5 µM $^{15}NH_4^+$	4	4	0.03162	0.00320	5.10	17.13	1.73	**4.28**	0.43
AS-PN	5 µM $^{15}NH_4^+$	6	4	0.06137	0.00635	5.16	34.06	3.53	**5.68**	0.59
C-PN	5 µM $^{15}NO_2^-$	0	4	0.00350	0.00124	2.28	0.52	0.19		
C-PN	5 µM $^{15}NO_2^-$	4	4	0.00570	0.00198	1.66	0.64	0.22	**0.16**	0.06
C-PN	5 µM $^{15}NO_2^-$	6	4	0.00609	0.00088	1.52	0.62	0.09	**0.10**	0.02
AS-PN	5 µM $^{15}NO_2^-$	0	3	0.00162	0.00059	4.82	0.52	0.19		
AS-PN	5 µM $^{15}NO_2^-$	4	3	0.00297	0.00028	7.06	1.41	0.13	**0.35**	0.03
AS-PN	5 µM $^{15}NO_2^-$	6	3	0.00382	0.00068	6.82	1.76	0.31	**0.29**	0.05
C-PN	5 µM $^{15}NO_3^-$	0	3	0.00271	0.00043	1.63	0.63	0.10		
C-PN	5 µM $^{15}NO_3^-$	4	3	0.00525	0.00086	2.10	1.60	0.26	**0.40**	0.07
C-PN	5 µM $^{15}NO_3^-$	6	3	0.00488	0.00051	2.09	1.49	0.15	**0.25**	0.03
AS-PN	5 µM $^{15}NO_3^-$	0	3	0.00294	0.00024	6.87	2.99	0.11		
AS-PN	5 µM $^{15}NO_3^-$	4	2	0.00346	0.00054	8.36	4.27	0.67	**1.07**	0.17
AS-PN	5 µM $^{15}NO_3^-$	6	3	0.00341	0.00047	9.07	4.34	0.60	**0.72**	0.10

Table V-4 (cont.)

EXPERIMENTAL TRIAL N.2 : July 1991

Uptake of ammonium, nitrite and nitrate by using 0.5 and 2 μM $^{15}NH_4^+$ (99 % atom) and $^{15}NO_2^-$ (99 % atom).
Frozen-thawed sediment from IS3 site and mid-shelf water from SW7: AS = seawater with suspended sediment (frozen-thawed), C = control seawater.
PN = ^{15}N enrichment was measured in the form of particulate nitrogen.
* Atom % enrichment (dilution factor) was calcualted from ^{15}N addition.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % excess	Standard deviation	Average [^{15}N + ^{14}N PN], μM	Average [PN] yield, nM	SD	Uptake rate at each time interval, nM/h	SD
C-PN	0.5 μM $^{15}NH_4^+$	0	2	0.00397	0.00011	1.52	12.57	1.60		
C-PN	0.5 μM $^{15}NH_4^+$	3	2	0.01250	0.00020	1.10	28.59	0.23	**9.53**	0.08
C-PN	0.5 μM $^{15}NH_4^+$	6	2	0.02353	0.00009	1.18	57.67	9.12	**9.61**	1.52
AS-PN	0.5 μM $^{15}NH_4^+$	0	2	0.00256	0.00009	7.27	49.26	14.70		
AS-PN	0.5 μM $^{15}NH_4^+$	3	2	0.00362	0.00016	7.61	72.90	9.81	**24.30**	3.27
AS-PN	0.5 μM $^{15}NH_4^+$	6	2	0.00476	0.00020	7.90	99.68	9.48	**16.61**	1.58
C-PN	0.5 μM $^{15}NH_4^+$	0	2	0.00154	0.00023	1.22	1.90	0.30		
C-PN	0.5 μM $^{15}NO_2^-$	3	2	0.00227	0.00019	1.50	3.44	0.65	**1.15**	0.22
C-PN	0.5 μM $^{15}NO_2^-$	6	2	0.00226	0.00013	1.58	3.61	0.88	**0.60**	0.15
AS-PN	0.5 μM $^{15}NO_2^-$	0	2	0.00285	0.00036	8.43	24.32	3.91		
AS-PN	0.5 μM $^{15}NO_2^-$	3	2	0.00317	0.00001	7.62	24.37	0.11	**8.12**	0.04
AS-PN	0.5 μM $^{15}NO_2^-$	6	2	0.00299	0.00035	10.87	32.84	2.95	**5.47**	0.49
C-PN	2 μM $^{15}NH_4^+$	0	2	0.00522	0.00011	1.67	11.60	0.77		
C-PN	2 μM $^{15}NH_4^+$	3	2	0.01480	0.00023	1.22	24.08	0.23	**8.03**	0.08
C-PN	2 μM $^{15}NH_4^+$	6	2	0.03276	0.00020	0.99	43.31	11.72	**7.22**	1.95
AS-PN	2 μM $^{15}NH_4^+$	0	2	0.00280	0.00017	7.88	33.44	19.90		
AS-PN	2 μM $^{15}NH_4^+$	3	2	0.00584	0.00028	11.38	100.68	20.55	**33.56**	6.85
AS-PN	2 μM $^{15}NH_4^+$	6	2	0.00602	0.00006	10.76	98.06	13.13	**16.34**	2.19
C-PN	2 μM $^{15}NO_2^-$	0	2	0.00220	0.00026	1.52	3.37	0.46		
C-PN	2 μM $^{15}NO_2^-$	3	2	0.00334	0.00003	1.18	3.99	0.52	**1.33**	0.17
C-PN	2 μM $^{15}NO_2^-$	6	2	0.00289	0.00015	0.90	2.63	0.38	**0.44**	0.06
AS-PN	2 μM $^{15}NO_2^-$	0	2	0.00266	0.00030	9.14	24.58	1.92		
AS-PN	2 μM 15NO2	3	2	0.00244	0.00087	11.99	29.53	4.15	**9.84**	1.38
AS-PN	2 μM 15NO2	6	2	0.00187	0.00037	10.82	20.44	5.67	**3.41**	0.95

