PESTICIDE AND HEAVY METAL CONCENTRATIONS IN GREAT BARRIER REEF SEDIMENT, SEAGRASS AND DUGONGS (*DUGONG DUGON*).

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Doctor of Philosophy in the Botany Department,
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David Haynes

PAPERS ARISING FROM THIS THESIS

Chapter 1.
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Chapter 3.
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ABSTRACT

Dugong populations in the southern Great Barrier Reef Region have undergone a major population decline over the last 10 years. Anthropogenic influences including capture in fishing nets, hunting, loss of seagrass habitat and local water quality degradation caused by coastal and hinterland development all threaten dugong populations. Pesticides including organochlorine compounds have been extensively applied by Queensland's intensive coastal agriculture industry. The persistent nature of many of these types of compounds raises the potential for continued long-term chronic exposure of Great Barrier Reef seagrasses and dugongs. This is important as organochlorines may affect marine mammal reproduction and immune system functioning, and have been implicated in marine mammal population declines elsewhere. Herbicide runoff from agricultural lands has the potential to impact seagrass, the major food consumed by dugongs.

Analysis of sediments and seagrass collected from 15 intertidal and 52 subtidal sites between Torres Strait and Moreton Bay in a region-wide survey of pollutants indicated that concentrations of herbicide (atrazine and diuron) and insecticide (lindane, dieldrin, DDT, and DDE) contamination were typically low. Contaminants were mainly detected in samples collected in subtidal muds along the high rainfall, tropical coast between Townsville and Port Douglas. Of the contaminants detected, diuron and dieldrin occurred at concentrations high enough to present an environmental risk to local biota. Heavy metal concentrations were generally low and are unlikely to present an environmental risk to local biota. Polychlorinated dibenzo-p-dioxins (PCDDs) were also detectable in sediments from 5 Great Barrier Reef sites sampled selectively for dioxins. These results were unexpected, and provide evidence that an unidentified source for higher chlorinated dioxins exists along the Queensland coast.

The impact of diuron at concentrations present along the Queensland coast on photosynthetic activity in three tropical seagrasses was assessed in the laboratorory using a PAM fluorometer. Exposure of Cymodocea serrulata, Halophila ovalis and Zostera capricorni to low (10 and 100 μg L^{-1}) diuron concentrations resulted in a decline in effective quantum yield within 2 hours of exposure to the herbicide.

Effective quantum yield depression was present for extended periods after plants exposed to 10 and 100 µg L^{-1} diuron for 5 days were returned to fresh seawater. These results indicate that exposure to herbicide concentrations present in nearshore Queensland sediments present a potential risk to seagrasses and, as a consequence, an indirect risk to dugongs.

Samples of liver and blubber were salvaged from 31 carcasses of dugong stranded along the Queensland coast between 1996-2000 and analysed for a range of heavy metals and organochlorine compounds (including dioxins) to assess the role of pollutants in local dugong population declines. Concentrations of metals in livers were generally low and within the range typically found in marine mammals, although elevated concentrations of chromium and nickel were detected in liver samples from several animals collected from the southern Queensland coast. Dieldrin, DDT and/or DDE were detected in 72% of blubber samples. Concentrations of organochlorines were low in comparison to concentrations recorded from marine mammal tissues collected elsewhere in the world, and are unlikely to pose a major threat to Great Barrier Reef dugong populations. In contrast, octachlorinated dibenzodioxin was found at concentrations higher than reported for other marine mammals. Accumulation of dioxins in tissues of dugongs is believed to be associated with sediment ingestion during feeding. Dioxins are known teratogens and carcinogens, and the environmental implications of accumulated dioxin concentrations in dugongs are presently unknown.

The most important consequences of coastal pollutant contamination for Great Barrier Reef dugong populations are likely to be through the bioaccumulation of dioxins and indirectly through impacts of the herbicide to their nearshore seagrass food resource. Future research efforts should be directed at further identifying sources, fates and impacts of dioxins and herbicides in the dugong ecosytem. Maintenance of long-term monitoring programs utilising innovative data acquisition techniques should also be regarded as a priority. Collection of these data will enable assessment of change in concentrations of these pollutants over time. However, improved land management practices, which include an immediate minimisation of vegetation clearance and responsible use of pesticides in Queensland, are essential if water quality in the Great Barrier Reef World Heritage Area is to be maintained and its populations of dugongs protected.

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Chapter 1: General introduction

GBRMPA

The dugong (*Dugong dugon)*

CHAPTER ONE: GENERAL INTRODUCTION

1.1. Introduction

Nearshore seagrass beds within Moreton Bay and the Great Barrier Reef Marine Park and World Heritage Area, Queensland, provide important habitat and feeding grounds for a significant proportion of existing world stocks of dugongs (*Dugong dugon*) (Great Barrier Reef Marine Park Authority 1981; Marsh 1992; Preen 1993). Aerial surveys of dugong numbers within the Marine Park have been conducted regularly since November 1984 (Marsh and Saalfeld 1989; Marsh and Saalfeld 1990; Marsh 1992; Marsh *et al.* 1993; Marsh *et al.* 1995). Surveys carried out in Marine Park waters south of Cape Bedford (Central and Capricorn Marine Park Zones) in November 1992 and repeated in November 1994 of have indicated that there has been a dramatic decline in dugong numbers in southern park waters from 1984 to 1994 (Marsh *et al.* 1994; Marsh *et al.* 1995). It is estimated that the population decline is in the order of 50-80% over the survey interval (Marsh *et al.* 1994; Marsh *et al.* 1995). This is of particular concern as the dugong has been endangered or exterminated over much of its worldwide range (Heinsohn *et al.* 1977; Preen and Marsh 1995) and although large populations of dugongs still exist in Australia (Preen 1993), the species is considered to be vulnerable to extinction (IUCN 1996). Reasons for the reported decline in dugong numbers in southern Great Barrier Reef Marine Park waters are unclear, although a number of human influences threaten dugong populations. These include indigenous hunting and accidental capture in gill nets, loss of seagrass habitat and water quality degradation caused by coastal and hinterland development (Anon 1993; Marsh *et al.* 1994; Preen *et al.* 1995; Gribble *et al.* 1998).

1.2. Dugong Biology

The dugong *Dugong dugon* (family Dugonidae, order Sirenia) is the only living herbivorous mammal that spends its entire lifespan in marine waters (Heinsohn 1983; Macdonald 1986; Marsh *et al.* 1999). It is long lived (up to 70 years) and has a low reproductive rate (Marsh *et al.* 1984). The species inhabits warm, shallow tropical and sub-tropical coastal waters of the Indian and Western Pacific Oceans (UNEP 1996),

with its range spanning waters of over 40 countries (Marsh *et al.* 1995). Knowledge of the biology of dugongs has been obtained principally through carcass examination and field observations (Marsh *et al.* 1982; Marsh *et al.* 1984; Marsh and Saalfeld 1989; Marsh and Saalfeld 1990; Preen 1993; Lanyon and Marsh 1995; Preen 1995a; Preen and Marsh 1995) and has recently been reviewed (Marsh *et al.* 1999).

There are large herds (>5000 animals) of dugongs present in Australia, located principally in the northern region of the Great Barrier Reef, Torres Strait, the Gulf of Carpentaria, the northern Northern Territory and Shark Bay, Western Australia (Preen 1998). There is also a large concentration of dugongs in Moreton Bay, Queensland (Preen 1993). Major concentrations of dugongs in the Great Barrier Reef Marine Park and World Heritage Area occur in the vicinity of shallow (< 5 m), inshore seagrass beds, particularly in bays sheltered from south-east trade winds (Marsh 1992; Marsh *et al.* 1993). Recent observations have also associated dugongs with deeper, off-shore seagrass beds (Lee Long *et al.* 1993). The home-range of the dugong is as yet un-defined, and may vary from 30 km^2 in tropical waters to 60 km^2 in sub-tropical waters (Preen 1993), although individuals have been tracked making journeys of between 100 to 400 km (Heinsohn 1983; Preen 1993; Marsh and Corkeron 1997). Dugongs feed almost exclusively on seagrass, and spend much of their time feeding in shallow waters (Heinsohn and Birch 1972). Both seagrass leaves and rhizomes are consumed, and over 90% of seagrass biomass may be removed from an area during feeding (Preen 1995a; 1995b). A total of 8 genera and 14 species of seagrass occur within the dugong's tropical and subtropical Australian range (Lanyon *et al.* 1989). Of these, the genera *Halodule* and *Halophila* have commonly been identified in the stomach contents of dugongs (Marsh *et al.* 1982; Erftemeijer *et al.* 1993). These genera are comparatively high in nitrogen and low in fibre and it has been postulated that these are fed on preferentially by dugongs for this reason (Preen 1995a; Preen 1995b). *Halodule uninervis* and *Halophila spinulosa* are two of the four species (which also include *Cymodocea serrulata* and *Zostera capricorni*) which contribute most of the Queensland seagrass abundance between Hervey Bay and Cape York (Lee Long *et al.* 1993). Dugongs also consume epiphytic diatoms and sessile invertebrates incidentally, or in the case of ascidians in sub-tropical waters, deliberately (Preen 1995a; Preen 1995b).

1.3. Dugong/Seagrass Management

Dugongs are vulnerable to anthropogenic impacts due to their low fecundity and restricted seagrass diet (Marsh and Corkeron 1997), and anecdotal evidence has linked fluctuations in dugong breeding patterns with variable food availability (Marsh 1995). Seagrass meadow decline in Australian waters has been associated with the general hypothesis of reduced plant photosynthesis caused by increased water turbidity, epiphyte growth and silt deposition. This is a consequence of nutrient enhancement, effluent discharges, and increasing suspended solids concentrations (Shepherd *et al.* 1989; Walker and McComb 1992; Abal and Dennison 1996). Seagrass decline in tropical and sub-tropical Australian waters has also been linked to dredging and trawling, as well as to natural phenomena associated with cyclonic activity including lowered salinities, smothering and loss of substrate (Preen *et al.* 1995). Land clearing and concomitantly increased erosion and sediment transport were implicated in massive losses of seagrass from Hervey Bay, Queensland, following cyclonic storms and flooding (Preen *et al.* 1995). This catastrophic seagrass loss was followed by mass migration and presumed mortality of a majority of the bays dugong population (Preen and Marsh 1995). Ongoing seagrass decline has also been reported for Moreton Bay, with sand movement and substratum disturbance or reduced water quality associated with foreshore and hinterland development being suspected causal factors (Hyland *et al.* 1989; Abal and Dennison 1996).

Current management initiatives for dugongs in the Great Barrier Reef World Heritage Area are designed to contribute to the maintenance of dugong populations at current or higher levels throughout their range in the Great Barrier Reef Region (Great Barrier Reef Marine Park Authority 1994). This is to be achieved via establishment of dugong reserves, tighter controls or bans on gill netting and tighter controls on indigenous hunting. Research into dugong biology and factors such as water quality (including this project) which may impact on dugong and dugong habitat is also to be sponsored. It is distressing to realise that these management imperatives were first identified in 1981 (Heinsohn and Marsh 1981), and are only just beginning to be comprehensively acted on (Great Barrier Reef Marine Park Authority 1994; Great Barrier Reef Marine Park Authority 1996; Anon 1997).

1.4. Organochlorine and Metal Pollutants

Agriculture, public health and industrial activities around the world have contributed to the widespread contamination of global ecosystems with organochlorine compounds and heavy metals (Fowler 1990; Tatsukawa *et al.* 1990). Both of these types of pollutants are conservative and are essentially permanent additions to the environment (Clark 1992). They are also often highly toxic to biota (Richardson 1995).

Chlorinated organic compounds (or organochlorines) are organic (carbon based) chemicals which contain bound chlorine. A majority of these compounds are artificial and enter the environment through human activities, although it is now recognised that marine algae and invertebrates, and natural processes such as forest fires also contribute large and variable quantities of organochlorines (and other halogenated organics) to the environment (Leach *et al.* 1985; Enell and Wennberg 1991; Gribble 1994). Chlorinated organic compounds have a wide range of industrial and agricultural applications. They include pesticides such as DDT (dichloro-diphenyl-trichloroethane) and lindane (γ-HCH or gamma-hexachlorocyclohexane) and polychlorinated biphenyls (PCBs) which were, and are still used in a range of industrial applications including dielectrics in electrical transformers. The few studies of the impact of organochlorine compounds carried out on Australian freshwater and marine environments indicate that environmental contamination by organochlorine substances has occurred at relatively low concentrations in Australia, and that highest concentrations have been associated with centres of urbanisation (Connell 1993; Richardson 1995). This contamination pattern is similar to the findings of studies elsewhere which have identified chlorinated organic compounds in estuarine and marine sediments near major metropolitan areas along the eastern coast of the United States (NRC 1989), and at a wide range of locations in Europe and Asia associated with human settlement (Mohapatra *et al.* 1995; Alvarez Piñeiro *et al.* 1995; Agnihotri *et al.* 1996; Thompson *et al.* 1996).

In contrast, heavy metals are natural constituents of rocks and soils and enter the environment as a consequence of weathering and erosion (Förstner 1989). Many metals are biologically essential, but all have the potential to be toxic to biota above certain threshold concentrations. Following industrialisation, *unnatural* quantities of metals such as arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni)

and zinc (Zn) have been released, and continue to be released into the aquatic environment through stormwater and wastewater discharges. As, Cd, Cu, Hg and Zn are the five metals with most potential impact that are added to the environment in elevated concentrations as a consequence of agricultural activity. Zn and Cu are used in small amounts as fertilisers in some soils deficient in these elements, and As, Cd and Hg are constituents of some fungicides (Hunter 1992). Cu is also used as an algicide and Cd and Zn occur as contaminants of phosphatic fertilisers (Rayment *et al.* 1989). As a consequence, potential impacts from heavy metals are generally restricted to locations adjacent to major cities or industrialised areas on the coastal fringe (Batley 1995), and to sites draining areas of intensive agriculture. Results of Australian studies of marine environmental metal contamination indicate that surficial sediments adjacent to most urbanised and industrialised estuaries are contaminated with metals, particularly Pb and Zn (Connell 1993; Batley 1995).

1.5. Pollutant Movement and Impact

Organochlorine pesticides enter the environment via a number of routes following their release or application (Figure 1.1). They may enter the atmosphere directly during spraying, and later following volatilisation of deposited spray from both foliage and surface soil (Nash and Hill 1990). Volatilisation rates are related to the vapour pressure of the compound as well as to other environmental factors such as temperature and soil moisture content (Nash and Hill 1990). Pesticides may also enter the atmosphere adsorbed to wind-blown dust particles (Clark 1992). Airborne pesticides are ultimately re-deposited to land or water. Applied and deposited pesticides are transported from application and depositional sites to the aquatic environment in overland flows and ground leachate following rainfalls (Clendening *et al.* 1990). Organochlorine compounds can also enter the environment as contaminants contained in effluent discharges and in urban stormwater runoff. Organochlorine compounds are highly hydrophobic and once in the water column, tend to adsorb to fine particulates or are bioaccumulated into lipids in aquatic biota (Olsen *et al.* 1982). The final distribution of organochlorine compounds between different phases in the aquatic environment is complex, and is dependent on partitioning co-efficients that are defined by the properties of the organochlorine compound (Connell 1995).

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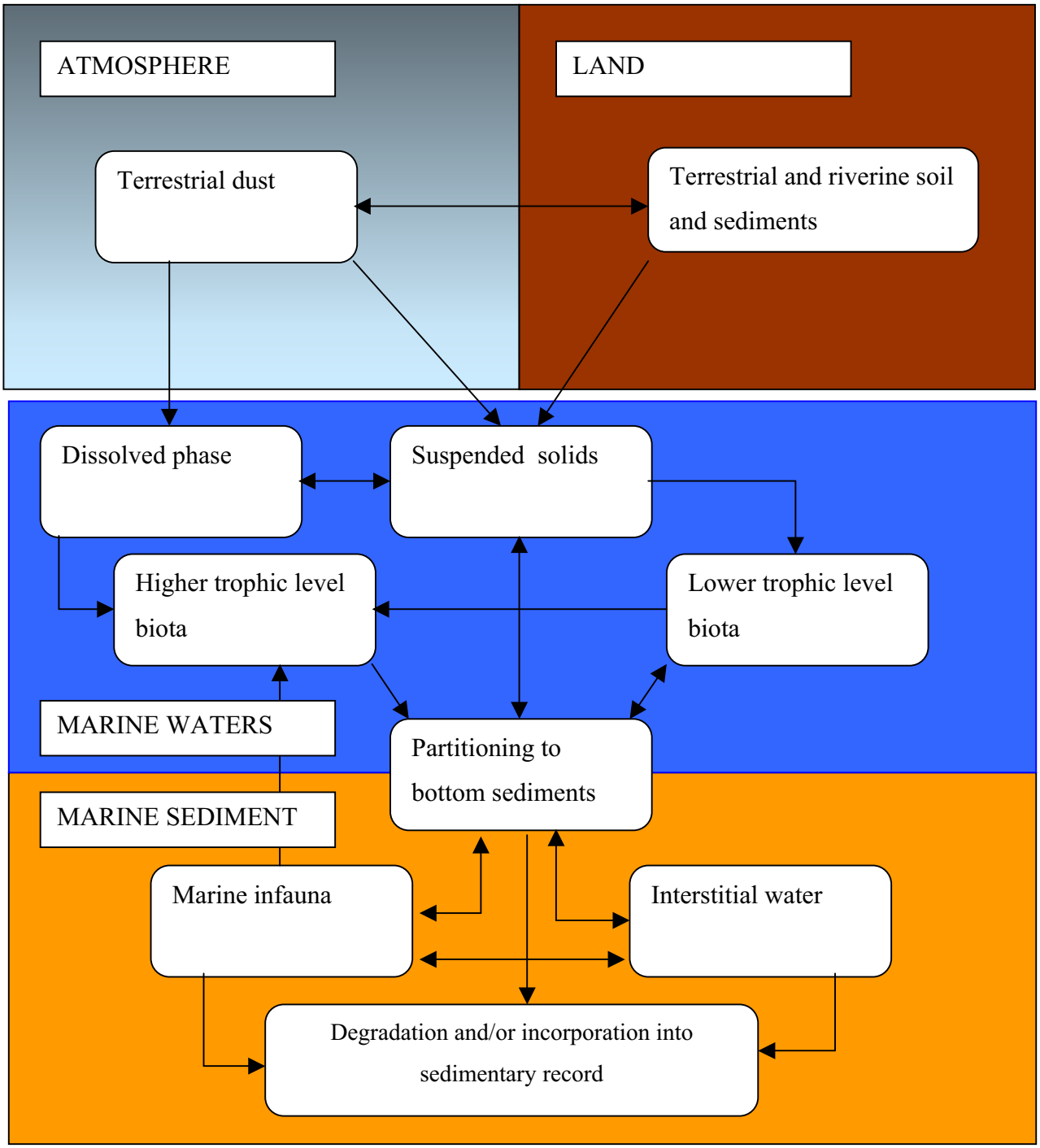

Figure 1.1. Conceptual model of pollutant movement and partitioning in the marine environment.

The consequences of organochlorine tissue accumulation are also complex (Clark 1992), and organochlorine pesticides and polychlorinated biphenyls (PCBs) have been implicated in reproductive and immunological abnormalities in terrestrial bird populations and in marine mammal populations (Kubiak *et al.* 1989; Boon *et al.* 1992; Kuiken *et al.* 1994; Johnston *et al.* 1996).

Metals are also strongly associated with particulates and enter the marine environment in a similar fashion to organochlorine compounds. The major routes of environmental entry include atmospheric transport of dust and sediment movement in overland flows and in waterways (Bryan 1971). Additional quantities of metals are also added to the environment via the discharge of effluent and urban stormwater. Particulate metals in suspension and in bottom sediments are not generally directly available to aquatic organisms. (The exception to this are sediment bound metals which can be accumulated following solubilisation in the acidic juices of a sediment-feeders gut (Waldichuk 1985)). The rates at which metals are solubilised from particulates is dependent on environmental factors including dissolved oxygen concentrations, pH, salinity and temperature (Waldichuk 1985). Once solubilised in the water column, metals may be accumulated by marine invertebrates from solution via passive uptake across permeable surfaces such as gills and the digestive tract (Rainbow 1990). Metals may also be accumulated from food. Cellular metal toxicity is primarily due to the chemical inactivation of cellular enzymes (Förstner 1989), with organism growth, reproduction and behavior all being potentially affected by elevated environmental concentrations of metals (Langston 1990).

Contamination of nearshore environments by pollutants may be an additional stress on seagrass meadows (Walker and McComb 1992) and their potential role in seagrass decline has not been investigated in Queensland waters. Similarly, the impact of concentrations of pollutants in tissues of dugongs have not been investigated in detail in Queensland (Marsh and Corkeron 1997).

1.6. Great Barrier Reef Marine Park Pollutant Concentrations

The Great Barrier Reef is the largest system of coral reefs and associated life forms anywhere in the world (Craik 1992). It extends approximately 2000 km parallel to the Queensland coast between 9^{o} and 24^{o}S latitude and covers approximately 350 000 km^{2} (Figure 1.2). It is a largely unspoiled environment with much of the adjacent coastline relatively unimpacted by coastal development (Lucas *et al*. 1997). Principal coastal population centres and/or port developments are located at Cairns, Mourilyan (near Innisfail), Lucinda (near Ingham), Townsville, Abbot Point (near Bowen), Mackay, Hay Point, Rockhampton, Gladstone and Bundaberg. Little is known about pollutant concentrations in the largely remote Great Barrier Reef Region. Published data are summarised below.

1.6.1. Air and Seawater

As is the case for most areas of the world (Phillips and Spies 1988), little information is available on the concentrations of chlorinated hydrocarbons in air and seawater in the Great Barrier Reef region.

Relatively low concentrations of HCHs (hexachlorocyclohexanes) and DDT and its breakdown products were reported in air and water samples collected from the Coral Sea in 1981 (Tanabe *et al.* 1982), particularly compared with concentrations in eastern American waters. Concentrations of γ-HCH exceeded α-HCH, implying local contamination from agricultural lindane application rather than from southern-moving airborne contaminants from Asia. This was in contrast to a later study where α-HCH was detected in relatively high concentrations in Coral Sea seawaters in 1987 (Kurtz and Atlas 1990). Because of the limited sampling undertaken at this time, it was unclear whether the high concentrations detected in 1987 were a short-term increase caused by improper local pesticide disposal or were indicative of long-term regional contamination.