Table V-4 (cont.)

EXPERIMENTAL TRIAL N.3 : September 1991

Uptake of ammonium and nitrite by using 0.5 µM $^{15}NH_4^+$ (99 % atom) and $^{15}NO_2^-$ (99 % atom).
Sediment used from IS5 site and mid-shelf water from SW8.
C = control seawater; AS = seawater with suspended sediment (frozen-thawed); FS = seawater with suspended sediment (freshly collected).
PN = ^{15}N enrichment was measured in the form of particulate nitrogen.
* Atom % enrichment (dilution factor) was calculated from the ^{15}N addition.

Water sample	Isotope addition	Incubation time interval (h)	No. of replicates	Average atom % excess	Standard deviation	Average [^{15}N-PN + ^{14}N-PN] µM	Average [PN] yield nM	SD	Uptake rate at each time interval nM/h	SD
C-PN	0.5 µM $^{15}NH_4^+$	0	2	0.00318	0.00021	1.21	0.92	1.35		
C-PN	0.5 µM $^{15}NH_4^+$	3	2	0.00919	0.00042	0.75	16.44	2.00	5.48	0.67
C-PN	0.5 µM $^{15}NH_4^+$	6	2	0.01390	0.00017	0.95	31.46	2.25	5.24	0.37
FS-PN	0.5 µM $^{15}NH_4^+$	0	2	0.00355	0.00022	12.74	114.40	7.17		
FS-PN	0.5 µM $^{15}NH_4^+$	3	2	0.00616	0.00314	15.23	229.09	88.34	76.36	29.45
FS-PN	0.5 µM $^{15}NH_4^+$	6	2	0.00545	0.00048	17.71	249.32	138.03	41.55	23.00
AS-PN	0.5 µM $^{15}NH_4^+$	0	2	0.00219	0.00070	13.66	72.42	14.90		
AS-PN	0.5 µM $^{15}NH_4^+$	3	2	0.00344	0.00111	15.57	132.37	3.38	44.12	1.13
AS-PN	0.5 µM $^{15}NH_4^+$	6	2	0.00367	0.00126	15.30	138.57	46.45	23.10	7.74
AS-PN	0.5 µM $^{15}NO_2^-$	0	2	0.00231	0.00008	9.56	2.56	0.52		
AS-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00215	0.00007	10.23	24.07	0.08	8.02	0.03
AS-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00212	0.00038	14.73	33.83	2.02	5.64	0.34

Table V-4 (cont.)

EXPERIMENTAL TRIAL N.4 : November 1991

Uptake of ammonium, nitrite and nitrate by using 0.5 µM $^{15}NH_4^+$ (99 % atom), $^{15}NO_2^-$ (99 % atom) and $^{15}NO_3^-$ (95 % atom).
Sediment used from IS6 site and mid-shelf water from SW9.
C = control seawater; AS = seawater with suspended sediment (frozen-thawed), FS = seawater with suspended sediment (freshly collected).
PN = ^{15}N enrichment was measured in the form of particulate nitrogen.
* Atom % enrichment (dilution factor) of the medium was measured directly for $^{15}NH_4^+$, but calculated from $^{15}NO_2^-$ and $^{15}NO_3^-$ additions.

Water sample	Isotope addition	Incubation time interval, h	No. of replicates	Average atom % excess	Standard deviation	Average [^{15}N-PN+^{14}N -PN], µM	Average [PN] yield, nM	SD	Uptake rate at each time interval, nM/h	SD
C-PN	0.5 µM $^{15}NH_4^+$	3	2	0.01668	0.00344	1.59	66.84	2.68	**22.28**	0.89
C-PN	0.5 µM $^{15}NH_4^+$	6	2	0.03546	0.00922	1.25	234.46	32.33	**39.08**	5.39
FS-PN	0.5 µM $^{15}NH_4^+$	3	2	0.00403	0.00027	8.57	113.05	14.92	**37.68**	4.97
FS-PN	0.5 µM $^{15}NH_4^+$	6	2	0.00861	0.00018	10.49	493.43	20.12	**82.24**	3.35
AS-PN	0.5 µM $^{15}NH_4^+$	3	2	0.00365	0.00002	11.25	105.74	4.77	**35.25**	1.59
AS-PN	0.5 µM $^{15}NH_4^+$	6	2	0.54006	0.00052	10.77	359.90	2.47	**59.98**	0.41
C-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00121	0.00031	1.44	1.76	0.41	**0.59**	0.14
C-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00184	0.00022	1.27	2.36	0.44	**0.39**	0.07
FS-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00101	0.00013	8.88	9.09	1.94	**3.03**	0.65
FS-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00144	0.00069	11.66	16.77	7.08	**2.79**	1.18
AS-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00161	0.00004	12.00	19.47	0.62	**6.49**	0.21
AS-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00204	0.00016	11.01	22.61	0.83	**3.77**	0.14
C-PN	0.5 µM $^{15}NO_3^-$	3	2	0.00116	0.00002	1.60	3.10	0.50	**1.03**	0.17
C-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00210	0.00046	1.37	4.77	0.93	**0.79**	0.31
FS-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00208	0.00057	14.90	50.48	11.40	**16.83**	3.80
FS-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00204	0.00001	17.42	58.25	5.65	**9.71**	0.94
AS-PN	0.5 µM $^{15}NO_2^-$	3	2	0.00170	0.00000	17.36	49.59	3.47	**16.53**	1.16
AS-PN	0.5 µM $^{15}NO_2^-$	6	2	0.00206	0.00004	15.08	52.31	0.64	**8.72**	0.11

APPENDIX VI

Table VI-1

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing Inhibitor-sensitive dark C-bicarbonate uptake (ISDCBU) rates measured between treatment (in control seawater {C} and seawater with abiotic sediment added {AS}, and between inhibitors (N-serve, ATU). "Sig." means significant at $P < 0.05$, "Ns." means not significant at $P > 0.05$, * means interact between factors.

Source	df	Mean Square	F-value	P-value	Result
Treatment	1	7.16	5.51	0.03	Sig.
Inhibitor	1	6.02	4.63	0.04	Sig.
Treatment * inhibitor	1	1.45	1.12	0.31	Ns.
Residual	16	1.30			
Treatment	N	Mean rate	Std. Dev.	Std. Error	Tukey Test at 0.05
Control water	10	0.87	0.40	0.13	
AS	10	2.07	1.73	0.55	AS > C
Inhibitor					
N-serve	10	2.02	1.73	0.55	N-serve > ATU
ATU	10	0.92	0.53	0.17	

Table VI-2

Resuts of a Paired t-test between rates calculated over 0-3 hrs (X) and 0-6 hrs (Y) time periods.

Rates	df	Y-X	Std error	T-Value	P-Value
Ammonium oxidation	10	-0.16	0.47	0.39	0.71
Nitrite oxidation	14	-0.32	0.25	-1.32	0.21
Ammonium uptake	11	0.34	6.01	0.06	0.96
Nitrite uptake	8	-1.53	0.70	-2.17	0.06
Nitrate uptake	4	-3.13	1.77	-1.77	0.15
Over all	52	0.58	1.34	-4.30	0.67

Table VI-3

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing ammonium oxidation rates among trials and treatments (control seawater {C}, seawater with frozen-thawed sediment {AS}, seawater with freshly collected sediment {FS}).