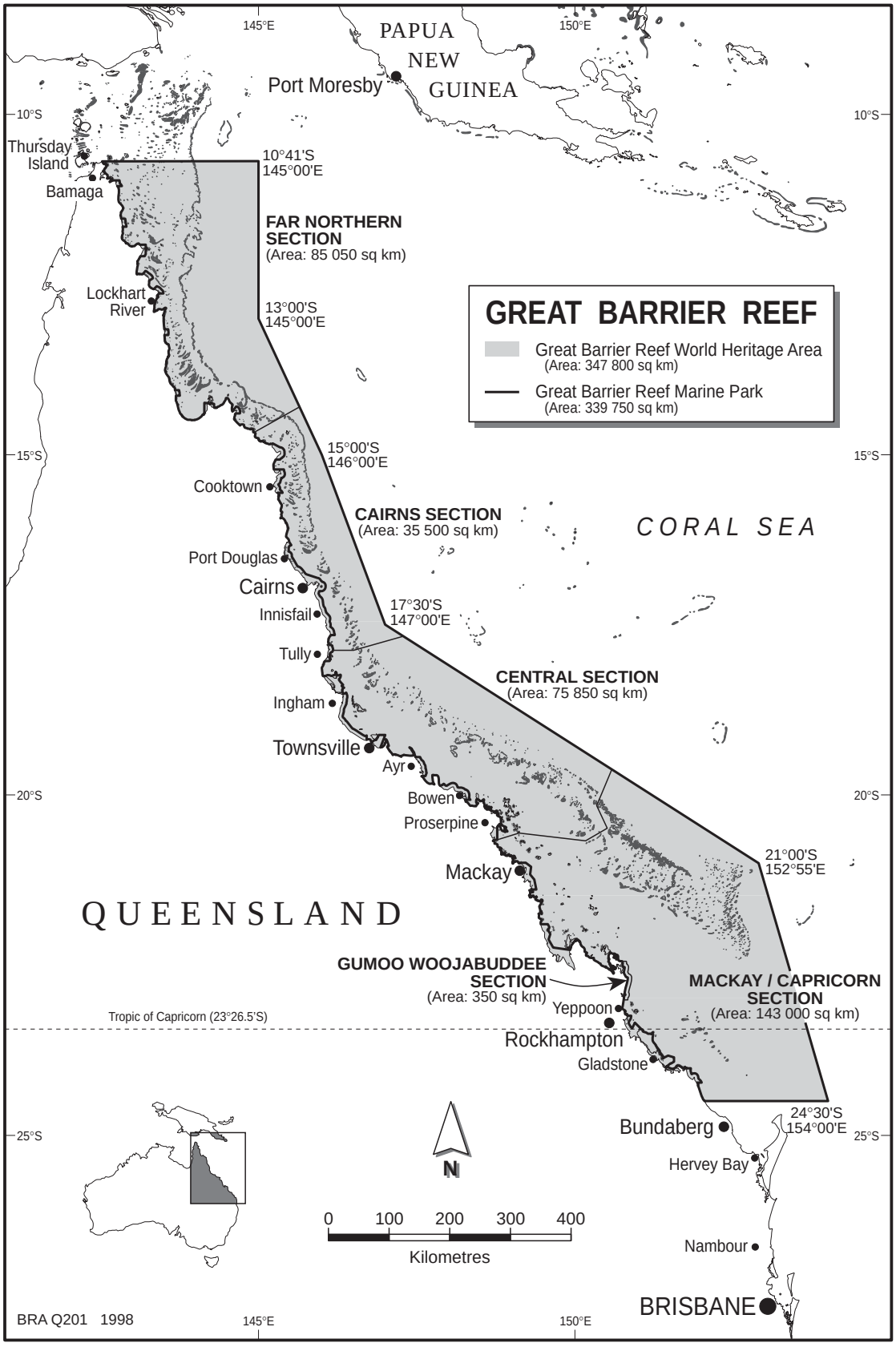

Figure 1.2. The Great Barrier Reef World Heritage Area, Queensland, Australia.

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Concentrations of metals in Great Barrier Reef seawaters are also relatively unstudied. Metal concentrations in seawater samples collected in nearshore waters between 1976-1977 in Cleveland and Bowling Green Bays and between Townsville and Cardwell in 1979 were found to be similar and were within the range of mean world data reported at that time (Burdon-Jones *et al.* 1982; Klumpp and Burdon-Jones 1982). The exception was Zn, which was elevated in seawaters collected near Townsville compared with a control site in Bowling Green Bay. Metal concentrations in seawater around Lizard, Orpheus and Heron Islands in 1982-1983 were also similar to concentrations reported for unpolluted sites (Denton and Burdon-Jones 1986b). Concentrations of Cd, Cu, Ni and Zn varied both temporally and spatially at island collection sites. Concentrations of Cu and Zn were highest at Orpheus Island, and the authors attributed this to the island's relative proximity to urban and industrial activity. Highest Cd concentrations were present at the end of the wet season at all sites.

1.6.2. Coastal Sediments

Organochlorine compounds and heavy metals tend to partition to sediments, and as a consequence, marine sediments are usually regarded as the ultimate sink for persistent pollutants discharged into the environment (Gibbs 1973). A majority of studies carried out to determine pollutant concentrations in Great Barrier Reef sediments have been initiated in response to port and harbour developments or dredging of shipping channels. Low concentrations of several metals have been detected in surficial sediments in Cairns Harbour, Port of Mourilyan, Port of Townsville, Hay Point and the Port of Gladstone (Reichelt and Jones 1993; Gladstone Port Authority 1994; Anon 1996; Cairns Port Authority 1998). Elevated concentrations of copper, which were attributed to past use of copper-based marine anti-foulant paint, have also been found in Cairns Harbour (Brady *et al.* 1994). Elevated concentrations of Ni, Cr, Fe and Zn which were associated with nickel ore loading berths have also been detected in the Port of Townsville (Reichelt and Jones 1993). Nearshore marine sediments collected in the vicinity of the Keppel Island Group have been analysed for metal concentrations using techniques to report both biologically available and total metal concentrations (Ahlers and Szymczak 1993). Marine sediments collected from Torres Strait during 1992 and 1993 have also been analysed for heavy metal concentrations (Gladstone 1996).

This study concluded that metal concentrations in sediments were low and comparable with concentrations found elsewhere in unpolluted tropical marine sediments. Offshore sediments in the vicinity of Raine Island are predominantly comprised of calcium carbonate and contained very low concentrations of heavy metals (Barry and Rayment 1992).

A limited number of Great Barrier Reef sediments have also been analysed for organochlorine contamination. Lindane (γ-HCH) was detected in sediments from the mouth of the Burdekin River in 1984 and 1985 (Dyall and Johns 1985). However, organochlorine pesticides were not detected in sediment samples collected in Bowling Green Bay or at Lizard Island during this survey. The authors concluded that from the limited sampling carried out, sedimentary accumulation of organochlorines was confined to within close proximity of coastal sugarcane growing area. Analysis of marine sediment cores dated circa 1960-1980 collected offshore from the Herbert and Burdekin Rivers failed to detect any organochlorine compounds (Cavanagh *et al.* 1999).

1.6.3. Invertebrates

Bioaccumulation of organochlorines and metals by invertebrates is variable, with some groups such as bivalve molluscs accumulating many pollutants to very high concentrations. Other groups such as crustaceans have the ability to regulate body burdens of certain pollutants (Phillips and Rainbow 1993). Pollutant concentrations present in Great Barrier Reef invertebrates have only been investigated in a limited number of species. Concentrations of p,p'- DDT and dieldrin were determined in gonad tissue from crown of thorns starfish (*Acanthaster planci*) collected from Slasher's Reef and the Bunker Group in 1970 and 1971 (McCloskey and Duebert 1972). Pesticide residue concentrations were low and similar to those in starfish collected from Guam. Low concentrations of γ-HCH, heptachlor and DDT were reported in hard corals (*Fungia* sp. and *Acropora* sp.) and a bivalve mollusc *(Tridacna crocea*) collected from inner shelf reefs between Heron and Lizard Islands in 1976 and 1977 (Olafson 1978).

Metal (Cd, Cu, Pb, Ni, Zn) concentration in various species of soft (octocorallian) and hard (scleractinian) corals from Heron, Orpheus and Lizard Islands were examined

between 1980 and 1983 (Denton and Burdon-Jones 1986b). Of the two groups, the octocorals accumulated significantly higher concentrations of all detectable metals. The soft coral *Sarcophyton* sp. contained highest concentrations of Cd at the southern Heron Island site. Little is known about the impact of metals on coral ecology, although exposure to metals may be an added stress connected with zooxanthellae loss and coral bleaching (Harland and Brown 1989). This response has been observed under laboratory conditions for *Galaxea fascicularis* at Heron Island (Ballestrin 1993). More recently the utility of a number of scleractinian corals (*Pocillopora* sp., *Acropora* sp., *Goniastrea* sp. and *Montastrea* sp.) resident in Townsville harbour and around Heron Island to act as biomonitors of ambient metal concentrations were assessed (Esslemont 1997). It was concluded that *G. aspera* and *P. damicornis* were suitable sentinel organisms for monitoring metal loads in Great Barrier Reef waters.

Extremely high concentrations of arsenic have been observed in the tissues of various bivalves collected from Great Barrier Reef waters (Benson and Summons 1981). This accumulation is a consequence of the metabolism of arsenate by micro-algae under low nutrient conditions. Although arsenic accumulation in algae is not excessive, it is bioaccumulated to high concentrations in the tissues (particularly in the kidney) of filter feeding bivalves such as *Tridacna* sp. which use the algae as a food source. Background tissue concentrations of Ag, Cd, Cu, Co, Pb, Ni and Zn have also been assessed in tissues of 9 species of tropical bivalves (*Arca ventricosa, Chama isotoma, Lithophaga teres, Pinctada margiritfera, Pycnodonte hyotis, Spondylus ducalis, Modiolus auriculatus, Trichomya hirsuta* and *Ustularca renuta*) collected from the greater Townsville region in 1979 (Klumpp and Burdon-Jones 1982). This study concluded that most of the bivalve species studied were strong accumulators of metals, although accumulation was variable between sampling locations. The relationships between concentration in tissues of bivalves, location and environmental impact were not assessed. More recently, trace metal concentrations in 7 species of bivalves (*Tridacna crocea*, *T. maxima*. *Pinctata margaritifera*, *Hyotissa hyotis*, *Chama plinthota*, *Trochus niloticus* and *Strombus luhuanus*), the gastropod *Polmesoda erosa* and the sea cucumber *Stichopus chloronotus* were assessed in animals collected from Torres Strait (Dight and Gladstone 1993; Gladstone 1996). *P. erosa* and *T. crocea* were identified as suitable heavy metal bioindicators for the Torres Strait.region.

1.6.4. Algae and Seagrasses

Marine and estuarine macroalgae and angiosperms concentrate metals from surrounding waters (Ward *et al.* 1986; Phillips 1994). Accumulation is thought to occur through both active and passive processes, and many metals are believed to be accumulated in proportion to environmental concentrations (Bryan 1971). Most metals are not significantly toxic to algae or seagrass at concentrations likely to be present in coastal seawaters (Ward 1989; Phillips 1994). Trace metal concentrations (Zn, Cu, Cd, Ni, Pb and Hg) in 48 species of reef algae collected in Great Barrier Reef waters between Lizard and Heron Islands in 1980 were low and indicative of an unpolluted environment (Denton and Burdon-Jones 1986a). Metal concentrations have also been assessed in a number of seagrass species collected from Shoalwater and Upstart Bays, Townsville, Cape York and Torres Strait in 1975 and 1991 (Denton *et al.* 1980; Dight and Gladstone 1993). Concentrations of Mn and Zn were relatively high in samples collected from the Townsville sites. All northern Australian samples contained high concentrations of Fe. Torres Strait samples were lower in Fe and Zn. Metal concentrations in the seagrass *Halophila ovalis*, *H. uninervis* and *Cymodocea serrulata* collected from the Townsville and Gladstone regions have also recently been assessed (Mauger 1997; Prange and Dennison 2000). These studies concluded that there was no direct relationship between metal concentrations in seagrass and their associated concentrations in sediments and that rainfall events and anthropogenic disturbance influenced metal concentrations in seagrass.

The major responses in marine plants to organochlorine pollutants are often decreased photosynthesis and either respiration inhibition or enhancement and growth reduction (Butler 1977). Different species of algae and seagrass vary in their sensitivity to exposure to organochlorine compounds (Ramachandran *et al.* 1984). The site and mechanism of pollutant action has not been clearly demonstrated, although inhibition of cyclic phosphorylation and suppression of electron transport and ATP turnover have been documented (Ramachandran *et al.* 1984). Macroalgae and seagrass have rarely been used to monitor trace organic contaminants (Phillips and Rainbow 1993), and there are no published data on organochlorine concentrations in algae or seagrass in Great Barrier Reef waters.

1.6.5. Fish

With the exception of mercury, fish are generally able to regulate accumulation of most metals (Phillips and Rainbow 1993). In contrast, organochlorines are not regulated, and may bioaccumulate in fish (Phillips and Rainbow 1993; Vassilopoulou and Georgakopoulos-Gregoriades 1993; Pastor *et al.* 1996), although concentrations are related to lipid concentrations in tissues as well as environmental factors such as salinity (Phillips and Rainbow 1993). Liver and muscle from coral trout (*Plectropoma maculatum*) and surf parrot fish (*Scarus fasciatus*) collected between Heron and Lizard Islands in 1976 and 1977 were analysed for organochlorine compounds (Olafson 1978). Lindane (γ-HCH) and DDT and its metabolites were detected in these samples, although concentrations were an order of magnitude lower than those reported for the Brisbane River (Thomson and Davie 1974). Runoff from the sugar cane industry was proposed as the source of contamination (Olafson 1978). Reef sharks were found to contain an average of 36 ng g^{-1} PCB (wet wt of muscle tissue), which was considered to be in the range of concentrations in biota sampled from more contaminated waters (Smillie and Waid 1985). Average concentrations of chlorinated organics (PCBs, DDTs, HCHs, aldrin, dieldrin and chlordanes) in muscle of coastal marine fish collected in the vicinity of Townsville between 1989 and 1993 were low compared to samples from the Brisbane region and other urbanised centres (Kannan *et al.* 1995). Further sampling was carried out in 1992 and 1993. Livers from 142 individual fish of a wide range of species were collected in the central section of the Great Barrier Reef Marine Park (von Westernhagen and Klumpp 1995). Low concentrations of DDE and dieldrin were detected in 8% of samples. Metal concentrations in 50 species of Great Barrier Reef fish were assessed in 1981 (Denton and Burdon-Jones 1986c). This study concluded that concentrations of metals in tissueswere low compared with other localities. Fifteen species of fish collected from Torres Strait were also assessed for metal concentrations in 1992-93 and were also found to contain very low concentrations of heavy metals (Gladstone 1996).

1.6.6. Marine Mammals (Sirenia)

Denton and co-workers reported metal concentrations in muscle, liver, kidney, lung and brain and in the blood of 48 dugongs collected from Torres Strait and Townsville

between 1974 and 1978 (Denton *et al.* 1980; Denton 1981; Denton and Breck 1981). These studies detected unusually high concentrations of Fe and Zn in liver and high concentrations of Cd in kidney. Concentrations of Cu, Cd, Co and Ag were also elevated in the liver compared with concentrations in other species of marine mammals. Concentrations of Fe, Zn, Cd and Co in the liver and Cd in the kidney were positively correlated with age. It was considered unlikely that the high metal concentrations accumulated by dugongs were a reflection of anthropogenic impacts, given the remoteness of the sampling sites (Denton *et al.* 1980). Similar concentrations of metals were reported in muscle, kidney and liver of 3 dugongs stranded following a cyclone in northern Australia in 1984 (Marsh 1989). More recently, metal concentrations in muscle, liver, kidney and intestine sampled from 3 dugong collected from Mabuiag Island, Boigu Island and Daru (Torres Strait) between October and December 1992 were assessed (Gladstone 1996). Metal concentrations in some tissues were high enough to have health implications for human consumers (Gladstone 1996). Three dugongs caught in the Gulf of Carpentaria in 1992 and 1993 (Parry and Munksgaard 1992; Parry and Munksgaard 1993) were also analysed for a range of heavy metals (As, Cd, Cu, Hg, Pb, Se and Zn). As found in previous studies, kidney and liver contained the highest concentrations of metals.

Very low concentrations of lindane and dieldrin were reported in the liver of four dugongs collected from Townsville in 1977 (Heinsohn and Marsh 1978), and PCB concentrations in the muscle, liver and blubber of a single dugong caught at Magnetic Island in the early 1980s have also been reported (Smillie and Waid 1985). There are no contemporary studies of the concentrations or impact of organochlorine pollutants on dugongs (Marsh and Corkeron 1997).

1.7. Moreton Bay Pollutant Concentrations

Moreton Bay is a 1,400 km^2 embayment on the southern Queensland coast which is protected by high sand islands. It is a semi-enclosed estuary and has extensive shallow waters with restricted water circulation (Mortimer and Hughes 1991). The embayment is the common estuary of a number of rivers which drain agricultural areas as well as carry urban runoff and treated domestic and industrial effluent from the greater Brisbane region (Moss *et al.* 1992a). A bulk of locally leached and discharged agricultural and

urban wastewaters are transferred to the Bay via the Brisbane River. PAHs and PCBs from urban centres have been widely distributed in waters and sediments of the Brisbane River (Shaw and Connell 1980; Kayal and Connell 1989). River discharges have also resulted in past contamination of Northern Bay sediments and bivalves with metals (Zn, Pb and Cu) and pesticides (Clegg 1974; Wallace and Moss 1979). Fish collected from the Brisbane River during the 1970s and 1980s were also contaminated with PAHs and PCBs (Shaw and Connell 1980; Kayal and Connell 1989). Intensive surveys of Moreton Bay carried out in the late 1990s concluded that the Bay is still contaminated with a range of organochlorines and heavy metals (Dennison and Abal 1999).

1.8. Thesis Objectives

Organochlorine and metal pollutants have been recorded from the waters, sediments and biota of the Great Barrier Reef region. However, they have only been detected in low concentrations where they occur, and sampling programs for their detection have often been restricted. Contemporary concentrations of pollutants have not been comprehensively quantified over the wider region, and little is known about the cycling and fate of these pollutants through the Great Barrier Reef environment. In particular, transfer of pollutants through Great Barrier Reef sediments and seagrass to local marine mammals is currently poorly defined, and has particular relevance to current concerns about dugong management. Accordingly, the objectives of this study are:

- To document the concentrations of trace metals and pesticides in intertidal and subtidal sediments and/or seagrasses along the Great Barrier Reef coasts;
- To investigate the toxicity of widely distributed pesticides to common seagrass species;
- To document the concentrations of pesticides in carcases of dugong stranded along the Queensland coast; and
- To carry out a risk evaluation of pollutants to the Great Barrier Reef environment in general and to local dugong in particular.

Thesis objectives are summarised in Figure 1.3, and section 1.9.

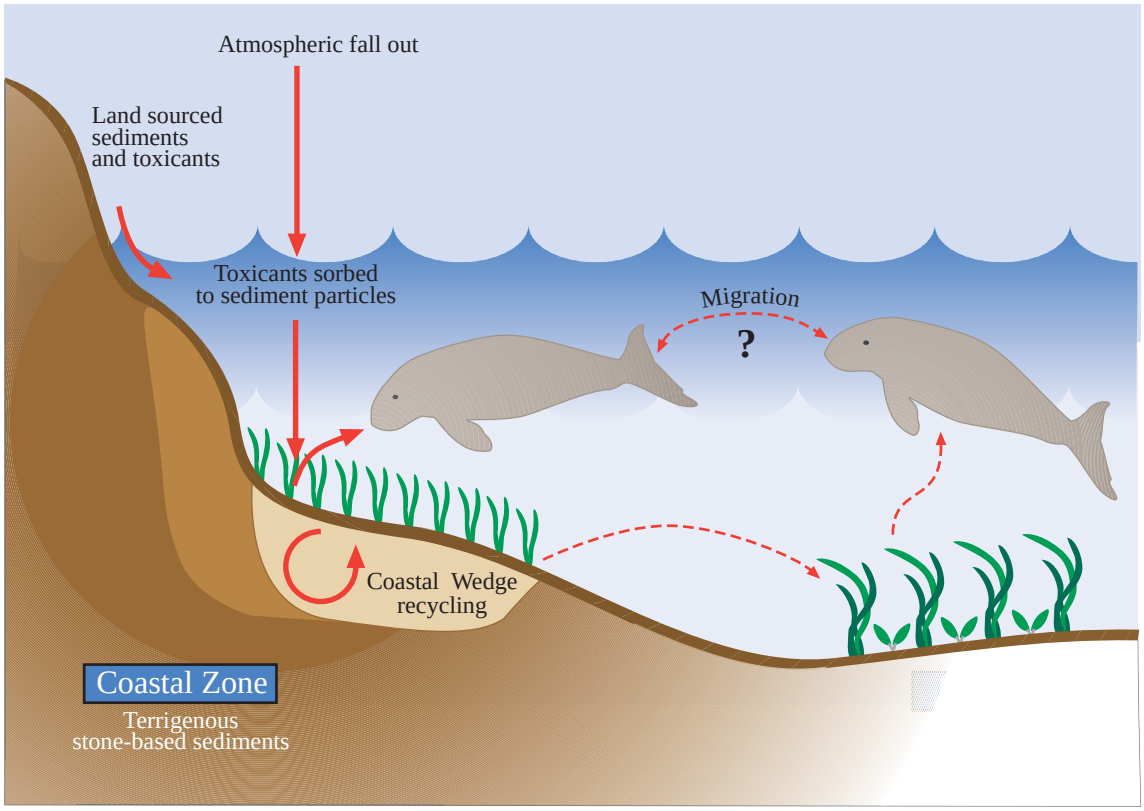

Figure 1.3. Conceptual model of pollutant movement in the Great Barrier Reef environment and the dugong foodchain.

1.9. Thesis Outline

Chapter 2 describes heavy metal and organochlorine concentrations in sediment samples collected in 1997 from 15 intertidal sites between Torres Strait and Moreton Bay. Relationships between environmental pollutant concentrations, sampling site and sampling matrix are explored and implications for dugong management presented.

Chapter 3 describes the distribution of heavy metals and organochlorines in sediments collected from 52 subtidal locations between Torres Strait and Gladstone in 1998 and 1999. Pollutant concentrations in sediments are compared with environmental guidelines and a risk evaaluation of subtidal pollutant concentrations is completed.

Chapter 4 considers the impact of the herbicide diuron on seagrass health using PAM fluorometry and places this in context with concentrations detected in Great Barrier Reef nearshore marine sediments.

Chapter 5 describes pollutant (organochlorines, PCBs, and heavy metals) concentrations in blubber and liver samples collected from 31 dugong carcasses stranded along the Queensland coast between 1996-2000, and discusses the relative risk posed to dugongs by different pollutants.

Chapter 6 describes the distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Great Barrier Reef World Heritage Area, including concentrations present in sediments, seagrasses and dugong tissue.

Chapter 7 provides concluding discussion which considers aquatic contaminant movement to the marine environment and discusses Great Barrier Reef Marine Park water quality management and monitoring into the future, with particular reference to protection of dugong.

Chapter 2: Intertidal sediment and seagrass pollutant concentrations

GBRMPA

Intertidal seagrass, Upstart Bay 1997

CHAPTER TWO: INTERTIDAL SEDIMENT AND SEAGRASS POLLUTANT CONCENTRATIONS

2.1. Introduction

Dugongs are marine herbivores that feed almost exclusively on preferred genera (*Halophila*, *Halodule* and *Cymodocea*) of seagrass (Marsh *et al.* 1982). Dugongs are believed to graze predominantly on inshore seagrass beds (Johnstone and Hudson 1981; Marsh *et al.* 1982; Preen 1993), although deeper water foraging trails have also been observed off the Queensland coast (Lee Long *et al.* 1993). Over 90% of seagrass biomass may be removed from an area during feeding by dugongs and both seagrass leaves and subsurface rhizomes and roots being consumed (Preen 1995a).