Source	df	Mean Square	F-Value	P-Value	Result
Trial	4	6.69	9.89	0.00	Sig.
Treatment	2	4.43	6.56	0.01	Sig.
Trial * Treatment	5	1.75	2.58	0.08	Ns.
Residual	12	0.68			
Trials	**N**	**Mean**	**Std. Dev.**	**Std. Error**	**Tukey Test at 0.05**
Trial N.1	4	4.02	0.71	0.36	Trial N.1 > trial N.2 =
Trial N.2 (0.5 µM added)	4	1.42	0.32	0.16	trial N.3 = trial N.4
Trial N.2 (2 µM added)	4	2.43	1.03	0.52	
Trial N.3	6	1.11	0.88	0.36	
Trial N.4	6	2.28	1.83	0.75	
Treatment	**N**	**Mean rate**	**Std. Dev.**	**Std. Error**	**Tukey Test at 0.05**
Control water	10	1.62	1.20	0.38	C < AS = FS
AS	10	2.52	1.34	0.42	
FS	4	2.59	2.20	1.10	

Table VI-4

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing nitrite oxidation rates among trials and treatments (control seawater {C}, seawater with frozen-thawed sediment {AS}, seawater with freshly collected sediment {FS}).

Source	df	Mean Square	F-Value	P-Value	Results
Trials	5	1.78	3.74	0.02	Sig.
Treatment	2	2.21	4.65	0.03	Sig.
Trial * Treatment	7	1.27	2.66	0.04	Ns.
Residual	15	0.48			
Treatment	**N**	**Mean rate**	**Std. Dev.**	**Std. Error**	**Tukey Test at 0.05**
Control water	12	0.41	0.46	0.13	C < AS = FS
AS	12	1.10	0.70	0.20	
FS	6	1.47	1.85	0.76	
Trials					
Trial N.1 + 5 µM $^{15}NH_4^+$	4	0.79	1.18	0.59	Trial N.1 = trial N.2 =
Trial N.2 + 2 µM $^{15}NH_4^+$	4	0.29	0.13	0.07	trial N.3 = trial N.4
Trial N.2 + 0.5 µM $^{15}NH_4^+$	4	0.91	0.39	0.19	
Trial N.3 + 0.5 µM $^{15}NH_4^+$	6	0.54	0.47	0.19	
Trial N.4 + 0.5 µM $^{15}NH_4^+$	6	0.65	0.42	0.17	Trial N.4: $^{15}NH_4^+$< $^{15}NO_2^-$
Trial N.4 + 0.5 µM $^{15}NO_2^-$	6	1.99	1.66	0.68	

Table VI-5

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing ammonium uptake rates among trials and treatments (control seawater {C}, seawater with frozen-thawed sediment {AS}, seawater with freshly collected sediment {FS}).

Source	df	Mean Square	F-Value	P-Value	Results
Trials	4	566.25	2.85	0.07	Ns.
Treatment	2	1784.97	8.99	0.00	Sig.
Trial * Treatment	5	118.02	0.59	0.71	Ns.
Residual	12	198.53			
Treatment	N	Mean rate	Std. Dev.	Std. Error	Tukey Test at 0.05
Control	10	11.31	11.18	3.54	C = DS
Seawater with frozen-thawed sediment	10	26.05	16.71	5.28	AS < FS
FS	4	59.46	23.09	11.55	C < FS

Table VI-6

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing nitrite uptake rates among trials and treatments (control seawater {C}, seawater with frozen-thawed sediment {AS}, seawater with freshly collected sediment {FS}).

Source	df	Mean Square	F-Value	P-Value	Results
Trials	3	11.38	3.59	0.06	Ns.
Treatment	2	34.00	10.74	0.00	Sig.
Trial * Treatment	3	7.19	2.27	0.15	Ns.
Residual	6	3.17			
Treatment	N	Mean	Std. Dev.	Std. Error	Tukey Test at 0.05
Control	8	0.60	0.44	0.16	
Seawater with frozen-thawed sediment	8	4.72	3.44	1.22	C < AS, AS = FS, C = FS
Seawater with freshly collected sediment	2	2.91	0.17	0.12	

Table VI-7

Results of a two-way analysis of variance (ANOVA) and Tukey test comparing nitrate oxidation rates among trials and treatments (control seawater {C}, seawater with frozen-thawed sediment {AS}, seawater with freshly collected sediment {FS}).

Source	df	Mean Square	F-Value	P-Value	Results
Trials	1	75.89	6.78	0.04	Sig.
Treatment	2	65.87	5.89	0.04	Sig.
Trial * Treatment	1	62.05	5.55	0.07	Ns.
Residual	5	11.19			
Treatment	N	Mean	Std. Dev.	Std. Error	Tukey Test at 0.05
Control	4	0.62	0.36	0.18	
Seawater with frozen-thawed sediment	4	6.76	7.49	3.74	C = AS, AS = FS, C < FS
FS	2	13.27	5.04	3.56	
Trials					
Trial N.1	4	0.61	0.36	0.18	Trial N.4 > trial N.1
Trial N.4	6	8.94	7.06	2.88	

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