Inshore seagrass meadows are often significantly contaminated by a range of pollutants including heavy metals and pesticides (Pulich 1980; Brix *et al.* 1983; Tiller *et al.* 1989; Pergent and Pergent-Martini 1999). This is generally a consequence of the proximity of anthropogenic activity and the weak dispersion patterns present in semi-enclosed and nearshore marine environments where seagrass are found (Neff 1997). As yet, little evidence of adverse effects to seagrasses resulting from exposure to pollutants other than nutrients has been observed (Short and Wyllie-Echeverria 1996), although the sublethal toxicity of elevated concentrations of copper and zinc to *Halophila ovalis* (Ralph and Burchett 1998) and the toxicity of herbicides to seagrass has been demonstrated (Delistraty and Hershner 1984; Jones and Winchell 1984; Mitchell 1987; Ralph 2000). Pollutants incorporated into seagrasses have the potential to be transferred to seagrass consumers (Pulich 1980; Ward 1989; Gordon *et al.* 1998) and sediment associated metals and organochlorines also have the potential to be bioaccumulated (Heinsohn and Marsh 1978; Miyazaki *et al.* 1979; O'Shea *et al.* 1984; Ames and Van Vleet 1996; McKenzie *et al.* 1999).

Studies of metal concentrations in sediments in Queensland marine ecosystems are limited and have been usually initiated in response to port and harbour developments or the dredging of shipping channels (Reichelt and Jones 1993; Brady *et al.* 1994; Gladstone Port Authority 1994; Anon 1996; Cairns Port Authority 1998).

Similarly, few studies of metal concentrations in Queensland seagrasses have been completed (Denton *et al.* 1980; Mauger 1997). No contemporary information is available on the concentrations of pesticides in Queensland intertidal seagrasses or intertidal sediments. The present study was carried out to provide the first comprehensive survey of metal and pesticide concentrations in intertidal sediments and seagrass from dugong habitat along the tropical and sub-tropical Queensland coast.

2.2. Materials and Methods

2.2.1. Sample Collection

Sediment and seagrass samples were collected from 15 Queensland intertidal (<1m deep) sites between Cape York and Moreton Bay (Figure 2.1). Samples were collected between February and May 1997. All sampling sites (with the exception of Cairns) are in the vicinity of important dugong habitat (Marsh and Saalfeld 1989; Marsh and Saalfeld 1990; Preen 1993; Marsh *et al.* 1995; Marsh and Corkeron 1997), and were relatively easily accessible for sampling purposes without the use of a boat. Three replicate 2 litre sediment samples and three replicate 2 litre seagrass samples were collected from each sampling site. (The number of samples collected for analyses were limited by cost constraints). Samples for heavy metals analysis were collected in acid-washed plastic containers, and samples collected for chlorinated hydrocarbon analyses were collected in solvent-washed glass containers. Each sediment sample was a composite of multiple surficial sediment samples collected randomly over an area of approximately 400 m^2. Replicate random samples of the dominant seagrass (*Cymodocea serrulata*, *Halodule uninervis* or *Zostera capricorni*) were also collected over the same area. Entire plants (leaves, roots and rhizomes) were sampled. Plant material was vigorously washed in local seawater prior to storage. Sediment and seagrass samples were frozen following collection.

Figure 2.1. Intertidal sediment and seagrass sampling sites, 1997.

1. Lloyd Bay, 2: Princess Charlotte Bay, 3: Flinders Island, 4: Bathurst Bay, 5: Cairns, 6: Cardwell, 7: Pallarenda, 8: Cleveland Bay, 9: Upstart Bay, 10: Newry Bay, 11: Shoalwater Bay, 12: Gladstone, 13: Hervey Bay, 14: Moreton Bay west, 15: Moreton Bay.

2.2.1. Metals Analyses

Frozen sediments were transported to the analytical laboratory where the samples were thawed and divided in two. One portion was wet sieved in plastic sieves and separated into four size fractions (>2000 μm, 200-2000 μm, 63-200 μm and <63 μm) and weighed. The second portion was ground to <50 μm using a shatter box grinding mill. Ground sediment samples were pelleted using the pressed powder technique (Gladstone 1996) and analysed by X-ray fluorescence (ARL XRF 8480) for aluminium (Al), arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), silica (Si) and zinc (Zn) concentrations. Selenium (Se) determination samples were digested using nitric:perchloric:sulphuric acid (13:1:2) and analysed by hydride generation atomic absorption spectometry (AAS, Perkin Elmer 4100ZL). Cadmium (Cd) and mercury (Hg) determination samples were digested with nitric:hydrochloric acid (6:2) following 2 hours digestion in a steam bath. Cadmium was analysed by graphite furnace AAS, and mercury by hydride generation AAS (Perkin Elmer 4100ZL).

Seagrass samples were washed in ultra pure water to remove associated sediment, dried at 65^{o}C and ground to <1 mm in a stainless-steel mill and analysed for trace metals. Seagrass sample dissolution was achieved using a nitric acid microwave digestion procedure (Dight and Gladstone 1993) followed by analytical determination for Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn using Inductively Coupled Plasma Mass Spectrometry (ICP-MS (Thermo-Jarrell Ash Iris ICPOES)).

2.2.3. Pesticide Residue and PCB Analyses

Samples for pesticide and polychlorinated biphenyl (PCB) analysis were analysed at the NATA certified pesticide laboratory of Queensland Health and Scientific Services, Brisbane, using routine laboratory methods. For the majority of compounds which included aldrin, atrazine, chlorpyrifos, endosulfan (α, β and endosulfan sulfate), dieldrin, DDTs (pp-DDD, pp-DDE and pp-DDT), diuron (DCMU [3-(3',4'-dichlorophenyl)-1,1-dimethylurea]), hexachlorobenzene, heptachlor, heptachlorepoxide, lindane and PCBs, approximately 100 g aliquots of the thawed and homogenised sediments were weighed into an extraction vessel.

These were then extracted into 100 mL acetone/n-hexane (1:1) on a shaker, overnight. The extract was then centrifuged and the supernatant decanted. Twenty mL of saturated NaCl was added to the extract prior to liquid/liquid partitioning with dichloromethane (150 mL). The dichloromethane fraction was filtered through anhydrous sodium sulfate and the partitioning steps were repeated. The combined fractions of dichloromethane containing the compounds of interest were concentrated, transferred into n-hexane and made up to a volume of 3 mL. One mL of the extract was set aside for analysis of diuron and atrazine, wheras the second fraction of 2 mL (67 % of extract) was subject to a clean-up in a column (18 mm I.D.) filled with 20 cm of Florisil™ (5 % deactivated with H_2O). Compounds of interest were eluted in two separate fractions using 120 mL of n-hexane/diethylether (94/6 V/V) followed by 90 mL of n-hexane/acetone (90/10 V/V).

The individual fractions were concentrated to 1 mL and the first fraction was analysed for chlorpyrifos using a gas chromatograph equipped with a flame photometric detector (GC-FPD, Hewlett-Packard 6890A) for quantification and a gas chromatograph equipped with nitrogen phosphorous detector (GC-NPD, Hewlett-Packard 6890A) for confirmation. The first fraction (n-hexane/diethylether eluate) was then subjected to a sulphur removal clean-up following US-EPA method 3660A. Samples were transferred to test tubes and 1 mL of tetrabutyl ammonium hydrogen sulfate saturated with anhydrous sodium sulphite, 2 mL isopropanol and small amounts of extra anhydrous sodium sulphite were added. After shaking (60 s), 5 mL of H_20 was added and the samples were again shaken (60 s). The top layer was transferred using an extra 2 mL of n-hexane and concentrated under a gentle stream of nitrogen to 1 mL. Both the first fraction (after sulphur removal clean-up), and the second fraction concentrated directly from the Florisil™ column were then analysed for aldrin, endosulfan (α, β and endosulfan sulfate), dieldrin, DDTs (pp-DDD, pp-DDE and pp-DDT), hexachlorobenzene, heptachlor, heptachlorepoxide, lindane and PCBs using a dual column gas chromatograph equipped with electron capture detectors (Shimadzu ECD GC-17A)

For the 1 mL fraction (33 % of extract) set aside for diuron and atrazine analysis, the solvent was exchanged by carefully evaporating the n-hexane and subsequently adding first water and then methanol.

The samples were made up to a final volume of 1 mL and analysed on a high performance liquid chromatography system coupled with a triple stage quadropole mass spectrometer (HPLC MS/MS). The HPLC MS/MS consisted of a LC-200 series pump, series 200 autosampler and API 300 MS/MS with atmospheric pressure chemical ionisation interface (Perkin-Elmer Sciex Instruments, Thornhill, Ontario, Canada). An Altima C18 column at 35^{o}C was used. Chromatography consisted of a linear gradient from 40-90% methanol over 5 mins, with a final isocratic stage holding at 9% methanol for 4 min. The total flow rate was 1 mL min^{-1}. The mobile phase was buffered to 5 mM with ammonium acetate. Injection volumes of 10 μL were used.

Samples were also analysed for 2,4-D ((2,4-dichlorophenoxy) acetic acid) and 2,4,5-T ((2,4,5-trichlorophenoxy) acetic acid). Subsamples of approximately 50 g were extracted using 100 mL of 0.1 M NaOH in H_2O on a shaker for 4 hours. The samples were centrifuged and the supernatant was decanted, and acidified to a pH < 2 using concentrated H_2SO_4. If precipitation occurred after acidification, the centrifugation was repeated. The compounds of interest were then extracted into diethylether (2 * 100 mL) using liquid-liquid partitioning. The diethylether was filtered through anhydrous sodium sulfate and the combined fractions concentrated to approximately 2 mL. The compounds of interest were instantaneously methylated using freshly prepared diazomethane which was collected in diethylether prior to use. The extract was then concentrated, transferred into n-hexane and made up to a final volume. The samples were analysed for 2,4,5-T using a gas-chromatograph coupled to a mass-spectrometer (Shimadzu GCMS-QP5050A). Quantification was performed in selective ion monitoring mode and confirmed using full ion scan.

Seagrass samples were thawed and one replicate from each sampling location was selected at random for analysis. Approximately 50 g (wet weight) of seagrass tissue was thoroughly washed in deionised water. Extraction, clean-up and quantification for the individual compound groups were similar to the methods described above for sediments. However, analysis of aldrin, chlorpyrifos, endosulfan (α, β and endosulfan sulfate), dieldrin, DDTs (pp-DDD, pp-DDE and pp-DDT), hexachlorobenzene, heptachlor, heptachlorepoxide, lindane and PCBs in seagrass required an extra filtration step prior to the liquid partition through a Whatman 542 filter. Furthermore, after the liquid partitioning step and before the florisil clean-up, gel permeation chromatography

(GPC) was used to purify the extracts. In brief, the 2 mL fraction after the liquid-liquid partitioning step was filtered through a 0.45 μm filter (Millex FH). The sample was then injected into the GPC (Envirogel) with dichloromethane as the mobile phase. The fractionation containing the compounds of interest were collected, reduced, transferred into n-hexane, further purified on florisil and analysed as described for sediments above.

For 2,4-D and 2,4,5-T analysis, seagrass samples were extracted into acetone by blending at high speed. The acetone was then filtered through a Whatman 542 filter, concentrated, transferred to a conical flask using diethylether and hydrolised with KOH (37 % w/v) on a water bath for 1 hour. Before liquid-liquid partitioning the pH was reduced to <2 using H_2SO_4 and the method was continued as described for sediment samples above.

2.2.4. Sediment Calcium Carbonate and Organic Carbon and Seagrass Lipid Analyses

Sediment calcium carbonate content was determined by a weight loss gravimetric method (Blakemore *et al.* 1987). For total organic carbon content (TOC) quantification in sediment samples, inorganic carbonates were first removed using an acid catalysed digestion (10% HCl, 1% $FeCl_2$ at 70^{o}C). The remaining material was dried and subjected to a combustion procedure (LECO induction furnace) with subsequent detection of CO_2 (LECO WR12 CO_2 detector). In order to determine the lipid content of the seagrass, the nonpolar extract was reduced to dryness after liquid-liquid partitioning and the lipid content determined gravimetrically.

2.2.5. Quality Assurance and Statistical Analysis

Blanks and certified reference materials (Marine Sediment Best-1, National Research Council, Canada; and *Ulva lactuca,* Commission of the European Communities Standard Reference Material) were analysed concurrently with sediment and seagrass samples to ensure consistency and accuracy of recoveries over metal analyses (Tables 2.1 and 2.2). All chlorinated hydrocarbon analytical methods were subject to standard QA/QC procedures. Blanks and a series of spikes, which contained known quantities of the analytes, were included in each analysis batch (usually 12 samples).

Table 2.1. Standard reference material (Marine Sediment Best-1, National Research Council, Canada) recoveries.

Metal	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Si	Zn
units	%	mg kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}
Best-1	8.61	17.6	1.5	0.26	11	118	36	4.32	0.102	344	48	17	25.6	182
Best-1	8.59	15.5	1.51	0.27	14	119	38	4.33	0.096	347	49	22	25.8	184
Best-1	8.92	18.7	1.57	0.25	17	117	35	4.43	0.094	358	50	19	26.4	187
Best-1	8.95	18.3	1.55	0.27	12	126	39	4.45	0.095	355	50	19	26.4	186
Best-1				0.25		114	34		0.109		51	21		183
Best-1				0.25		120	38		0.107		52	22		186
Analyses Mean	8.77	17.5	1.53	0.26	14	119	37	4.38	0.100	351	50	20	26.1	185
Analyses Std. Dev.	±0.19	±1.4	±0.03	±0.01	±3	±4	±2	±0.07	±0.007	±7	±1	±2	±0.4	±2
Certified value														
Mean	8.57	20.7	-	0.24	13.8	106	39.3	4.35	0.092	365	49.3	21.9	27.8	172
2 Std. Deviations	±0.26	±0.8	-	±0.01	±1.4	±8	±2	±0.22	±0.009	±21	±1.8	±1.2	±1.1	±16

*Table 2.2. Standard reference material (*Ulva lactuca, *Commission of the European Communities) recoveries.*

Metal	As	Cd	Cu	Pb	Se	Zn
Units	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Analyses value	3.00	0.28	12.7	13.9	0.57	50.0
Certified value						
Mean	3.09	0.274	13.14	13.48	0.593	51.3
2 Std. Deviations	±0.20	±0.022	±0.37	±0.36	±0.032	±1.2

Table 2.3. Percentage recovery of spiked organochlorine samples.

Compound	Intertidal sediments	Intertidal seagrass
OCs	70-100	70-100
PCBs	90	80
Chlorpyrifos	95	85
Atrazine	70	95
Diuron	70	90
2,4-D	85	nd

nd: not determined

The reporting limit was defined as 5 times the average values of the baseline noise signals and/or 3 times the concentration in a representative blank. QC/QA data are presented in Table 2.3. No contaminants were detected in reagent blanks.

Metal data were graphed and inspected for gross deviations from normality, and where necessary, transformed (Log_{10}) prior to analysis. Non-detectable values were set at half the detection limit for that metal for statistical analyses. Pearson correlation co-efficients and their associated Bonferroni-adjusted probabilities were calculated for sediment metals and physico-chemical. Regression analysis was used to explore relationships between metal concentrations in sediment and seagrass. Differences in metal concentrations between sediments and seagrasses at different sampling locations were compared using two-way analysis of variance (ANOVA). Significant differences in metal concentrations between sampling matrices were located using the Tukey HSD multiple comparison test with an experiment-wise type 1 error probability of 0.05 (Ott 1993). Metal data were standardised to *Z* scores and an agglomerative hierarchical algorithm using complete clustering was used to classify the sediment and seagrass metal data. Principal Component Analysis (PCA) was used to ordinate the data. Euclidean distances were utilized to calculate dissimilarities.

The presence of natural groupings in the data was defined by concurrence in both the classification and the ordination analyses (Clarke and Warwick 1994). All statistical computations were carried out with the aid of the SYSTAT V7.0 package (Wilkinson 1996).

2.3. Results

2.3.1. Sediment Physico-chemical Characteristics

Samples collected from all sites except Princess Charlotte Bay, Bathurst Bay and Cardwell were predominantly coarse grained (Figure 2.2). All sampling sites north of Cairns (except Lloyd Bay) contained comparatively high (>20 %) concentrations of calcium carbonate (Figure 2.2). These sites also had the lowest silica concentrations (Figure 2.2). All sites contained low concentrations of organic carbon (average <2%).

2.3.2. Heavy Metal Concentrations

With the exception of cadmium and mercury, all sediment metal concentrations were negatively correlated with coarser sediments and calcium carbonate content (Table 2.4). Conversely, all metals (except cadmium and mercury) were positively correlated with the fine (<63 μm) sediment fraction and organic carbon content.

Metal concentrations were highly variable between sampling matrix (sediment and seagrass) and sampling site (Figures 2.3 to 2.6). Significant differences were present in concentrations of all metals between sampling sites and (with the exception of arsenic and zinc) between the two sampling matrices (Table 2.5). No single sampling site had consistently highest metal concentrations. Average concentrations of aluminium, chromium, iron, manganese, nickel, and lead were highest in sediment samples and average concentrations of cadmium and mercury were highest in seagrasses. With the exception of chromium and mercury, concentrations of metals in sediments and seagrass samples were positively correlated with sediment metal concentration (Table 2.6). However, regression analysis indicated that the linear relationship between sediment and seagrass metal concentration was poor, with r^2 values for all metals below 0.5.

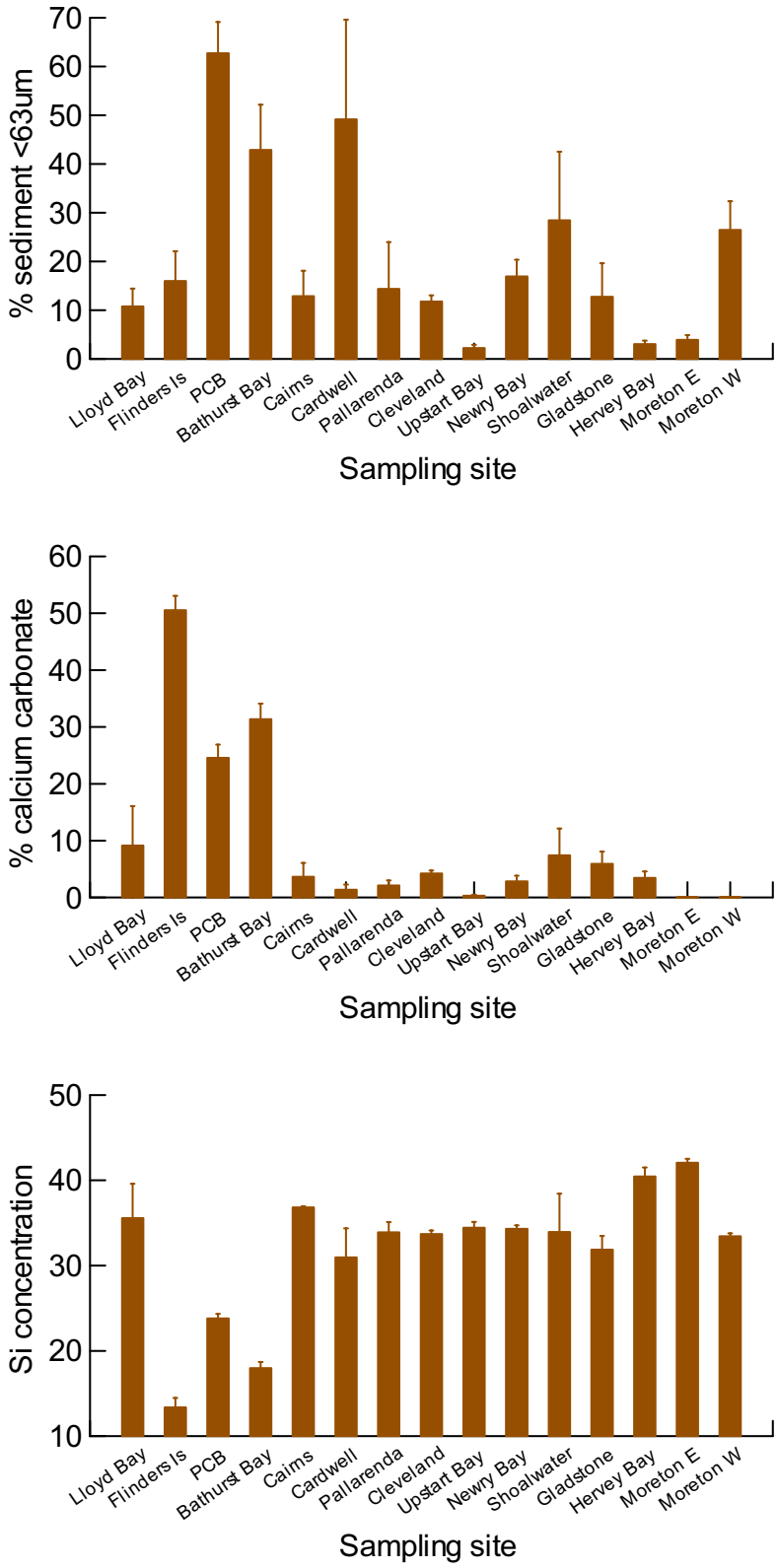

Figure 2.2. Physico-chemical characteristics of collected intertidal sediments. Silica mg kg^{-1} dry weight. (Error bars = 1 SEM, n=3).

Table 2.4. Pearson correlation coefficient matrix, including Bonferroni-adjusted probabilities for Log_{10} transformed sediment physico-chemical and metal concentrations.

	>2000µm	**200-2000 µm**	**63-200 µm**	**<63µm**	**Organic carbon**	**$CaCO_3$**	**Si**	**Ca**	**Al**
>2000µm	1.000								
200-2000 µm	0.326	1.000							
63-200 µm	**-0.554****	**-0.537****	1.000						
<63µm	0.044	**-0.595****	0.017	1.000					
Organic C	0.198	-0.290	-0.022	**0.686*****	1.000				
$CaCO_3$	0.471	-0.177	-0.404	0.347	0.152	1.000			
Si	-0.427	-0.211	**0.732*****	-0.053	0.020	**-0.574****	1.000		
Ca	**0.486***	-0.142	-0.473	0.408	0.255	**0.909*****	**-0.627*****	1.000	
Al	-0.202	-0.467	0.487*	0.480	**0.552****	-0.143	**0.511***	0.021	1.000
As	-0.292	**-0.500***	0.628	0.355	0.377	-0.034	**0.612*****	-0.021	**0.716*****
Cd	0.076	0.002	-0.082	0.401	**0.495***	-0.146	-0.089	0.079	0.375
Cr	-0.295	-0.378	**0.617*****	0.247	0.360	**-0.513***	**0.523***	-0.444	**0.537****
Cu	-0.260	-0.020	0.063	0.393	0.450	-0.317	0.133	-0.154	0.431
Fe	-0.074	-0.456	0.475	0.440	**0.506***	-0.040	**0.547****	0.129	**0.910*****
Hg	0.280	-0.290	-0.125	**0.718*****	**0.657*****	0.326	-0.168	**0.547****	**0.518***
Mn	-0.194	**-0.571****	0.427	0.356	0.366	0.023	0.215	0.202	**0.844*****
Ni	-0.335	-0.441	0.261	**0.613*****	0.480	-0.150	0.160	-0.029	**0.594****
Pb	-0.161	-0.469	0.275	**0.574****	**0.588****	-0.034	0.250	0.111	**0.827*****
Zn	-0.202	-0.435	0.346	**0.571****	**0.608*****	-0.069	0.216	0.118	**0.875*****

*0.05<p<0.01, **0.001<p<0.01, ***p<0.001

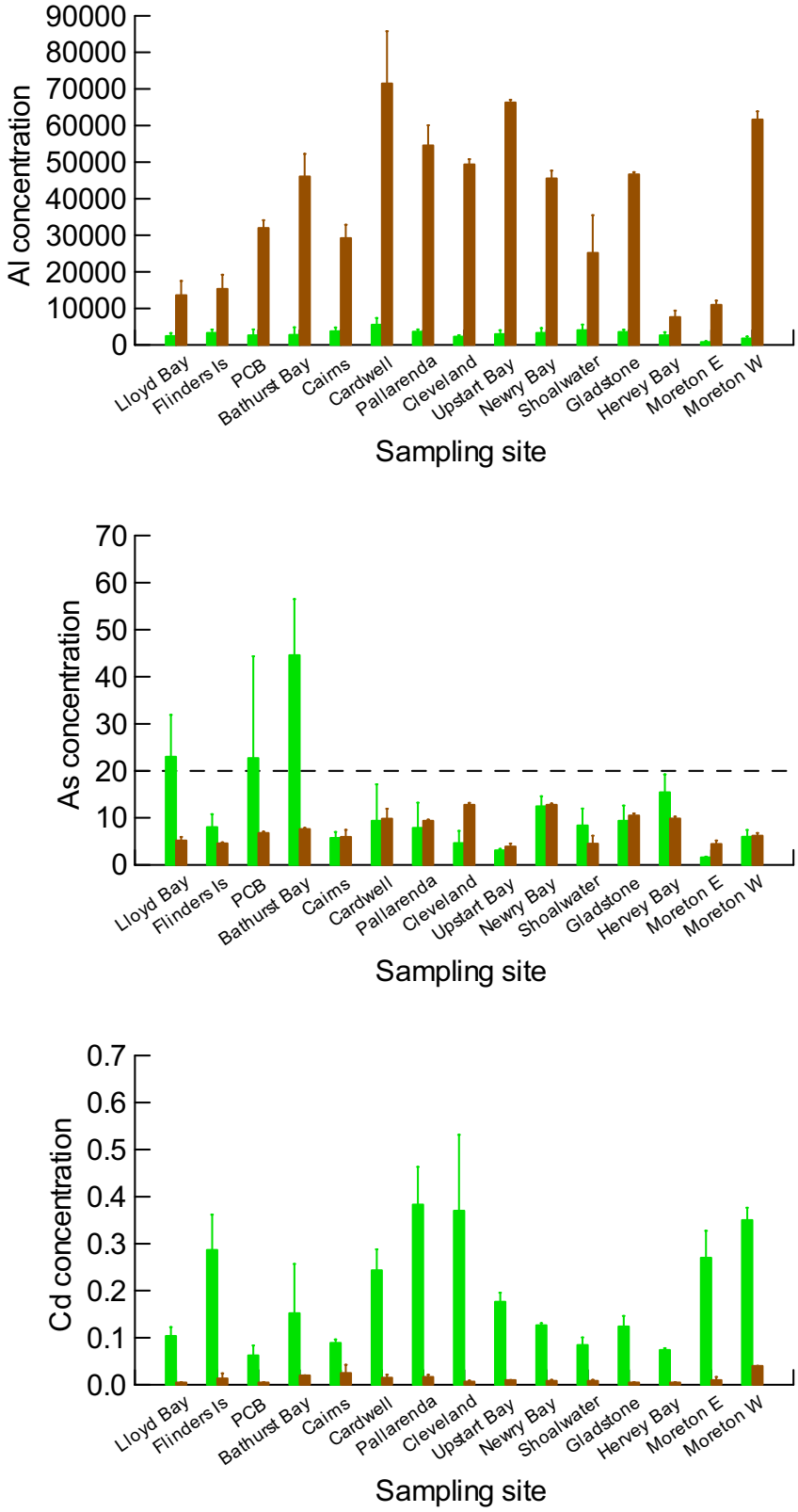

Figure 2.3. Concentrations of Al, As and Cd in intertidal sediments and seagrasses. All concentrations mg kg^{-1}dw. (Error bars = 1 SEM, n=3). Brown = sediment, green = seagrass.

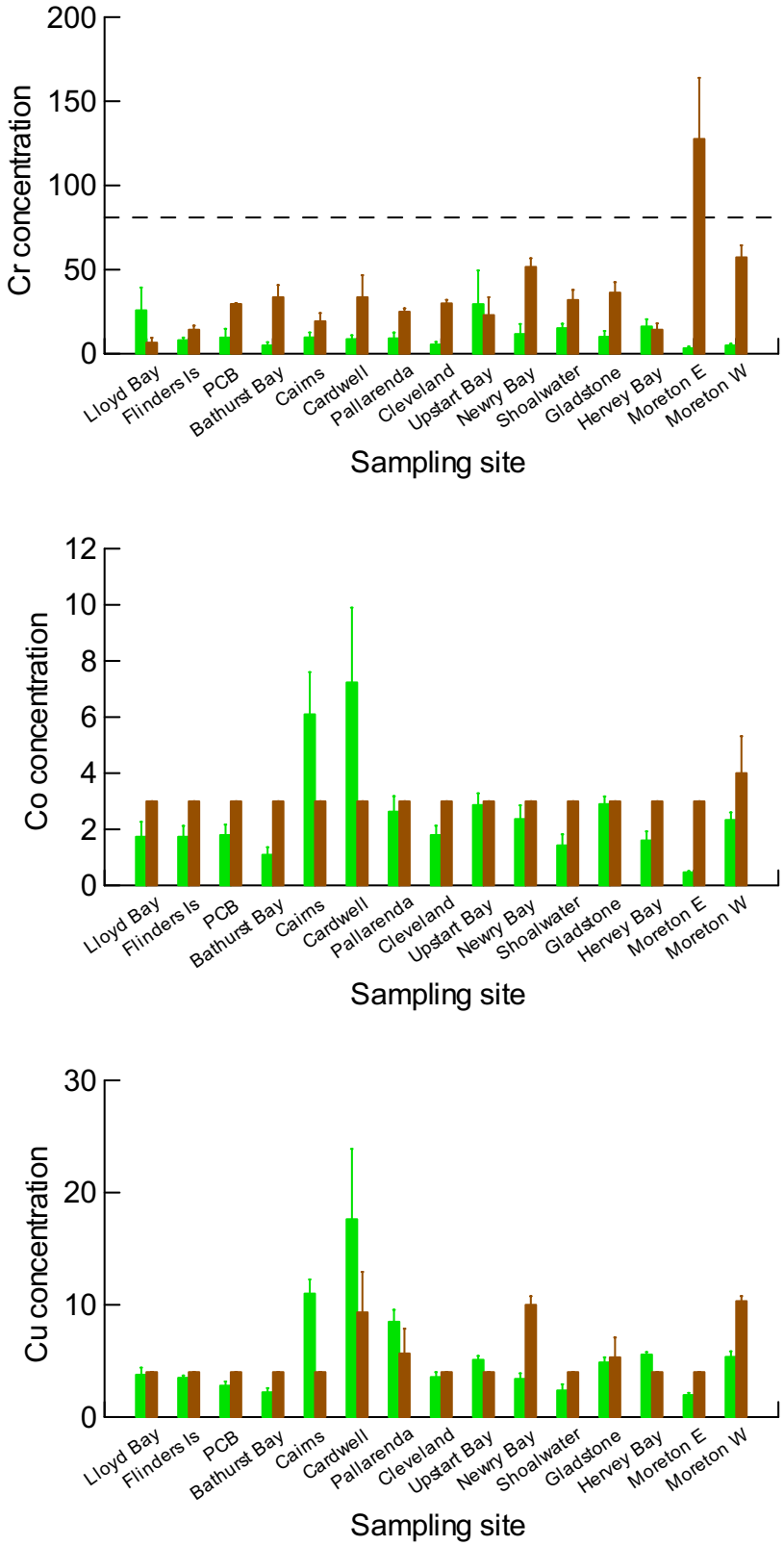

Figure 2.4. Concentrations of Cr, Co and Cu in intertidal sediments and seagrasses. All concentrations mg kg^{-1} dw. (Error bars = 1 SEM, n=3). Brown = sediment, green = seagrass.

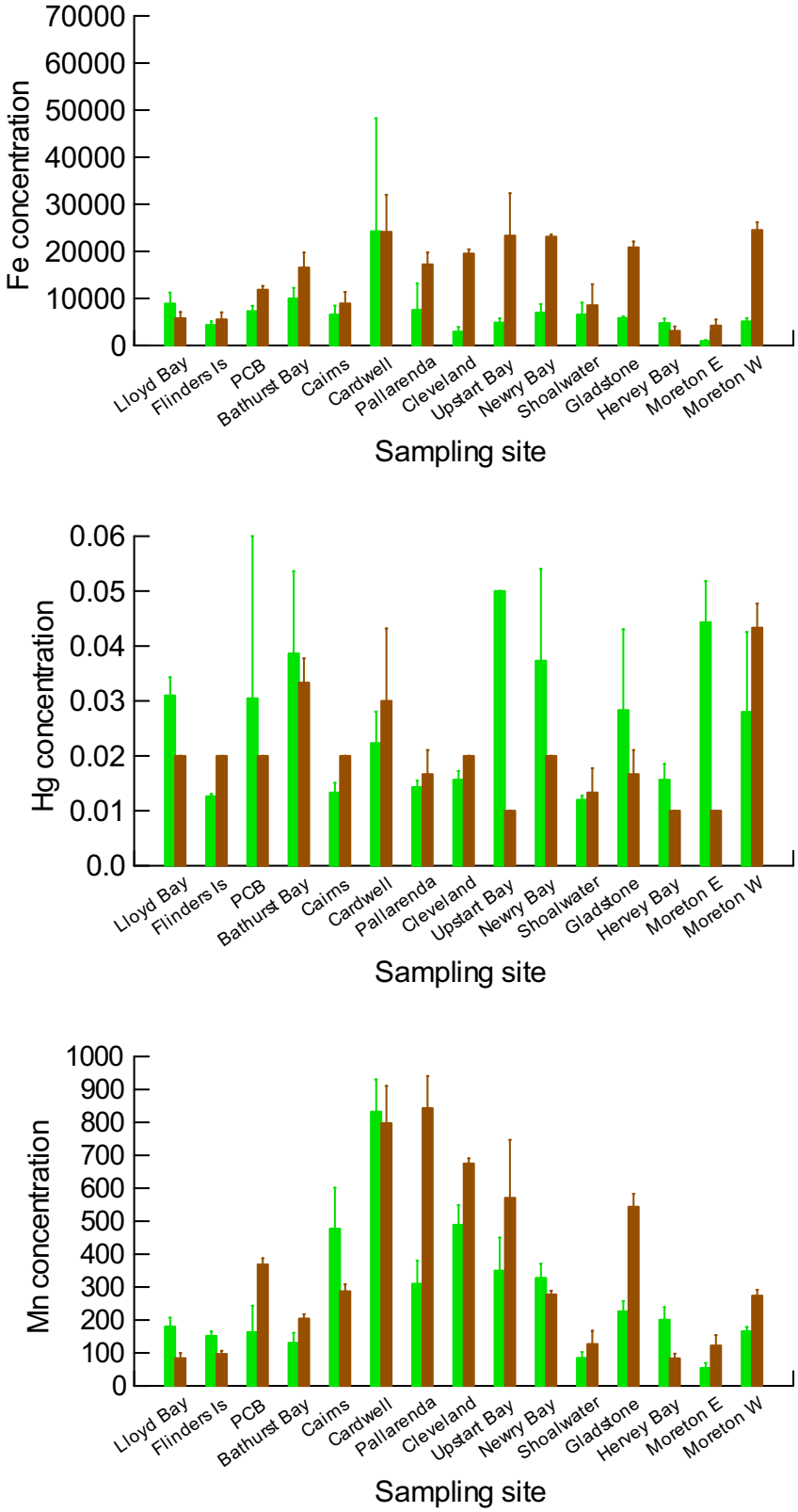

Figure 2.5. Concentrations of Fe, Hg and Mn in intertidal sediments and seagrasses. All concentrations mg kg^{-1} dw. (Error bars = 1 SEM, n=3). Brown = sediment, green = seagrass.

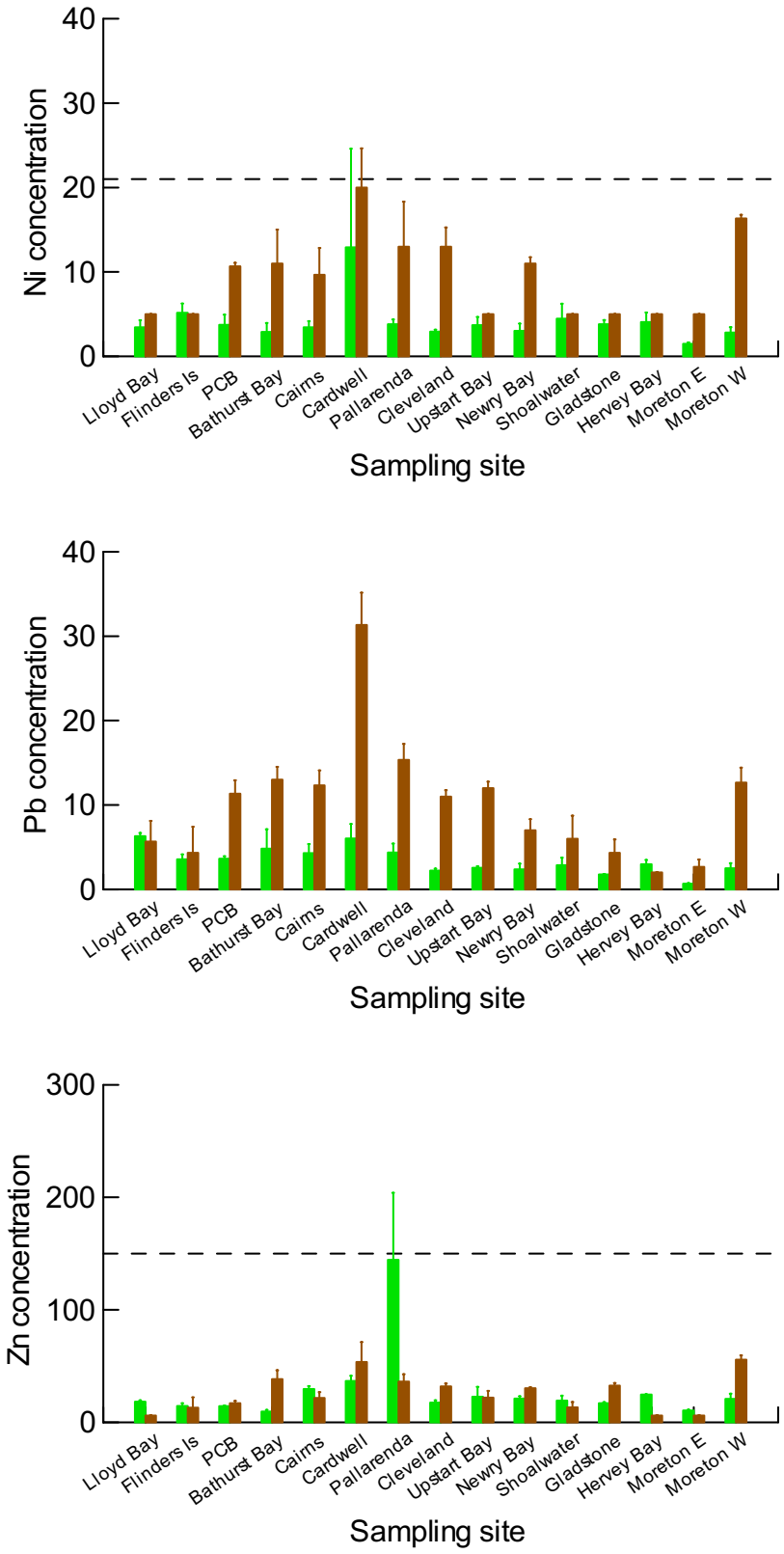

Figure 2.6. Concentrations of Ni, Pb and Zn in intertidal sediments and seagrasses. All concentrations mg kg^{-1} dw. (Error bars = 1 SEM, n=3). Brown = sediment, green = seagrass.

Table 2.5. Summary of results of ANOVAs of intertidal sediment and seagrass metal concentrations. (All data Log_{10} transformed prior to analysis).

Metal	Factor	*F* ratio	p
Al	Site	9.759	<0.001
	Matrix	926.135	<0.001
	Interaction	4.900	<0.001
As	Site	8.394	<0.001
	Matrix	2.388	0.128
	Interaction	5.561	<0.001
Cd	Site	7.908	<0.001
	Matrix	860.262	<0.001
	Interaction	3.015	0.002
Cr	Site	1.929	0.041
	Matrix	152.369	<0.001
	Interaction	11.049	<0.001
Co	Site	13.484	<0.001
	Matrix	77.787	<0.001
	Interaction	13.209	<0.001
Cu	Site	20.356	<0.001
	Matrix	5.605	0.021
	Interaction	10.596	<0.001
Fe	Site	8.328	<0.001
	Matrix	58.933	<0.001
	Interaction	3.842	<0.001
Hg	Site	4.080	<0.001
	Matrix	6.464	0.014
	Interaction	4.515	<0.001
Mn	Site	53.058	<0.001
	Matrix	15.305	<0.001
	Interaction	10.051	<0.001
Ni	Site	4.765	<0.001
	Matrix	113.705	<0.001
	Interaction	3.274	<0.001
Pb	Site	14.338	<0.001
	Matrix	146.084	<0.001
	Interaction	5.155	<0.001
Zn	Site	20.601	<0.001
	Matrix	1.336	0.252
	Interaction	11.222	<0.001

Table 2.6. Seagrass-sediment metal correlation coefficients and results of regression analysis.
(Data Log_{10} transformed prior to analyses).

Metal	***r***	***r²***	*p*
Al	0.562**	0.316	<0.001
As	0.300	0.090	0.032
Cd	0.142	0.020	0.322
Cr	-0.419	0.175	0.002
Cu	0.332	0.110	0.017
Fe	0.577	0.330	<0.001
Hg	-0.273	0.074	0.053
Mn	0.673***	0.454	<0.001
Ni	0.280	0.078	0.047
Pb	0.434	0.188	0.001
Zn	0.379	0.144	0.006

Bonferroni adjusted probabilities: **0.001<*p*<0.01, ***p<0.001

Table 2.7. Comparison of location variation in seagrass metal concentrations.
(All concentrations mg kg^{-1} dry weight).

Metal	Torres Strait[1]	Nth Qld[2]	Indonesia[3]	Denmark[4]	This study (mean)	This study (range)
Al		345-640[5]			3054	403-7800
As	**0.4-6.8**				**11.9**	**1.2-86**
Cd	0.37-3.0	0.2-1.1	0.05-1.2	0.09-2.92	0.196	0.016-0.61
Cr	**0.25-3.2**	**0.3-2.3**			**11.6**	**0.94-58.9**
Co	0.1-0.5	<0.4-4.0			2.6	0.41-11.2
Cu	2.9-13.3	2.4-9.0	1.2-18.9	1.82-19.29	5.5	1-27
Fe	**14-348**	**563-5250**			**7136**	**507-60600**
Hg						<0.01-0.05
Mn	18-41	44-1100			279	38-955
Ni	**1.1-4.3**	**0.6-4.9**			**4.1**	**0.94-30.6**
Pb	0.1-1.7	0.4-7.0	0.52-18.4	0.35-37.46	3.4	0.58-8.6
Zn	2.8-12	11-88	1.2-18.9	25-175	28	4.3-234

[1](Dight and Gladstone 1993); [2](Denton *et al*. 1980); [3](Nienhuis 1986); [4](Brix *et al*.1983)

Table 2.8. Results of the PCA analysis of intertidal sediment and seagrass metal concentrations.

Metal	Component I	Component II	Component III
Al	**0.920**	0.162	-0.043
As	**0.836**	0.288	0.161
Cd	**0.814**	0.435	0.007
Cr	**0.780**	0.489	0.052
Co	**-0.746**	0.389	0.274
Cu	0.140	**0.866**	-0.224
Fe	0.023	**0.681**	0.131
Hg	0.458	**0.676**	-0.035
Mn	0.187	**0.668**	-0.514
Ni	0.017	0.028	**0.693**
Pb	0.029	-0.165	**0.664**
Zn	0.494	-0.213	**-0.432**
Eigen value	4.844	1.991	1.475
% variation explained	32	24	13

Arsenic concentrations in seagrass at Lloyd Bay, Princess Charlotte Bay and Bathurst Bay (Figure 2.3), nickel concentrations in sediments and seagrass from the Cardwell site and zinc concentrations in seagrass from Pallarenda (Figure 2.6) all exceeded Australian sediment quality guidelines (ANZECC 1999). Sediment concentrations of chromium at the Moreton Bay east site (Figure 2.4) also exceeded Australian sediment quality guidelines. Seagrass concentrations of arsenic, chromium, iron and nickel were also higher than concentrations typically determined at other sampling locations ata number of sites (Table 2.7).

Principal Components Analysis was carried out using the combined sediment and seagrass metal concentration dataset. The first two components of the analysis accounted for 56% of the variance in the data (Table 2.8). Principal component I (32% of the variance) was positively correlated with metals including aluminium, arsenic, cadmium and chromium. Principal component II (24% of the variance) was correlated with copper, iron, mercury and manganese. The cluster dendrogram and PCA ordination tended to broadly separate sediment from seagrass samples, and distinctly separated the Cardwell and east Moreton Bay sediment samples and the Cardwell, Cairns and Pallarenda seagrass samples from the other sediment and seagrass samples (Figure 2.7).

2.3.3. Organochlorine Concentrations

Detectable concentrations (0.5-1.7 μg kg^{-1}) of diuron were present in sediments at 3 (Cairns, Cardwell and Moreton Bay West) of the 15 intertidal locations (Table 2.9). Organochlorines, PCBs, chlorpyrifos, atrazine and 2,4-D were not detected in intertidal sediment samples. Diuron was the only contaminant detected in intertidal seagrass samples, where its concentration ranged from 0.8 to 1.7 μg kg^{-1} (Table 2.9). The occurrence of diuron in seagrass was confined to samples collected between Townsville and Cairns and from western Moreton Bay. Detected seagrass tissue concentrations of diuron were usually higher than sediment concentrations. Organochlorines, PCBs, chlorpyrifos, and atrazine were not detected in intertidal seagrass samples (Table 2.10).

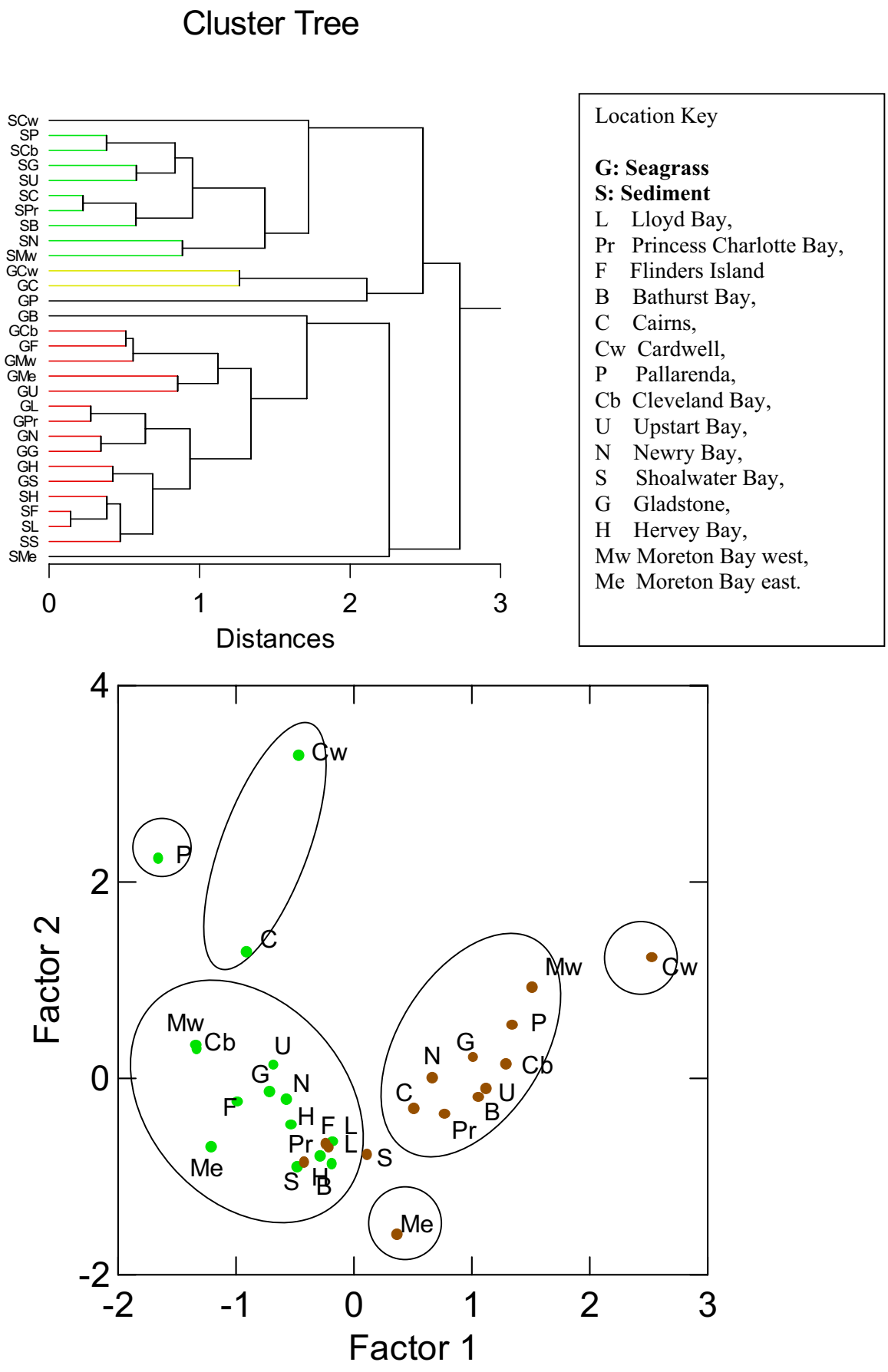

Figure 2.7. Classification and ordination of intertidal metal data.

Table 2.9. Pesticide concentrations, intertidal sediments 1997.

(All concentrations µg kg^{-1} dry weight).

Site	% $CaCO_3$	% org C	OCs	PCBs	Chlorpyrifos	Diuron	Atrazine	2,4-D
Lloyd Bay	9.2	0.34	<1.0	<50	<1.0	<0.5	<0.5	<10
Flinders Island	50.5	0.72	<1.0	<50	<1.0	<0.5	<0.5	<10
PC Bay	24.6	0.38	<1.0	<50	<1.0	<0.5	<0.5	<10
Bathurst Bay	32.3	0.76	<1.0	<50	<1.0	<0.5	<0.5	<10
Cairns	3.6	0.30	<1.0	<50	<1.0	**0.5**	<0.5	<10
Cardwell	1.4	2.2	<1.0	<50	<1.0	**1.7**	<0.5	<10
Pallarenda	2.1	0.11	<1.0	<50	<1.0	<0.5	<0.5	<10
Cleveland Bay	4.2	0.29	<1.0	<50	<1.0	<0.5	<0.5	<10
Upstart Bay	0.3	0.10	<1.0	<50	<1.0	<0.5	<0.5	<10
Newry Bay	2.9	0.68	<1.0	<50	<1.0	<0.5	<0.5	<10
Shoalwater Bay	7.4	0.18	<1.0	<50	<1.0	<0.5	<0.5	<10
Gladstone	5.9	0.07	<1.0	<50	<1.0	<0.5	<0.5	<10
Hervey Bay	3.5	0.06	<1.0	<50	<1.0	<0.5	<0.5	<10
E. Moreton Bay	<0.1	0.26	<1.0	<50	<1.0	<0.5	<0.5	<10
W. Moreton Bay	<0.1	0.52	<1.0	<50	<1.0	**0.6**	<0.5	<10

Table 2.10. Pesticide concentrations, intertidal seagrasses 1997.

(All concentrations µg kg^{-1} dry weight).

Site	Species	% lipid	OCs	PCBs	Chlorpyrifos	Diuron	Atrazine
Lloyd Bay	*H. uninervis*	0.90	<1.0	<50	<1.0	<0.5	<0.5
Flinders Island	*C. serrulata*	1.6	<1.0	<50	<1.0	<0.5	<0.5
PC Bay	*H. uninervis*	1.4	<1.0	<50	<1.0	<0.5	<0.5
Bathurst Bay	*C. serrulata*	na	<1.0	<50	<1.0	<0.5	<0.5
Cairns	*Z. capricorni*	1.2	<1.0	<50	<1.0	**0.6**	<0.5
Cardwell	*H. uninervis*	0.90	<1.0	<50	<1.0	**1.1**	<0.5
Pallarenda	*H. uninervis*	0.40	<1.0	<50	<1.0	**0.8**	<0.5
Cleveland Bay	*C. serrulata*	0.40	<1.0	<50	<1.0	<0.5	<0.5
Upstart Bay	*Z. capricorni*	0.90	<1.0	<50	<1.0	<0.5	<0.5
Newry Bay	*Z. capricorni*	0.30	<1.0	<50	<1.0	<0.5	<0.5
Shoalwater Bay	*Z. capricorni*	0.40	<1.0	<50	<1.0	<0.5	<0.5
Gladstone	*Z. capricorni*	0.30	<1.0	<50	<1.0	<0.5	<0.5
Hervey Bay	*Z. capricorni*	0.30	<1.0	<50	<1.0	<0.5	<0.5
E. Moreton Bay	*C. serrulata*	0.50	<1.0	<50	<1.0	<0.5	<0.5
W. Moreton Bay	*Z. capricorni*	0.40	<1.0	<50	<1.0	**1.7**	<0.5

na: not available

2.4. Discussion

2.4.1. Intertidal Sediment Pollutant Concentrations

A majority of sediments collected from intertidal sites were relatively coarse grained, and had concomitantly low concentrations of heavy metal and organochlorine pollutants associated with them. A majority of sites also contained high concentrations of silica, and low concentrations of $CaCO_3$, indicative of their predominantly terrigenous source. Fine-grained sediments tend to be transported further offshore (Larcombe *et al.* 1996), and it would be predicted that highest pollutant concentrations would occur at these offshore depositional sites (see Chapter 3). There were two exceptions. Nickel concentrations in a single sample from Cardwell which exceeded ANZECC (1999) guidelines for this metal in sediments and concentration of chromium in sediments from the eastern side of Moreton Bay also exceeded ANZECC (1999) sediment guidelines. High chromium concentrations have also been detected in bivalves from Moreton Bay (A. Moss, pers comm). Elevated concentrations of nickel are likely to be due to natural sources as Cardwell is relatively remote from urban influences, and adjacent to igneous bedrock source material. The source(s) of chromium in Moreton Bay is unknown. Intertidal sediments were also relatively uncontaminated with pesticide residues. The low concentrations of diuron detected in sediments from the wet tropics region and Moreton Bay are likely to be from runoff from sugar-cane growing areas (Hamilton and Haydon 1996).

2.4.2. Intertidal Seagrass Pollutant Concentrations

Intertidal seagrasses contained relatively high concentrations of arsenic, chromium, iron and nickel compared with values recorded previously in marine angiosperms. As a majority of the sampling sites are remote from human influence, it must be assumed that seagrass (and sediment) metal concentrations are largely from natural sources. The weak relationship between seagrass and sediment metal concentrations has been related elsewhere to temporal variability in tissue metal concentrations as well as spatial variability in sediment metal concentrations (Ward *et al.* 1986).

2.4.3. Pollutant Impacts on Intertidal Seagrass Environments

Pollutants present in intertidal (and subtidal) seagrass environments have the potential to impact dugong populations directly following bioaccumulation of contaminants via seagrass consumption, or, indirectly by impacting on seagrass health to reduce the availability of the animals food resource. As yet, there is little evidence of adverse effects to seagrasses resulting from heavy metal exposure (Short and Wyllie-Echeverria 1996). However, the sublethal toxicity of elevated concentrations of copper and zinc to *Halophila ovalis* has been demonstrated (Ralph and Burchett 1998), and laboratory studies have demonstrated that zinc, iron, and copper may inhibit growth of bacteria associated with *Zostera marina* and *Halodule wrightii* rhizomes (Smith *et al.* 1982). Mercury, nickel and lead will also significantly reduce nitrogen fixation (acetylene reduction) by symbiotic nitrogen fixing bacteria associated with the roots and rhizomes of *Z. marina,* potentially affecting the supply of nutrients to seagrass (Brackup and Capone 1985). Concentrations of metals detected in intertidal sediments in this study, were, however, an order of magnitude lower than the concentrations predicted to result in either of these types of impacts.

2.4.4. Intertidal Pollutant Monitoring

The utility of seagrasses as biomonitors of pollutant concentrations has been assessed with conflicting results. Some studies of seagrasses have supported the concept that these plants can act as efficient bioaccumulators of metals in coastal waters (Bryan and Langston 1992; Warnau *et al.* 1996; Nicolaidou and Nott 1998; Schalcher-Hoenlinger and Schlacher 1998; Muse *et al.* 1999). In contrast, other studies have recommended that only specific metals be monitored using seagrass tissue (Brix and Lyngby 1983; Ward *et al.* 1986; Güven *et al.* 1993). The lack of correlation between sediment and seagrass metal concentrations together with the generally higher sediment metal concentrations found in this study implies that with the exception of cadmium and mercury, metal concentrations present in sediment samples are a more appropriate indicator of metal status of intertidal Great Barrier Reef sites. Depending on any seasonal variability, environmental concentrations of cadmium and mercury may be more accurately monitored using seagrass tissue concentrations.

However, quantification of metal concentrations in seagrass may help in monitoring metal availability to these animals, as dugongs feed almost exclusively on seagrasses, and as a consequence, the plants are probably a major source of metals for these animals (Denton *et al*. 1980; Ward 1989). Regional differences in seagrass and sediment metal concentrations suggest that metal concentrations in dugong tissue may be influenced by local metal concentrations. However, it has been postulated that this has not adversely impacted dugong health, because metal concentrations accumulated are within the animals tolerance thresholds (Denton *et al.* 1980). Although much data have been collected on the variability of metal concentrations in marine mammals (Denton *et al.* 1980; Thompson 1990; Wood and Van Vleet 1996; Holsbeek *et al.* 1998; Parsons 1999), with the exception of mercury, no experimental or field collected data has demonstrated a toxic impact of accumulated metals in these animals (O'Shea 1999). Diuron was the only organochlorine compound detected in intertidal sediments or seagrasses in this study and intertidal organochlorine concentrations are unlikely to represent a significant direct threat to dugong populations. The potential long-term environmental impact of diuron on local intertidal seagrasses is essentially unknown and is assessed further in Chapter 4.

2.5. Conclusions

Great Barrier Reef intertidal sediments are relatively coarse grained and contain a low organic carbon content. As a consequence they carry low concentrations of heavy metal and pesticide pollutants. These contaminants are more likely to be concentrated further offshore in muddy depositional zones of the Great Barrier Reef (Chapter 3). Based on current understanding, concentrations of pollutants detected in intertidal sediments are, unlikely to present a direct threat to dugong populations. The indirect impact of intertidal herbicide concentrations to dugongs through impact on seagrass health is considered further in Chapter 4.

Chapter 3: Subtidal sediment pollutant concentrations

J Mueller

Subtidal sediment sampling, Repulse Bay, Dec 1999

CHAPTER THREE: SUBTIDAL SEDIMENT POLLUTANT CONCENTRATIONS

3.1. Introduction

Some 25 major river catchments discharge directly into the Great Barrier Reef World Heritage Area (Moss *et al.* 1992b). The bulk of their terrigenous inputs are deposited within 10 km of the Queensland coast (Larcombe *et al.* 1996), and this nearshore deposition zone containing mangroves, soft-bottom communities, seagrass and fringing reef environments is, as a consequence, most at risk from anthropogenic contaminants. These include heavy metals and organochlorines sourced from Queensland coastal catchments.

Although most organochlorine contaminants were banned for use in Queensland in the late 1980s, compounds including lindane (γ-HCH), aldrin, heptachlor, chlordane, DDT and dieldrin were used extensively in Queensland agricultural for the control of insects (Hamdorf 1992; von Westernhagen and Klumpp 1995) and for a wide range of domestic, public health and agricultural purposes in urban areas (Mortimer 1998). As a consequence, these pollutants have been detected as contaminants of northern Australian estuarine sediments (Dyall and Johns 1985; Mortimer 1998) and marine biota (McCloskey and Duebert 1972; Olafson 1978; Hamdorf 1992; von Westernhagen and Klumpp 1995; Kannan *et al.* 1995; Moss and Mortimer 1996; Mortimer 2000). Seafoods for human consumption collected along the tropical north-eastern Australian seaboard have also been shown to be contaminated with low concentrations of PCBs, DDT and its metabolites, chlordane compounds and lindane isomers (Kannan *et al.* 1994).

Heavy metal contaminants including arsenic, cadmium, copper, mercury, lead, nickel and zinc have also been released, and continue to be released, into the aquatic environment through urban stormwater and wastewater discharges and as a consequence of agricultural activity. Zinc and copper are used in small amounts as fertilizers in some soils deficient in these elements, and arsenic, cadmium and mercury are constituents of some fungicides (Hunter 1992).

Arsenic, cadmium and zinc also occur as contaminants of phosphatic fertilisers applied to Queensland soils (Rayment *et al.* 1989; Tesiram 1995). In addition, a number of triazine (atrazine) and phenylurea and chlorophenoxy acid organochlorine herbicides (diuron and 2,4-D) and organophosphate pesticides (chlorpyrifos) are in wide use by the Queensland sugar cane industry (Hamilton and Haydon 1996).

The persistent nature of many of these and related contaminants, together with possible continued illegal use of banned organochlorine compounds raises the potential for continued long-term chronic exposure to plants and animals of the Great Barrier Reef. The data presented here represent the first comprehensive survey of contemporary concentrations of heavy metal and organochlorine pollutants in subtidal marine sediments collected along the Great Barrier Reef coastline.

3.2. Materials and Methods

3.2.1. Sample Collection

Sediment samples were collected from 52 Queensland subtidal sites located between Cape York and Gladstone in June 1998 and December 1999 (Figure 3.1). Sampling sites included major estuarine areas, and northward facing embayments as well as open coastal areas. Sampling sites were generally in shallow (<10 m) waters. Samples were collected using a modified van-Veen grab sampler or by SCUBA diver (Figure 3.2). At each site, two replicate samples were collected. Replicate samples were collected approximately 500 to 1000 m apart. Each replicate consisted of a sample composited from 3 grab samples. Samples for heavy metals analysis were collected in acid-washed plastic containers and samples collected for chlorinated hydrocarbon analyses were collected in solvent-washed glass containers. Sediment samples were frozen following collection.

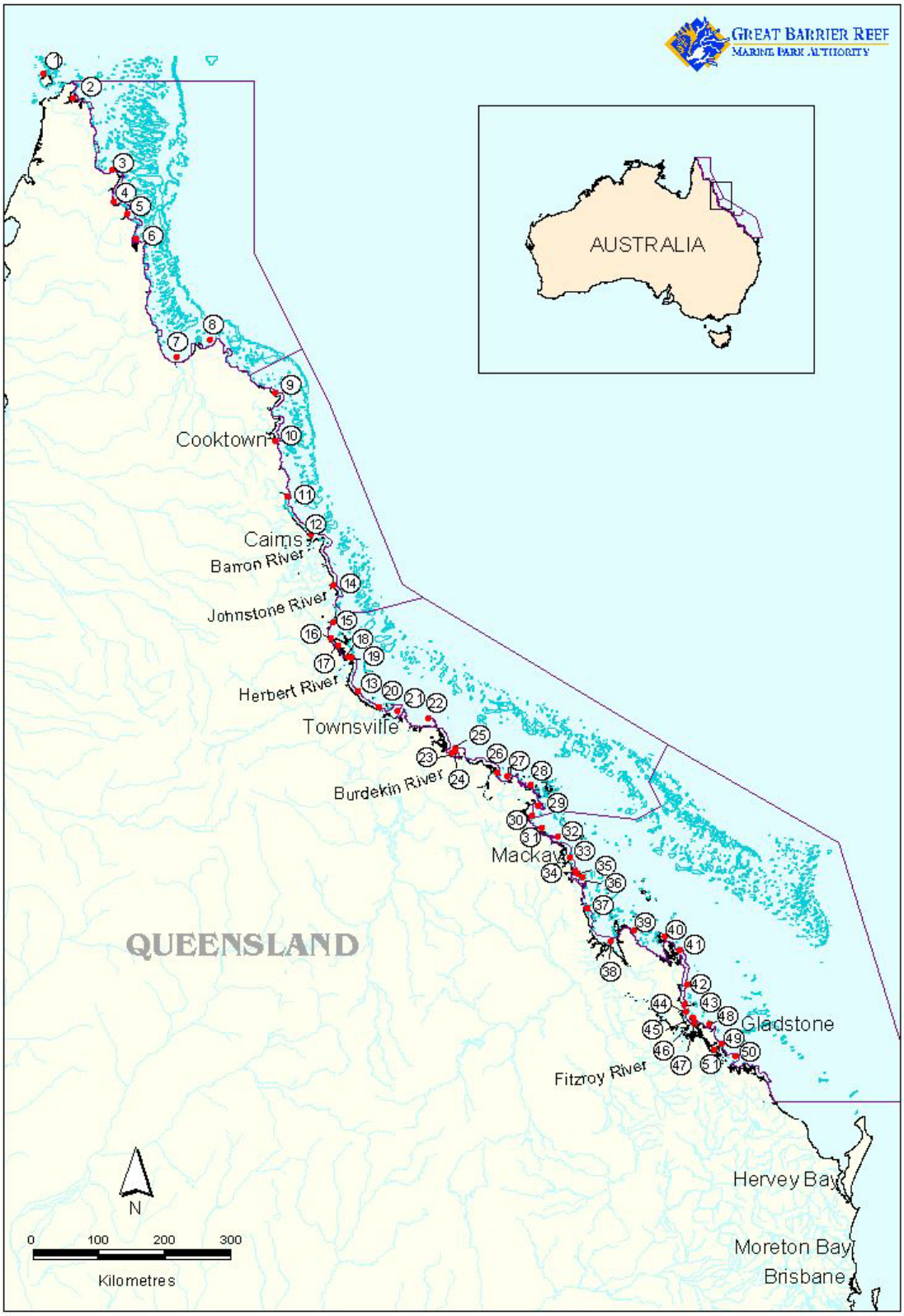

Figure 3.1. Subtidal sediment sampling sites, Queensland, 1998 and 1999.

(Locations are detailed in Tables 3.8 and 3.9).

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Figure 3.2. Subtidal sediment sampling, on the northern and central Queensland coast, 1998 and 1999.

3.2.2. Heavy Metal Analysis

Samples for heavy metals analysis were analysed at the NATA certified metals laboratory of the Queensland Department of Natural Resources, Brisbane. Frozen sediments were transported to the analytical laboratory where the samples were thawed and divided in two. One portion was wet sieved in plastic sieves and separated into four size fractions (>2000 μm, 200-2000 μm, 63-200 μm and <63 μm) and weighed. The second portion was ground to <50 μm using a shatter box grinding mill. Ground sediment samples were pelleted using the pressed powder technique (Gladstone 1996) and analysed by X-ray fluorescence (ARL-XRF 8480) for aluminium (Al), arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), silica (Si) and zinc (Zn) concentrations. Samples for selenium (Se) determination were digested using nitric:perchloric:sulphuric acid (13:1:2) and analysed by hydride generation atomic absorption spectometry (AAS, Perkin Elmer 4100ZL). Cadmium (Cd) and mercury (Hg) determination samples were digested with nitric:hydrochloric acid (6:2) following 2 hours exposure to a steam bath. Cadmium was analysed by graphite furnace AAS, and mercury by hydride generation AAS (Perkin Elmer 4100ZL).

3.2.3. Pesticide Residue and PCB Analyses

Samples for pesticide and PCB analysis were analysed at the NATA certified pesticide laboratory of Queensland Health and Scientific Services, Brisbane, using routine laboratory methods. Both replicate samples collected from each site in the 1998 survey were analysed, whereas with the exception of samples collected from Repulse Bay, cost constraints only allowed one of the two replicates collected from each site in the 1999 survey to be analysed. For the majority of compounds (which included aldrin, atrazine, chlorpyrifos, endosulfan (α, β and endosulfan sulfate), dieldrin, DDTs (pp-DDD, pp-DDE and pp-DDT), diuron (DCMU [3-(3',4'-dichlorophenyl)-1,1-dimethylurea]), hexachlorobenzene, heptachlor, heptachlorepoxide, lindane and PCBs), approximately 100 g aliquots of the thawed and homogenised sediments were weighed into an extraction vessel and extracted into 100 mL acetone/n-hexane (1:1) on a shaker, overnight. The extract was then centrifuged and the supernatant decanted.

Twenty mL of saturated NaCl was added to the extract prior to liquid/liquid partitioning with dichloromethane (150 mL). The dichloromethane fraction was filtered through anhydrous sodium sulfate and the partitioning steps were repeated. The combined fractions of dichloromethane containing the compounds of interest were concentrated, transferred into n-hexane and made up to a volume of 3 mL. One mL of the extract was set aside for analysis of diuron and atrazine, while the second fraction of 2 mL (67 % of extract) was subject to a clean-up in a column (18 mm I.D.) filled with 20 cm of Florisil™ (5 % deactivated with H_2O). Compounds of interest were eluted in two separate fractions using 120 mL of n-hexane/diethylether (94/6 V/V) followed by 90 mL of n-hexane/acetone (90/10 V/V).

The individual fractions were concentrated to 1 mL and the first fraction was analysed for chlorpyrifos using a gas chromatograph equipped with a flame photometric detector (GC-FPD, (Hewlett-Packard 6890A) for quantification and a gas chromatograph equipped with nitrogen phosphorous detector (GC-NPD, Hewlett-Packard 6890A) for confirmation. The first fraction (n-hexane/diethylether eluate) was then subjected to a sulphur removal clean-up following US-EPA method 3660A. Samples were transferred to test tubes and 1 mL of tetrabutyl ammonium hydrogen sulfate saturated with anhydrous sodium sulphite, 2 mL isopropanol and small amounts of extra anhydrous sodium sulphite were added. After shaking (60 s), 5 mL of H_20 was added and the samples were again shaken (60 s). The top layer was transferred using an extra 2 mL of n-hexane and concentrated under a gentle stream of nitrogen to 1 mL. Both the first fraction (after sulphur clean-up), and the second fraction concentrated directly from the Florisil™ column were then analysed for aldrin, endosulfan (α, β and endosulfan sulfate), dieldrin, DDTs (pp-DDD, pp-DDE and pp-DDT), hexachlorobenzene, heptachlor, heptachlorepoxide, lindane and PCBs using a dual column gas chromatograph equipped with electron capture detectors (Shimadzu ECD, GC-17A).

For the 1 mL fraction (33 % of extract) set aside for diuron and atrazine analysis, the solvent was exchanged by carefully evaporating the n-hexane and subsequently adding first water and then methanol. The samples were made up to a final volume of 1 mL and analysed on a high performance liquid chromatography system coupled with a triple stage quadropole mass spectrometer (HPLC MS/MS).

The HPLC MS/MS consisted of a LC-200 series pump, series 200 autosampler and API 300 MS/MS with atmospheric pressure chemical ionisation interface (Perkin-Elmer Sciex Instruments, Thornhill, Ontario, Canada). An Altima C18 column at 35^{o}C was used. Chromatography consisted of a linear gradient from 40-90% methanol over 5 mins, with a final isocratic stage holding at 9% methanol for 4 min. The total flow rate was 1 mL min^{-1}. The mobile phase was buffered to 5 mM with ammonium acetate. Injection volumes of 10 µL were used.

Samples were also analysed for 2,4 D and 2,4,5 T. Subsamples of approximately 50 g were extracted using 100 mL of 0.1 M NaOH on a shaker for 4 hours. The samples were centrifuged and the supernatant was decanted, and acidified to a pH < 2 using concentrated H_2SO_4. If precipitation occurred after acidification, the centrifugation was repeated. The compounds of interest were then extracted into diethylether (2 * 100 mL) using liquid-liquid partitioning. The diethylether was filtered through anhydrous sodium sulfate and the combined fractions are concentrated to approximately 2 mL. The compounds of interest were instantaneously methylated using freshly prepared diazomethane which was collected in diethylether prior to use. The extract was then concentrated, transferred into n-hexane and made up to a final volume. The samples were analysed using a gas-chromatograph coupled to a mass-spectrometer (Shimadzu GCMS-QP5050A). Quantification was performed in selective ion monitoring mode and confirmed using full ion-scan.

3.2.4. Sediment Calcium Carbonate and Organic Carbon Analyses

Sediment calcium carbonate content was determined by a weight loss gravimetric method (Blakemore *et al.* 1987). For total organic carbon content (TOC) quantification in sediment samples, inorganic carbonates were first removed using an acid catalysed digestion (10% HCl, 1% $FeCl_2$ at 70^{o}C). The remaining material was dried and subjected to a combustion procedure (LECO induction furnace) with subsequent detection of CO_2 (LECO WR12 CO_2 detector).

3.2.5. Quality Assurance and Statistical Analysis

All chlorinated hydrocarbon analytical methods were subject to standard QA/QC procedures. Blanks and a series of spikes, which contained known quantities of the analytes, were included in each batch (usually 12 samples). The reporting limit was defined as 5 times the average values of the baseline noise signals and/or 3 times the concentration in a representative blank. QC/QA data are presented in Table 3.1. No contaminants were detected in reagent blanks. Blanks and certified reference materials (Marine Sediment Mess-2, National Research Council, Canada) were analysed concurrently with sediment samples to ensure consistency and accuracy of recoveries over metal analyses (Table 3.2).

Table 3.1. Percentage recovery of spiked organochlorine samples.

Compound	Subtidal sediments 1998	Subtidal sediments 1999
OCs	68-114	50-105
PCBs	nd	nd
Endosulphan	nd	84-91
Chlorpyrifos	77	69-75
Atrazine	53	80-93
Diuron	96	73-102
2,4-D	67	nd

nd: not determined

Metal data were graphed and inspected for gross deviations from normality and where necessary, transformed (Log_{10}) prior to analysis. Non-detectable values were set at half the detection limit for that metal for statistical analyses. Pearson correlation co-efficients and their associated Bonferroni-adjusted probabilities were calculated for sediment metals and physico-chemical parameters.

Table 3.2. Standard reference material (Marine sediment Mess-2, National Research Council, Canada) recoveries.

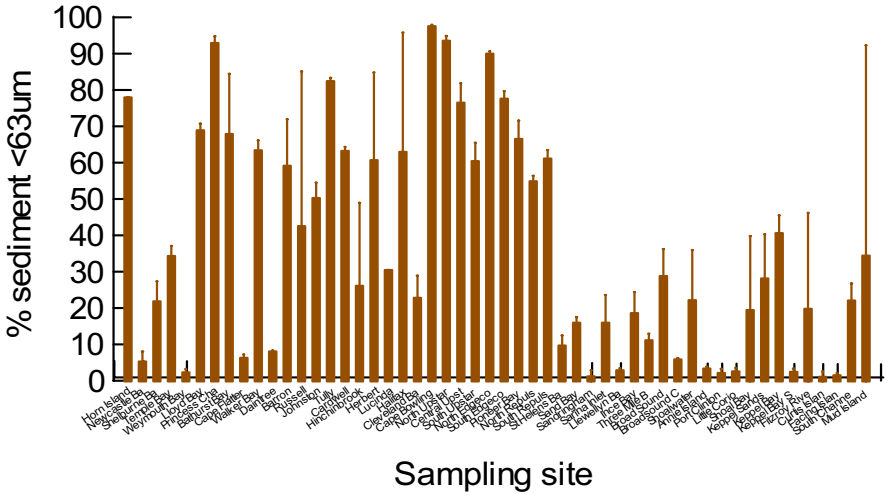
Metal 1998 analyses	Al %	As mg kg^{-1}	Ca %	Cd mg kg^{-1}	Co mg kg^{-1}	Cr mg kg^{-1}	Cu mg kg^{-1}	Fe %	Hg mg kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Pb mg kg^{-1}	Si %	Zn mg kg^{-1}
Mess 2	8.10	21.2	1.53	0.26	15	113	39	4.24	0.098	350	49	22	26.0	166
Mess 2	8.14	21.3	1.50	0.25	15	113	38	4.16	0.097	343	48	21	25.6	161
Mess 2	8.30	20.6	1.52	0.25	14	113	37	4.28	0.095	350	51	20	25.7	168
Mess 2	7.88	21.0	1.43	0.25	13	109	39	4.06	0.093	331	45	17	24.5	157
Mess 2	8.24	20.5	1.51	0.25	13	114	40	4.24	0.095	349	48	21	25.5	167
Analyses mean	8.13	20.90	1.50	0.25	13.64	112.40	38.82	4.19	0.10	344.48	48.18	20.18	25.44	163.76
Analyses SD	±0.16	±0.36	±0.04	±0.01	±0.88	±2	±1	±0.09	±0.007	±8	±2	±2	±0.6	±4
1999 analyses														
Mess-2	8.51	21.1	1.59	0.26	10.3	113	31.2	4.35	0.103	369	50.6	19.4	25.89	174
Mess-2	8.34	21.2	1.54	0.266	11.9	111	33	4.30	0.105	358	50.5	21.8	25.53	168
Analyses mean	8.42	21.1	1.56	0.26	11.1	112	32.1	4.32	0.104	363	50.5	20.6	25.7	171
Analyses SD	±0.12	±0.7	±0.03	±0.004	±1.1	±2	±1.3	±0.03	±0.001	±7	±0.07	±1.7	±0.26	±4
Certified value														
Mean	8.57	20.7	-	0.24	13.8	106	39.3	4.35	0.092	365	49.3	21.9	27.8	172
2 Std. Deviations	±0.26	±0.8	-	±0.01	±1.4	±8	±2	±0.22	±0.009	±21	±1.8	±1.2	±1.1	±16

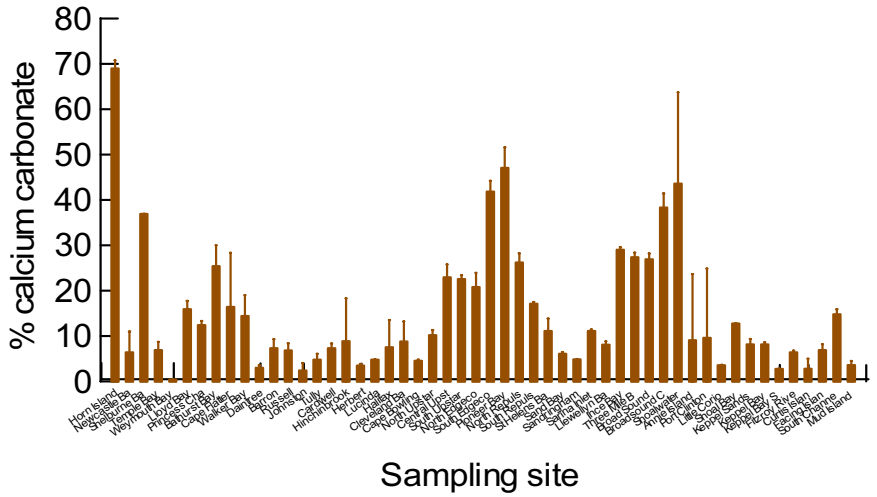
Regression analysis was used to explore the relationship between sediment aluminium and iron and other metal concentrations. Where a significant and strong correlation existed (r^2>0.6), aluminium or iron concentration was used as a metal normaliser to highlight anthropogenic enrichment of these metals (Windom *et al.* 1989; Loring 1991). Differences in metal concentrations between sampling locations were compared using two-way analysis of variance (ANOVA), with sampling geographic region (far northern, northern, central, southern and capricorn) and sampling site exposure regime (open coast or sheltered embayment) as analysis factors. Significant differences in metal concentrations were located using a Tukey HSD multiple comparison test with an experiment-wise type 1 error probability of 0.05 (Ott 1993). Sediment metal data were standardised to *Z* scores and an agglomerative hierarchical algorithm using complete clustering used to classify the sediment metal data and Principal Component Analysis (PCA) used to ordinate the data. Euclidean distances were utilized to calculate dissimilarities. The presence of natural groupings in the data was defined by concurrence in both the classification and the ordination analyses (Clarke and Warwick 1994). All statistical computations were carried out with the aid of the SYSTAT V7.0 package (Wilkinson 1996).

3.3. Results

3.3.1. Sediment Physico-chemical Parameters

Sediment samples were variable with respect to physico-chemical characteristics (Figure 3.3). Sampling sites situated in sheltered northward facing bays or adjacent to river mouths contained the highest concentrations of fine sediment. Sheltered sites also tended to contain lowest concentrations of calcium carbonate material and higher silica concentrations.





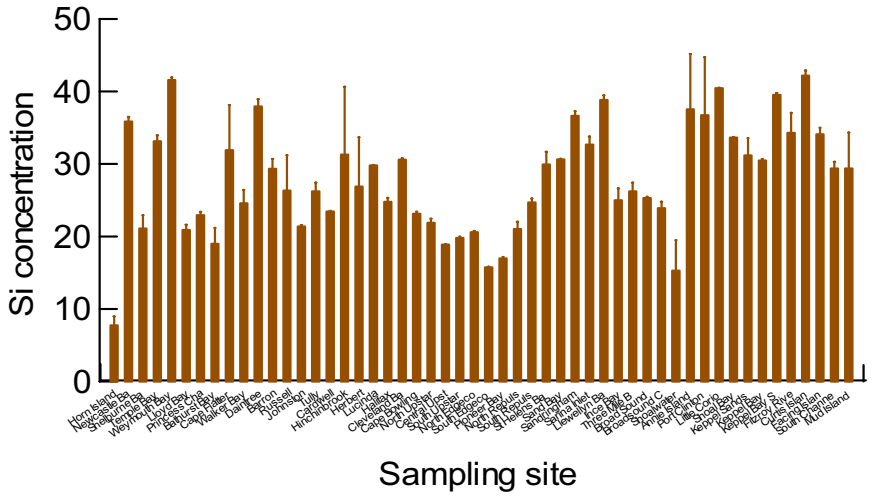


Figure 3.3. Subtidal sediment particle size, calcium carbonate and silica content. (Silica mg kg^{-1} dw, error bars = 1 SEM, n=2).

3.3.2. Sediment Metal Concentrations

Detectable concentrations of all metals analysed were present in subtidal sediment samples. All metal concentrations were positively correlated with the fine (<63 μm) sediment fraction, and with the exception of cadmium, all metal concentrations were negatively correlated with sediment calcium carbonate content (Table 3.3). Metal concentrations were generally low in comparison with concentrations detected in sediments from Queensland coastal waters in the past (Table 3.4), although sediment concentrations of chromium and nickel exceeded ANZECC (1999) sediment quality guideline (Figures 3.5 and 3.7 respectively).

Sediment metal concentrations were significantly variable amoung sampling regions and with degree of exposure (i.e. proximity to river mouth or open coast (Figures 3.4 to 3.7 and Table 3.5). Highest average concentrations of all metals were associated with sediments collected from more sheltered locations. Sampling sites located along the northern and central Great Barrier Reef coast (i.e. Mackay to Port Douglas) contained highest concentrations of all metals except cadmium and chromium. Highest average concentrations of cadmium were contained in sediments collected from far northern sites (north of Port Douglas). Highest average concentrations of chromium were present in sediments collected from both northern and capricorn (southern) sampling sites.

With the exception of arsenic and zinc, subtidal sediment metal concentrations were not strongly correlated with either aluminium or iron concentrations, precluding their use as normalisers of sediment metal concentrations (Table 3.6).

The first two components of a principal components analysis of standardised sediment metal concentrations accounted for 80% of the variance in the data (Table 3.7). Principal component I (40.4% of the variance) was associated with aluminium, lead, zinc, arsenic, iron, manganese, mercury and copper concentrations. Component II (39.3% of the variance) was associated with nickel, cobalt, chromium and cadmium concentrations. The cluster dendrogram and PCA ordination isolated samples collected adjacent to the Johnston River from other samples (Figure 3.8).

Table 3.3. Pearson correlation coefficient matrix, including Bonferroni-adjusted probabilities for Queensland sediment metal data.

	Depth	$CaCO_3$	>2mm	200-2000 µm	63-200 µm	<63µm	Al	Fe	Si
Al	-0.318	-0.223	-0.135	**-0.318*** **	**-0.559*** **	**0.754*** **		**0.907*** **	**-0.486*** **
As	-0.103	-0.257	-0.006	-0.259	-0.227	**0.381***	**0.657*** **	**0.681*** **	**-0.226**
Cd	-0.282	0.301	-0.156	-0.219	-0.272	**0.427****	**0.365***	**0.441****	**-0.532*** **
Co	-0.286	-0.242	-0.170	-0.107	-0.240	0.328	**0.547*** **	**0.764*** **	-0.234
Cr	-0.118	-0.230	-0.292	-0.300	-0.097	0.346	**0.494*** **	**0.729*** **	-0.197
Cu	**-0.427****	-0.226	-0.207	-0.224	**-0.454*** **	**0.610*** **	**0.774*** **	**0.865*** **	**-0.380***
Fe	-0.278	-0.234	-0.178	-0.325	**-0.464*** **	**0.678*** **	**0.907*** **		**-0.458*** **
Hg	**-0.393***	-0.162	-0.218	-0.288	**-0.495*** **	**0.691*** **	**0.818*** **	**0.883*** **	**-0.479*** **
Mn	-0.071	-0.331	-0.162	-0.211	-0.113	0.275	**0.646*** **	**0.724*** **	-0.142
Ni	-0.320	-0.270	-0.210	-0.190	**-0.365***	**0.506*** **	**0.732*** **	**0.876*** **	-0.322
Pb	**-0.442****	-0.290	-0.173	-0.179	**-0.458*** **	**0.576*** **	**0.816*** **	**0.650*** **	-0.283
Si	0.299	**-0.717*** **	0.184	**0.486*** **	**0.444****	**-0.766*** **	**-0.486*** **	**-0.458*** **	
Zn	**-0.373***	-0.215	-0.244	-0.303	**-0.533*** **	**0.742*** **	**0.945*** **	**0.942*** **	**-0.476*** **

*0.05<p<0.01, **0.001<p<0.01, ***p<0.001

Table 3.4. Comparison of Australian subtidal sediment metal concentration ranges.
(All metal concentrations mg kg^{-1}).

Parameter	Torres Strait[1]	Cleveland Bay[2]	Whitsundays[3]	Keppel Islands[4]	This study (range)	This study (mean)
Al	0.20-10.2		3.4-5.5		0.3-10.2	4.61
As	1-36		2.6-7.5		0.7-20	8.97
Cd	0.01-0.21		3.1-3.8	0.05-0.42	0.005-0.07	0.01
Co	1-17			4-20	3-36	4.80
Cr	5-103		39-59	5-75	5-207	43.46
Cu	2-44	9-70	19-46	5-28	4-32	7.95
Fe	900-48600	8000-48000	14558-28005	596-25282	20-67300	19600
Hg	<0.05-0.12				0.005-0.07	0.02
Mn	69-724	nd-1200	292-348	143-847	5-1006	373.47
Ni	4-52	3-178	18-48	8-61	5-90	14.22
Pb	0.5-24	<5-53	9.2-17.9	7-24	2-39	14.79
Zn	2-105	160-460	36-76	37-114	6-117	34.76

[1]Dight and Gladstone 1993; [2]Reichelt and Jones 1994; [3]Blake 1996; [4]Ahlers and Szymczak 1993.

Table 3.5. Summary of ANOVAs of subtidal metal concentrations. Regions joined by a line were not significantly different. (All data Log $_{10}$ transformed prior to analyis).

Metal	Factor	F	Multiple comparison
Al	Region	10.560***	CP S FN C N
	Exposure	7.463**	Exposed<Sheltered
	Interaction	0.313	
As	Region	6.211***	FN CP S C N
	Exposure	1.627	
	Interaction	0.708	
Cd	Region	2.339	
	Exposure	0.052	
	Interaction	3.202*	
Cr	Region	6.994***	
	Exposure	0.587	
	Interaction	3.464*	
Co	Region	3.461*	
	Exposure	11.262**	
	Interaction	3.461*	
Cu	Region	7.564***	S CP FN C N
	Exposure	4.224*	
	Interaction	0.136	
Fe	Region	6.195***	FN CP S N C
	Exposure	0.179	
	Interaction	0.563	
Mn	Region	15.634***	S CP FN C N
	Exposure	3.306	
	Interaction	0.780	
Hg	Region	21.168***	
	Exposure	0.290	
	Interaction	2.919*	
Ni	Region	12.338***	S CP FN C N
	Exposure	5.394*	Exposed<Sheltered
	Interaction	1.301	
Pb	Region	14.532***	S CP FN C N
	Exposure	5.597*	
	Interaction	1.388	Exposed<Sheltered
Zn	Region	18.465***	S CP FN C N
	Exposure	7.082 **	Exposed<Sheltered
	Interaction	1.461	

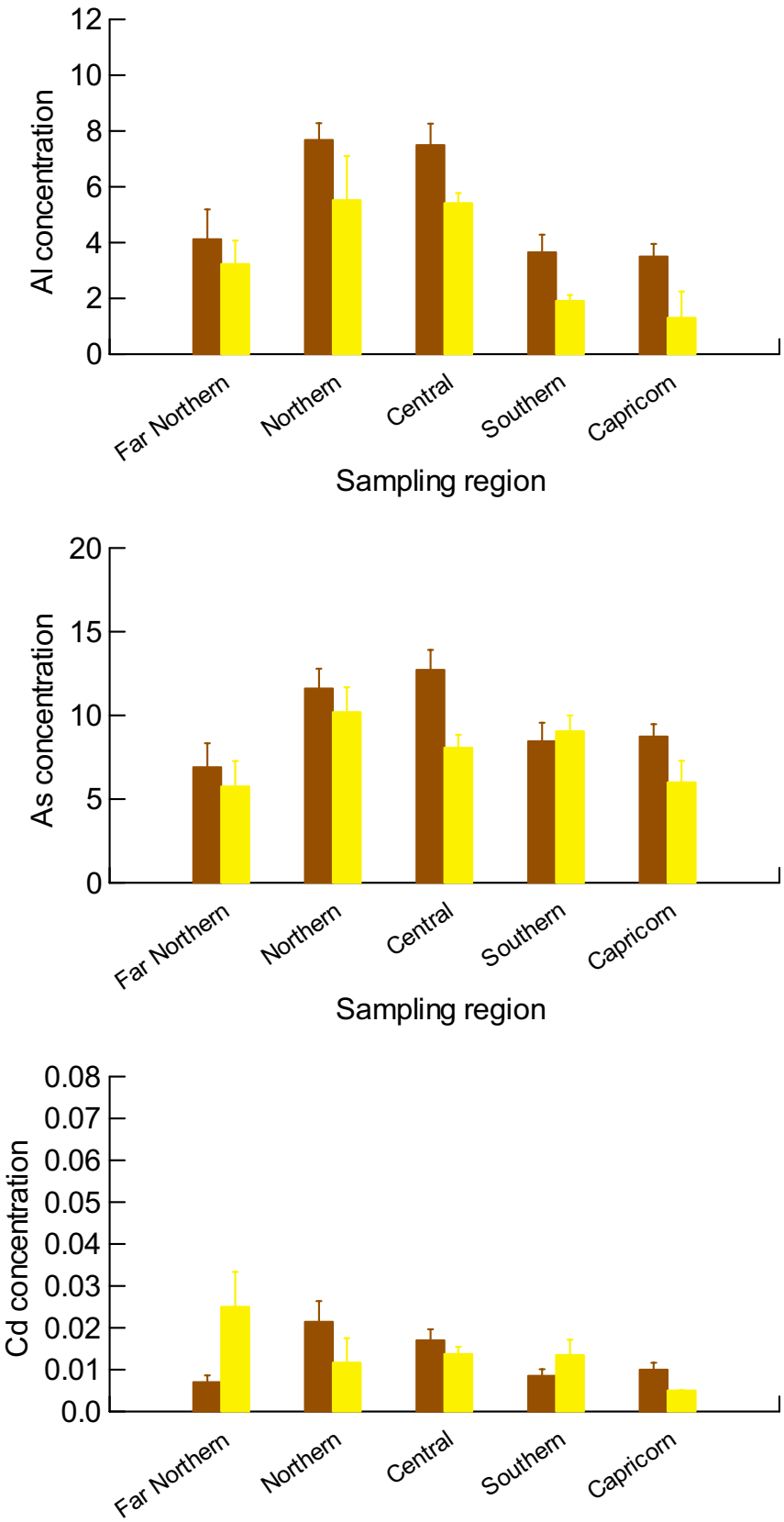


Figure 3.4. Queensland subtidal Al, As, and Cd concentrations.

(All conc. mg kg^{-1}, error bars = 1 SEM). Yellow = open coast, brown = embayments.

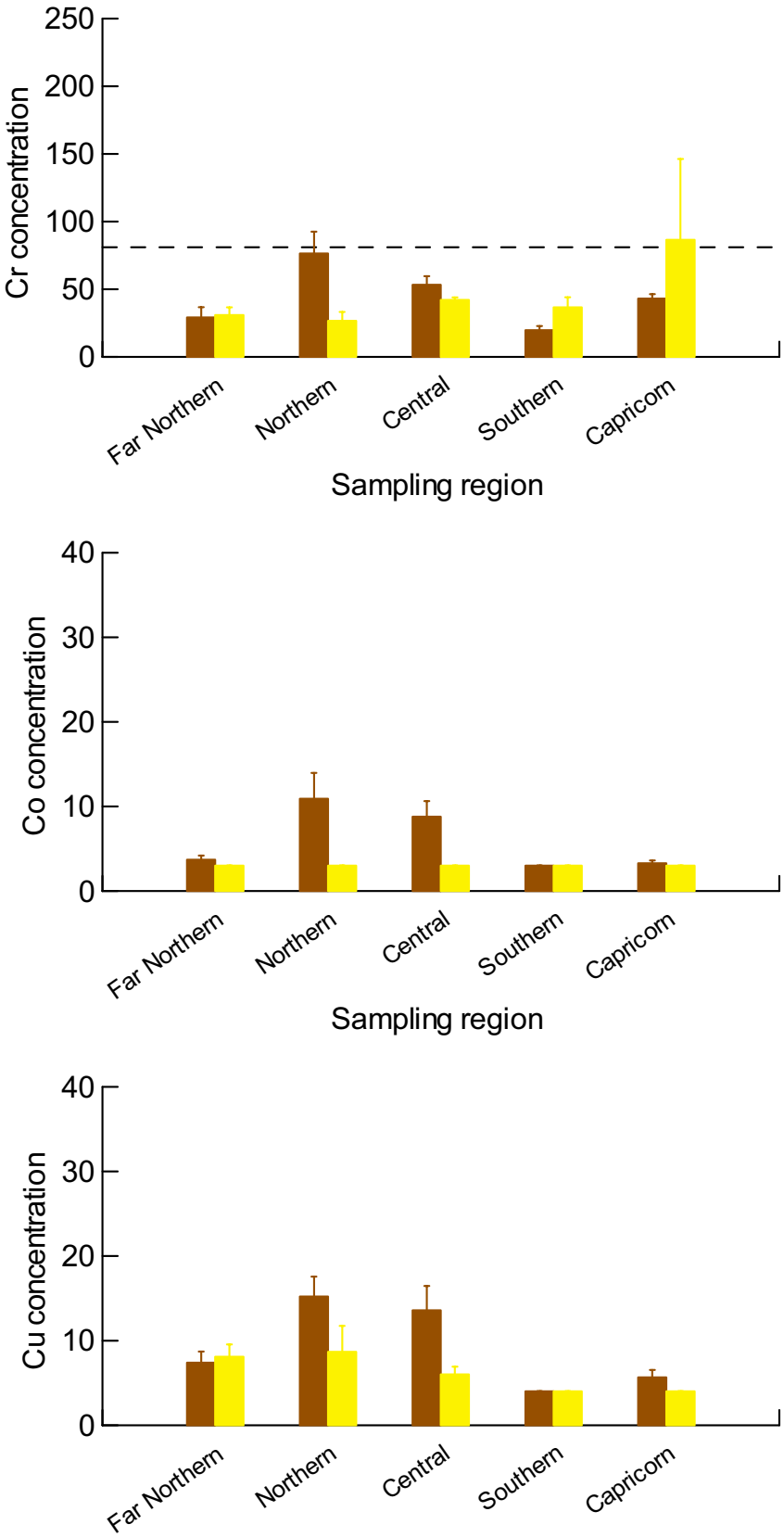


Figure 3.5. Queensland subtidal Cr, Co and Cu concentrations.

(All conc. mg kg^{-1}, error bars = 1 SEM). Yellow = open coast, brown = embayments.

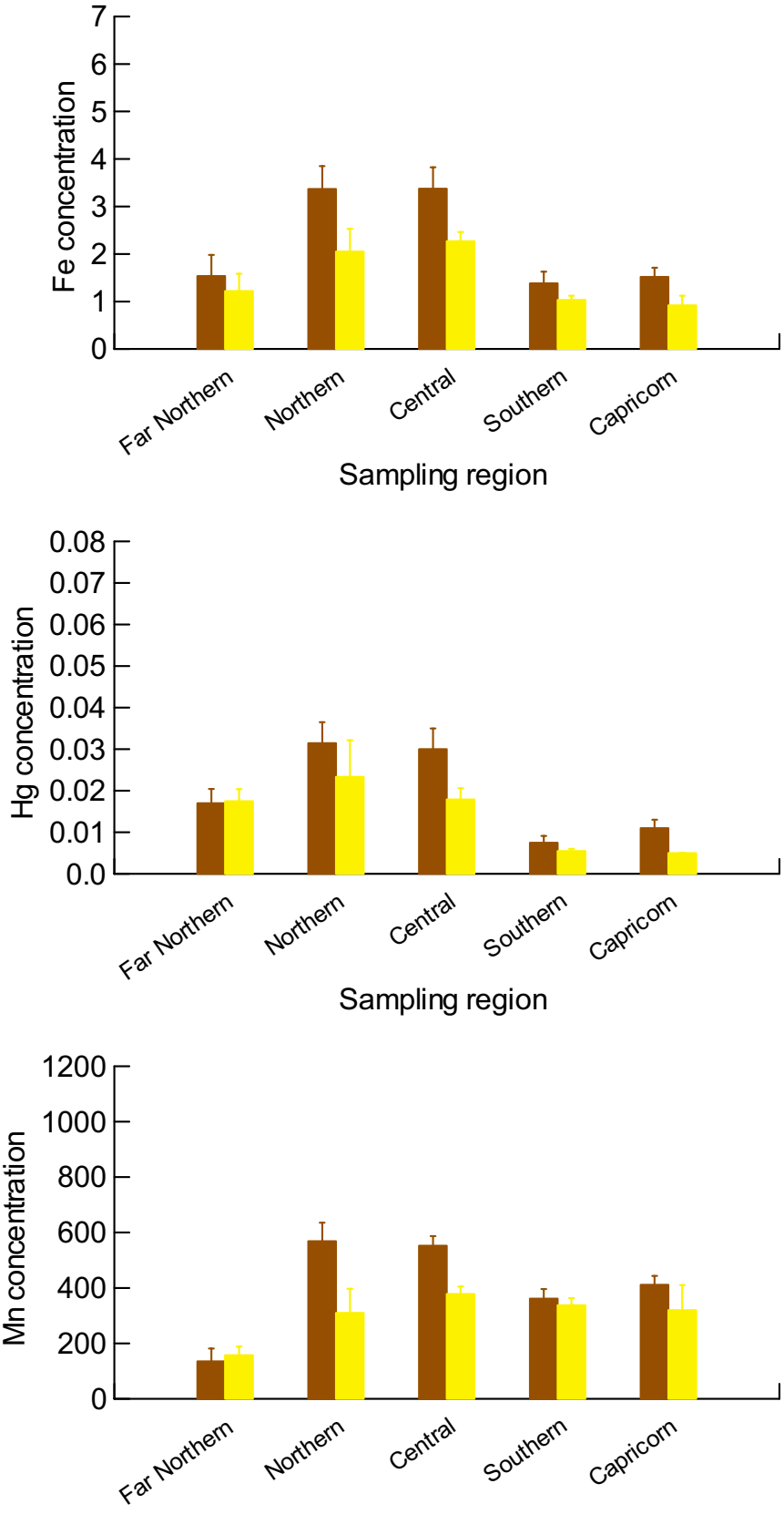


Figure 3.6. Queensland subtidal Fe, Hg and Mn concentrations.

(All conc. mg kg^{-1}, error bars = 1 SEM). Yellow = open coast, brown = embayments.

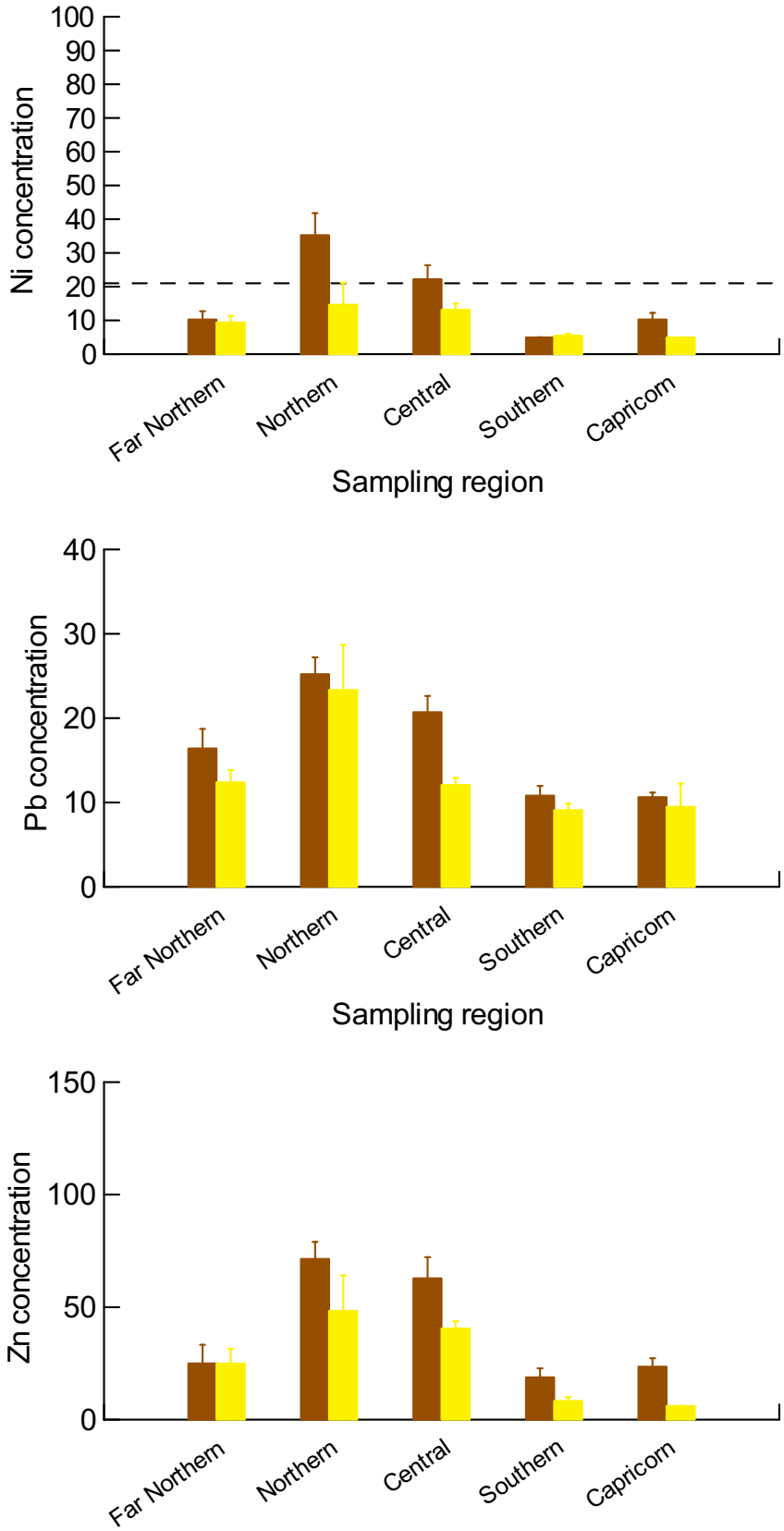


Figure 3.7. Queensland subtidal Ni, Pb and Zn concentrations.

(All conc. mg kg^{-1}, error bars = 1 SEM). Yellow = open coast, brown = embayments.

Table 3.6. Queensland subtidal sediment heavy metal concentration regression r^2 values.

	Aluminium	Iron
As	0.431	0.725
Cd	0.227	0.175
Co	0.211	0.159
Cr	0.235	0.521
Cu	0.438	0.268
Hg	0.527	0.350
Mn	0.311	0.526
Ni	0.546	0.344
Pb	0.588	0.186
Si	0.163	0.127
Zn	0.812	0.499

Table 3.7. Results of the PCA analysis of Queensland sediment metal concentrations.

Metal	Component I	Component II
Al	**0.888**	0.368
Pb	**0.829**	0.173
Zn	**0.808**	0.533
As	**0.781**	0.134
Fe	**0.732**	0.633
Mn	**0.668**	0.391
Hg	**0.662**	0.700
Cu	**0.574**	0.758
Ni	0.504	**0.817**
Co	0.284	**0.882**
Cr	0.272	**0.827**
Cd	0.097	**0.708**
% Variation	40.4	39.3
Eigen value	8.34	1.23

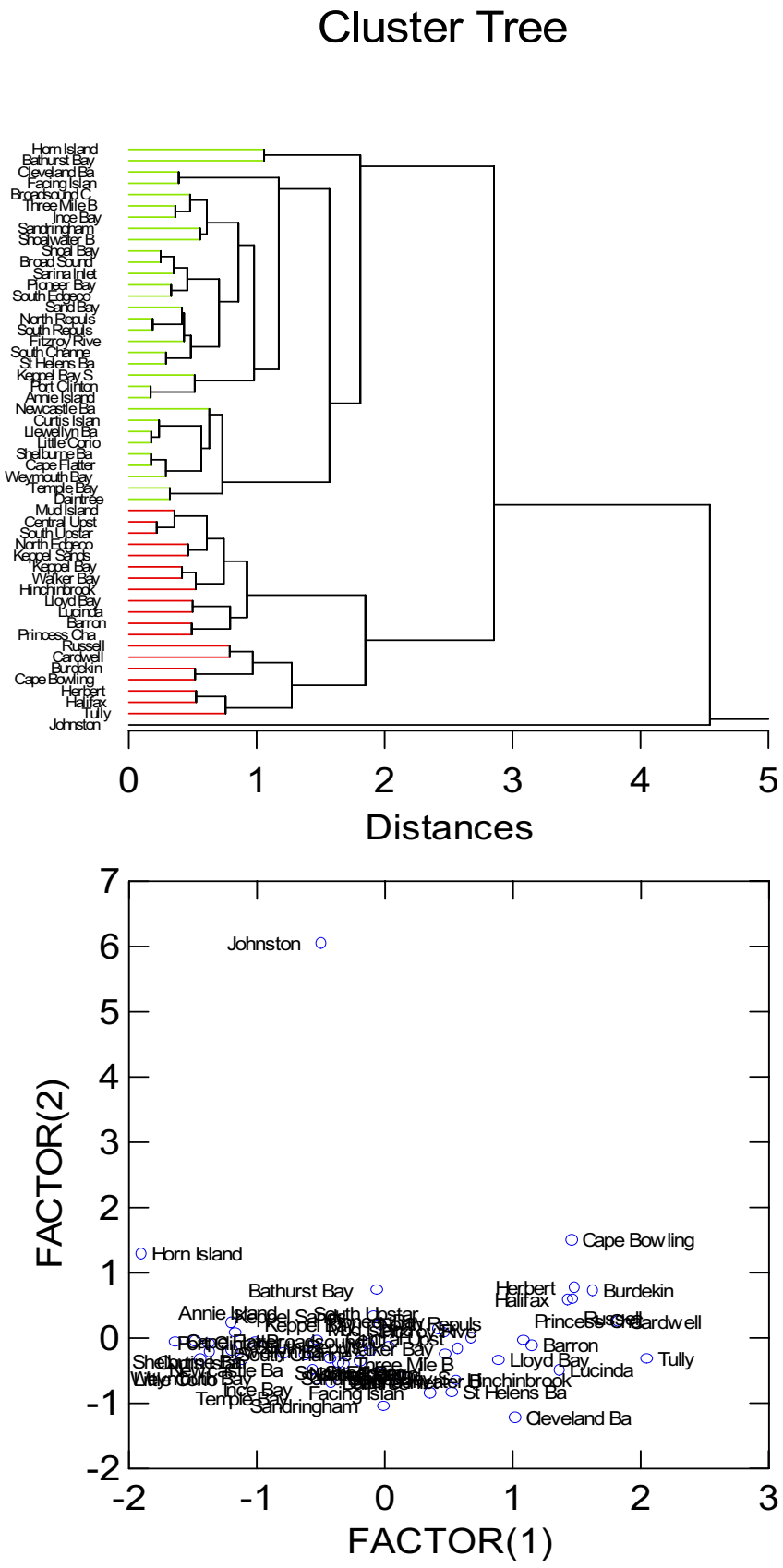


Figure 3.8. Classification and ordination of subtidal sediment metal concentrations.

3.3.2. Sediment Pesticide Concentrations

Atrazine, diuron, lindane, dieldrin, DDT and DDE were detected in sediments collected from subtidal sampling sites (Tables 3.8 and 3.9), with their occurrence being concentrated in wet tropics sampling sites between Townsville and the Daintree River. No herbicides or insecticides were detected at sites north of the Daintree River, or south of Townsville, with the exception of sediment samples collected in the vicinity of the mouths of the Burdekin and Fitzroy Rivers and in Repulse Bay. Chlorpyrifos (detection limit 1.0 μg kg^{-1}), HCB (detection limit 0.05 μg kg^{-1}), heptachlor (detection limit 0.05 μg kg^{-1}), aldrin (detection limit 0.05 μg kg^{-1}), endosulfan (detection limit 0.05 μg kg^{-1}), DDD (detection limit 0.05 μg kg^{-1}), and PCBs (detection limit 50 μg kg^{-1}) were not detected in any of the subtidal sediment samples analysed in this study. Considering only the sites at which the respective pesticide was above the limit of quantification, concentrations of atrazine ranged from 0.1-0.3 μg kg^{-1}, diuron from 0.2 to 10.1 μg kg^{-1}, lindane from 0.08 to 0.19 μg kg^{-1}, dieldrin from 0.05 to 0.37 μg kg^{-1} and DDT and DDE from 0.05 to 0.26 μg kg^{-1}.

Table 3.8. Pesticide concentrations in Queensland subtidal sediments 1998. (All concentrations are µg kg^{-1} dry weight and organic carbon %, n=2).

Site	Site No	Depth (m)	Atrazine	Diuron	Lindane	Dieldrin	DDT	DDE	OC
Horn Island	1	3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.8
		3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.7
Newcastle B	2	5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.3
		6	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.3
Shelburne B	3	3.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
		3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.4
Temple B	4	4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.4
		4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
Weymouth	5	3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.1
		4.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	na
Lloyd B	6	4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.5
		4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.6
PCB	7	4.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
		3.8	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
Bathurst B	8	4.2	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.1
		4.2	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.9
C. Flattery	9	3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
		4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.1
Walker B	10	3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.3
		3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.0
Daintree R	11	na	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
		na	<0.1	0.2	<0.05	<0.05	<0.05	<0.05	0.4
Barron R	12	3.6	<0.1	0.3	<0.05	<0.05	<0.05	0.15	0.6
		3.3	<0.1	0.4	<0.05	0.09	0.05	0.26	0.9
Russell R	13	5.1	<0.1	1.6	<0.05	<0.05	<0.05	<0.05	1.2
		4.2	<0.1	0.5	<0.05	<0.05	<0.05	<0.05	0.6
Johnstone R	14	3	<0.1	10.1	0.08	0.15	<0.05	0.16	2.5
		2.2	<0.1	9.8	0.19	0.37	<0.05	0.25	3.5
Tully R	15	4.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.3
		2.8	<0.1	1.4	<0.05	<0.05	<0.05	0.06	1.2
Cardwell	16	3.4	<0.1	0.8	<0.05	<0.05	<0.05	<0.05	1.7
		3.5	<0.1	0.8	<0.05	<0.05	<0.05	<0.05	1.7
H'brook	17	4.8	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
		3.6	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	1.8
Herbert R	18	1.5	0.1	1.1	<0.05	<0.05	<0.05	<0.05	2.2
		1.5	0.3	2.8	<0.05	<0.05	<0.05	<0.05	3.4
Lucinda	19	4.6	<0.1	1.6	<0.05	<0.05	<0.05	<0.05	1.5
Halifax Bay	20	2.9	<0.1	<0.1	<0.05	0.05	<0.05	0.05	0.5
		2.6	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.7
Cleveland B	21	2.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.1
		2.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
B. Green B	22	2.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.8
		2.6	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.9
Burdekin R	23	8	<0.1	<0.1	<0.05	<0.05	<0.05	0.11	0.6
		8.8	<0.1	<0.1	<0.05	<0.05	<0.05	0.1	0.9
Shoalwater	40	na	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
		na	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
Fitzroy R	48	na	<0.1	0.9	<0.05	<0.05	<0.05	0.10	0.7
		na	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.4

na: not available

Table 3.9. Pesticide concentrations in Queensland subtidal sediments, 1999.

(All concentrations are μg kg^{-1} dry weight and organic carbon %, n=1).

Site	Site No	Depth (m)	Atrazine	Diuron	Lindane	Dieldrin	DDT	DDE	OC
C. Bowling Green	22	6.4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.9
Burdekin R	23	5.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.9
Central Upstart B	24	5.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
S Upstart B	25	9.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6
N Edgecombe B	26	8.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.9
S Edgecombe B	27	3.4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.3
Pioneer B	28	9	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.4
North Repulse B	29	6.9	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.5
South Repulse B	30	8	<0.1	**0.6**	<0.05	<0.05	<0.05	<0.05	0.5
South Repulse B	30	8	<0.1	**1.0**	<0.05	<0.05	<0.05	<0.05	na
St Helens B	31	8	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.1
Sand B	32	11	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.3
Sandringham B	33	9.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Sarina Inlet	34	8.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
Llewellyn B	35	7.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Ince B	36	7.3	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
3 Mile Beach	37	7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Broad Sound	38	7.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
Broadsound Channel	39	10	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Annie Island	41	15	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Port Clinton	42	10	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Little Corio B	43	9	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Shoal B	44	5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Keppel Sands	45	4.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.1
Keppel B	46	13.9	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.3
Keppel B	47	3.5	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Fitzroy R	48	12.7	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
Curtis Island	49	8.8	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
Facing Island	50	10.9	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	<0.1
South Channel	51	16.4	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.2
Mud Island	52	2	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.6

3.4. Discussion

3.4.1. Heavy Metals

Metals in sediments collected from the subtidal along the Queensland coast are largely land-sourced and this is reflected in the positive correlation between metal concentrations and silica content and the negative correlation with calcium carbonate concentration. Terrestrial sediments are recognised as both a carrier and a possible source of metal contaminants in aquatic ecosystems (Förstner 1989). The relative importance of these is dependent on local catchment geology and the extent and type of adjacent catchment-based anthropogenic activity. The Johnston River catchment is a good example of this (Figure 3.8). Metal concentrations are relatively high in subtidal sediments adjacent to this catchment, a consequence of both local basaltic catchment geology, high local rainfall rates and the application of metal-contaminated phosphatic fertilisers in the catchment.

Sediment metal concentrations were, with the exception of chromium, cobalt and nickel, similar to values obtained in previous surveys along the Queensland coast (Ahlers and Szymczak 1993; Reichelt and Jones 1994; Blake 1996). The challenge in sediment metal monitoring is to differentiate sites containing unnaturally enhanced metal concentrations (Loring 1991). One approach to this is the use of reference element(s) which take into account the natural variability in sediment characteristics which influence metal concentrations. Normalisation of metal concentrations in sediments has utilised both geochemical as well as granulometric approaches (Loring 1991), with the former being the most useful as it compensates for mineralogical as well as granular variability in metal concentrations. Aluminium, (a major constituent of fine-grained aluminosilicates), the clay mineral indicator element iron, and the granitic indicator lithium have all been used with success as geochemical normalisers (Windom *et al.* 1989; Loring 1991; Din 1992). Metals in sediments collected from the Queensland subtidal zone in this study were only poorly correlated with aluminium and iron concentrations, precluding their use as reference elements. Studies elsewhere have indicated that lithium may be superior for the normalisation of metal data from most silica sediments (Loring 1991), and its use should be considered in future surveys.

3.4.2. Metal Risk Evaluation

An alternative approach to the use of sediment normalisers is to assess sediment metal concentrations in relation to reference values which have been derived from sites that are unimpacted by human activity (Luoma 1990; Batley 1994). Such a reference data set has been compiled for Queensland waters (Semple and Williams 1998). However the data-set on which it is based is limited with respect to estuarine and marine samples, and all data are derived from the <63 μm sediment fraction only (Moss and Costanzo 1998). Nonetheless, when compared with these reference values, samples collected adjacent to the Russell and Johnston Rivers and in Port Clinton contained elevated concentrations of chromium, and samples collected adjacent to a majority of the wet tropics rivers and to the Burdekin River contained elevated concentrations of nickel (Table 3.10). The comparatively high values of these metals are likely to be a consequence of the presence of ultramafic igneous rocks in these catchments, which result in naturally enhanced metal concentrations in local soils (Lottermosser 1997; Moss and Costanzo 1998).

However, the use of either reference values or normalised data fails to describe any potential biological impact resulting from sediment metal concentrations. This is necessary if an estimate of the toxicological and ecological significance of sediment metal concentrations to aquatic life is to be made (Anon 1995; Long *et al.* 1995). Based on toxicological data, chromium and nickel concentrations in many subtidal sediment samples may have some potential for environmental impact (Table 3.10). However, these reference data is derived for predominantly European and North American species, and its relevance to tropical Australian species is questionable, particularly given the largley natural elevated concentrations of a range of heavy metals present in eastern Australian marine sediments.

Table 3.10. Comparison od Queensland sediment metal concentrations with ecological health guidelines. (All data mg kg^{-1}).

Guideline	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Reference
Qld estuarine reference median range*	Na	0.5-1.5	**30-95**	5-23	<0.1	**5-23**	5-13	37-110	(Moss and Costanzo 1998)
Qld coastal reference median range*	Na	0.5-5.0	**66-100**	16-23	<0.1	**15-20**	5	52-100	(Moss and Costanzo 1998)
Australian effects range low (ERL)	20	1.5	**80**	65	0.15	**21**	50	200	ANZECC (1999)
Australian effects range median (ERM)	70	10	**370**	270	1.0	**52**	220	410	ANZECC (1999)
Maximum recorded this study	20	0.07	**207**	32	0.07	**90**	39	117	
Contaminated sites			Russell River and Johnston River			Wet tropics rivers and Burdekin River			
n			**5**			**24**			

*<63 μm fraction

3.4.3. Organochlorines

Organochlorine compounds tend to rapidly partition to the fine organic compartment of sediments or bioaccumulate into lipids of biota (Olsen *et al.* 1982; Miyamoto *et al.* 1990). As a consequence, estuarine and nearshore terrigenous muds are likely to contain the highest concentrations of any contaminants resulting from anthropogenic activity in coastal catchments. The herbicides atrazine and diuron and the pesticides lindane, dieldrin and DDT (and its breakdown product DDE) were all detected in nearshore marine samples collected along the Queensland coast.

Atrazine was only detected in sediments collected in the vicinity of the mouth of the Herbert River (Figure 3.1). In comparison with many other pesticides, atrazine has a relatively high aqueous solubility (30-33 mg l^{-1} at 20^{o}C) and only a moderate ability to adsorb onto soils (Huber 1993; Hamilton and Haydon 1996). As a consequence, an average of ~3% (and up to 18%) of applied atrazine is lost to aqueous environments through runoff (Huber 1993), where it can persist through freshwater and estuarine environments to contaminate marine ecosystems (Readman *et al.* 1993). The low concentrations of atrazine detected in this study (0.1-0.3 μg kg^{-1}) are likely to be a consequence of herbicide degradation rates being considerably enhanced by sunlight, and saline conditions (Brambilla *et al.* 1993), resulting in a half life of generally less than 30 days in estuarine (tidal) environments (Huber 1993). This is supported by microcosm trials which demonstrated rapid (15-20 day half-life) breakdown of atrazine in estuarine sediments (Jones *et al.* 1982). Rapid breakdown in tropical marine ecosystems together with the enhanced decomposition of atrazine under tropical soil conditions (herbicide half-life of 6-150 days (Akinyemiju 1991; Korpraditskul *et al.* 1992; Korpraditskul *et al.* 1993) imply that Queensland tropical marine ecosystems should remain relatively uncontaminated by agriculturally applied atrazine.

In contrast to atrazine, diuron was widely detectable in marine sediments along the wet-tropics coastline (Townsville to Port Douglas, Figure 3.1). Diuron is moderately mobile in soil (Lewis and Gardiner 1996) and has a soil half-life of 100 to 300 days (Hamilton and Haydon 1996; Lewis and Gardiner 1996). It has an aquatic half-life of approximately 120 days, and will degrade more rapidly in organically rich aquatic sediments (Howard 1991).

Photolysis is not a major degradation pathway for the herbicide (Lewis and Gardiner 1996). The widespread occurrence of diuron in Queensland coastal sediments is therefore likely to be a consequence of high local agricultural usage combined with moderate soil mobility and a relatively long aquatic half-life.

Lindane, dieldrin and DDT and its metabolites were also detected in low concentrations in subtidal sediment samples. Lindane was only detected in sediments collected in the vicinity of the mouth of the Johnstone River. Lindane was used extensively for the control of *Inopus* spp. and cane grubs (*Lepidiota* spp.) in Queensland catchments between the 1950s and the 1990s (Chessels *et al.* 1988; Just *et al.* 1990; Rayment *et al.* 1997). Past monitoring has indicated that lindane was a widely distributed contaminant in northern Queensland, with the pesticide detected in groundwaters (Brodie *et al.* 1984), air and seawater samples (Tanabe *et al.* 1982; Kurtz and Atlas 1990), marine sediments (Dyall and Johns 1985) and in freshwater and marine biota (Olafson 1978; Kannan *et al.* 1994; Kannan *et al.* 1995; Russell *et al.* 1996b). More recent monitoring has failed to detect the pesticide in freshwater and marine fish samples from northern Queensland (von Westernhagen and Klumpp 1995; Russell *et al.* 1996a; 1996b), although the pesticide is still detectable at low concentrations in northern Queensland agricultural soils and in sediments from irrigation drains (Cavanagh *et al.* 1999; Müller *et al.* 2000). Its limited distribution in nearshore sediments may, in part, be due to its relatively high vapour pressure and rapid volatilisation in tropical regions (Chessels *et al.* 1988; Kannan *et al.* 1995).

Dieldrin was detected in sediments collected from the mouth of both the Barron and Johnstone Rivers and in sediments from Halifax Bay. Dieldrin had broad usage in Australia until the late 1980s as a termiticide and for the control of soldier fly (*Inopus* spp.) in Queensland cane fields, and as a consequence, was a widely distributed contaminant of Queensland waterways and estuaries in the past (Clegg 1974; Kannan *et al.* 1995; Russell *et al.* 1996b; Rayment *et al.* 1997). It is still consistently detected in mud crabs (*Scylla serrata*) collected from estuaries adjacent to agricultural catchments between Moreton Bay and Cairns (Mortimer 2000), although concentrations present in freshwater fish have declined by an order of magnitude between the 1970s and 1990s (Russell *et al.* 1996b). It is also detectable in tissue of marine fish collected from the

central Queensland coast adjacent to agricultural activity (von Westernhagen and Klumpp 1995).

DDT and its metabolites were detected in low concentrations at the mouth of the Barron, Johnstone, Tully, Burdekin and Fitzroy Rivers and in Halifax Bay. Concentrations of DDE exceeded those of DDT at all sampling sites. It is estimated that up to 10,000 tonnes of DDT were used in Australia for insect control prior to its ban in the 1970s (Voldner and Li 1995; Mortimer 1998). Low concentrations of DDT and its metabolites have been detected in agricultural soils in the Herbert and Burdekin areas (Cavanagh *et al.* 1999; Müller *et al*. 2000). DDT has also been consistently detected in crabs (*Scylla serrata*) collected from Queensland estuaries adjacent to agricultural catchments (Mortimer 2000), although concentrations of DDT have declined in freshwater fish collected in northern Queensland waterways over the last 20 years (Russell *et al.* 1996b).

3.4.4. Organochlorine Risk Evaluation

Biological effects were not measured during this study. However, the concentrations of most detected pesticide pollutants in sediments were below the concentrations believed to evoke a toxic response in marine benthic organisms (Long *et al*. 1995; Lewis and Gardiner 1996). The exceptions were dieldrin and diuron.

Dieldrin is a cyclodiene pesticide with neurotoxic properties (Ware 1989). Where dieldrin was detected, its sediment concentration exceeded both the effects range low (ER-L) and effects range median (ER-M) for observed biological impacts to marine infauna (Table 3.11) (Long and Morgan 1995). As a consequence, it may also present a localised threat to nearshore marine organisms along the wet tropics Queensland coast.

Table 3.11. Comparison of ER-L and ER-M concentrations and Great Barrier Reef sediment pollutant concentrations.

Compound	GBR intertidal sediment range (µg kg^{-1})	GBR subtidal sediment range (µg kg^{-1})	ER-L[1] (µg kg^{-1})	ER-M[1] (µg kg^{-1})
Atrazine	<0.5	<0.1-0.3		
Diuron	<0.5-1.7	**<0.1-10.1**		
Lindane	<1.0	0.19		
Dieldrin	<1.0	**<0.05-0.37**	**0.02**	**8**
DDT	<1.0	0.05	1	7
DDE	<1.0	0.26	2	15
~~Ð~~DDT	<1.0	0.31	3	350

[1](Kennicutt *et al.* 1994)

Table 3.12. Predicted nearshore Great Barrier Reef diuron water column concentrations derived from partitioning co-efficients.

	Diuron (µg kg^{-1})	Organic Carbon (%)	Diuron C_{soc}	Diuron K_{oc}	Diuron C_w (µg L^{-1})*
Barron R	0.4	0.9	44	398	0.1
Russel R	1.6	1.2	133	398	0.3
Johnstone R	10.1	2.5	404	398	1.0
Tully R	1.4	1.2	117	398	0.3
Cardwell	0.8	1.7	47	398	0.1
Herbert R	2.8	3.4	82	398	0.2
Lucinda	1.6	1.5	107	398	0.3
Fitzroy R	0.9	0.7	129	398	0.3

$C_w = C_{soc} (K_{oc})^{-1}$ (Connell 1990); C_{soc} Concentration in sediments expressed in terms of organic carbon; K_{oc} Partitioning coefficient between organic carbon and water; C_w Water concentration

The herbicidal action of diuron is a consequence of inhibition of photosynthetic transport of electrons in photosystem II (see Chapter 4) (Molander *et al.* 1992). Diuron concentrations of 2 $\mu g\ L^{-1}$ and 10-170 $\mu g\ L^{-1}$ have been shown to result in reduction in photosynthesis in marine periphyton (Molander *et al.* 1992), and reduction in growth in marine phytoplankton (Mayer 1987). Predicted chronic water column diuron concentrations near the mouths of most wet tropics rivers range from 0.1 to 1.0 $\mu g\ kg^{-1}$ (Table 3.12) and concentrations are likely to be higher during rainfall periods over summer months. These predictions are based on partitioning co-efficients for diuron in marine sediments and their subsequent concentration in the overlying water column:

$$C_w = C_{soc} (K_{oc})^{-1} \text{ (Connell 1990);}$$

Where: C_{soc} *Concentration in sediments expressed in terms of organic carbon;*
K_{oc} *Partitioning coefficient between organic carbon and water; and*
C_w *Water concentration*

The potential to impact phytoplankton community structure and to inhibit photosynthesis and growth of seagrasses and coral zooxanthellae therefore exists. The influence of elevated water temperatures and reduced salinity during summer months on diuron toxicity to phytoplankton and seagrass is unknown.

3.5. Conclusions

Great Barrier Reef subtidal sediments present in sheltered environments tend to be fine grained and have the highest concentrations of pollutants adsorbed to them. The pesticides diuron and dieldrin were relatively widespread in nearshore sediments collected from the wet tropics region of the Great Barrier Reef at sites between Townsville and Port Douglas. Their distribution in marine sediments is a consequence of their relatively long chemical half-life and/or to their relatively high rate of application in adjacent catchments. Based on known toxicological data, dieldrin and diuron are present at concentrations high enough to present a potential biological risk at some sites. Concentrations of metals, although high at many sites, are likely to be mainly naturally elevated, and as a consequence are likely to present a minor ecological risk to local fauna.

Chapter 4: The impact of diuron (DCMU) on three species of tropical seagrass

GBRMPA

Intertidal Seagrass, Magnetic Island

CHAPTER FOUR: THE IMPACT OF DIURON (DCMU) ON THREE SPECIES OF TROPICAL SEAGRASS

4.1. Introduction

Sugar cane production is the largest intensive agricultural industry carried out in Queensland, Australia. It represents one of Australia's largest export industries and industry sales generated approximately AUS $1.2 billion in 1991 (Anon 1992). The industry is situated primarily along the coastal fringe and is concentrated in northern Queensland, adjacent to the Great Barrier Reef World Heritage Area. Sugar cane production is reliant on a range of pesticides to control insect pests and weed species in the growing area. Diuron (DCMU [3-(3',4'-dichlorophenyl)-1,1-dimethylurea]) is a phenylurea herbicide used extensively in the Queensland cane industry for pre-emergence weed control (Hamilton and Haydon 1996), and as a consequence, is a common contaminant of sugar cane growing soils (Müller *et al*. 2000), and the nearshore marine environment of the Great Barrier Reef (Chapters 2 and 3).

The toxic action of the herbicide diuron on plant photosynthesis is well understood (van Rensen 1989). The photosynthetic apparatus (PSI and PSII) consists of two independent reaction centres, (P680 and P700) which are supported by a complex of photosynthetic carotenoids and phicobilin pigments (Figure 4.1). The complex of pigments is joined by an electron transport chain. Each system has an electron acceptor and donor which allows light photons to impart energy to the reaction centres. PSII has a quinone molecule (Q) as the primary electron acceptor while PSI uses chlorophyll. Diuron binds specifically and with high affinity at the Q_B-binding site of the D_I protein of the PSII core complex and prevents Q_B from binding at this location. Exclusion of the Q_B from its binding site blocks electron transfer from Q_A to Q_B (Figure. 4.1), which limits electron flow in PSII (Sandmann and Bölger 1986). This can be observed as a decrease in measurable variable fluorescence (ΔF), and a concomitant decline in effective quantum yield ($\Delta F / F_{m'}$) in the affected plant.

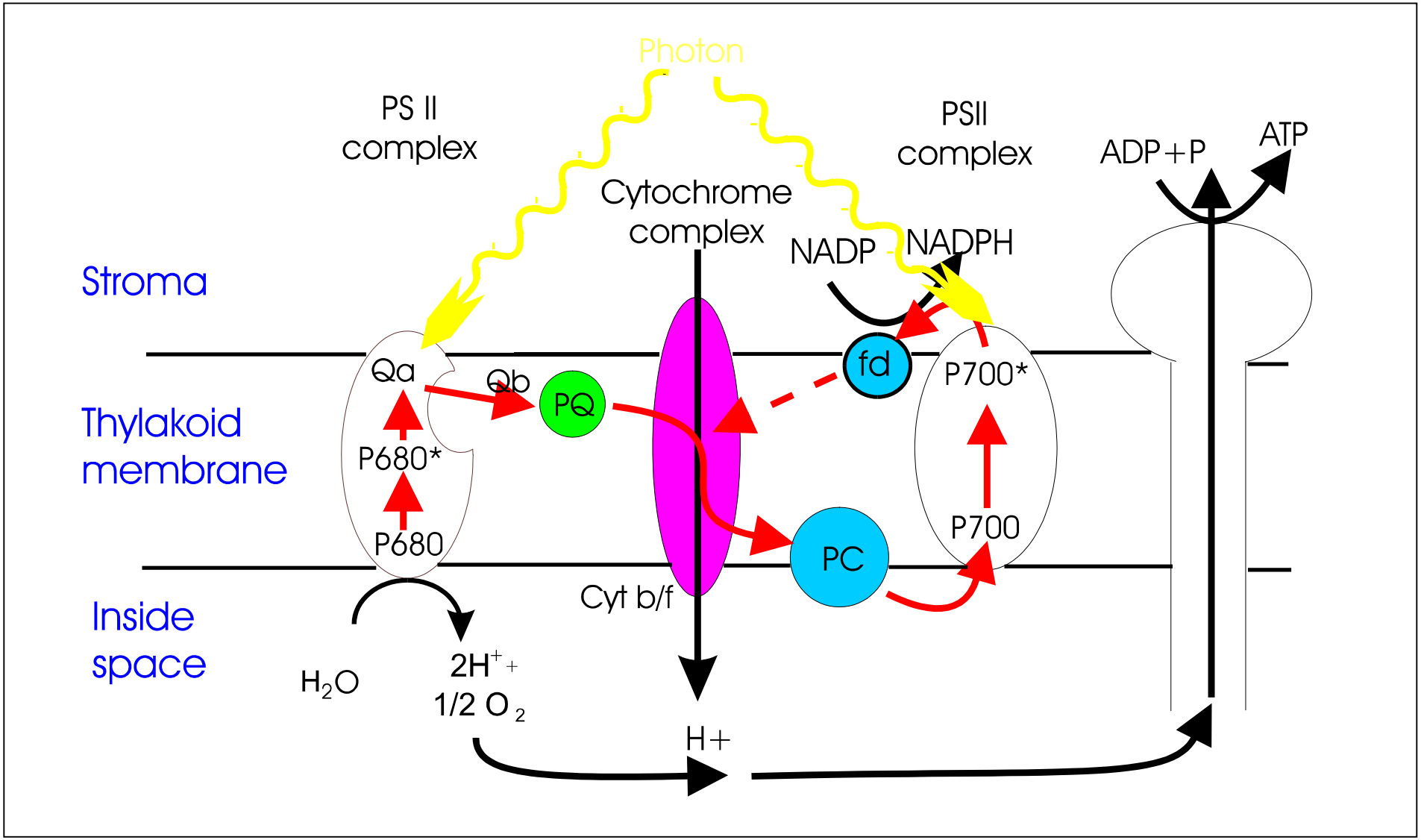


Figure 4.1. Electron and proton transport pathways in chloroplast photosynthetic electron flow (after van Rensen 1989).

Diuron's toxic effect on photosynthetic biochemical pathways has been extensively studied for over 30 years, particularly in terrestrial plants (van Rensen 1989). However, the (long-term) environmental impact of both chronic and acute diuron exposure are essentially unknown for the (Australian) marine environment. Extensive losses of seagrass beds have occurred worldwide in recent years (Walker and McComb 1992; Preen *et al.* 1995; Short *et al.* 1996). In Australia, the loss of 450 km^2 of seagrass beds over the last 10 years has been attributed to anthropogenic impacts (Kirkman 1997). The general hypothesis related to these losses is that a decrease in light reaching submerged plants reduces effective photosynthesis, ultimately leading to plant death. However, the possibility exists that low concentration chronic diuron contamination of the nearshore Queensland environment could affect the competitive fitness of local seagrasses, eventually leading to changes in community structure with major ecosystem flow-on impacts (Haynes *et al.* 1998).

The objective of this chapter was to assess the toxicity of a range of environmentally relevant diuron concentrations to three tropical seagrass species using chlorophyll fluorescence as a measure of photosynthetic efficiency (Dawson and Dennison 1996; Jones *et al.* 1999; Ralph 2000).

4.2. Materials and Methods

4.2.1. Plant Collection

Three species of tropical seagrass (*Halophila ovalis*, *Cymodocea serrulata* and *Zostera capricorni*) were collected in shallow water (<3 m) from Wanga Wallen Banks, Moreton Bay, Australia, (27°25' S, 153°22' E) in November 1998. Plants were collected using a 105 mm diameter PVC corer, and intact cores were transferred to 1L pyrex beakers and sealed in plastic bags to avoid excessive water loss during transportation to the laboratory. Plants were transferred to flow-through tanks and allowed to acclimate for 24 hrs prior to experimentation.

4.2.2. Experimental Arrangement

Specimens of each of the three acclimated seagrass species (and their associated sediment cores) were randomly placed in 10, 50 L glass aquaria and exposed to 5 replicated diuron treatments (0, 0.1, 1.0, 10 and 100 μg L^{-1}). Prior to use, all glass aquaria used in the trial were cleaned with anionic detergent and rinsed in 10% nitric acid followed by distilled water. The 50 L aquaria were housed inside larger outdoor flow-through (50 L h^{-1}) aquaria that minimised water temperature variation over the experimental period. There was no water exchange between the experimental and larger aquaria. Aquaria were covered with 50% neutral density shade screens and clear plastic covers to minimise rainwater dilution of experimental diuron concentrations. Aquaria containing seagrass were aerated over the experimental period.

Seagrass were exposed to diuron for a 5-day period, rinsed, and replaced in fresh seawater and monitored for a further 5-day recovery period. Tests were conducted under static conditions, with herbicide exposure a single dose addition to the water at the beginning of the experiment. Experimental diuron concentrations (0, 0.1, 1.0, 10 and 100 μg L^{-1}) were based on concentrations detected in nearshore marine sediments collected from the northern Queensland coast (Chapter 3). Standard solutions of diuron were prepared from technical grade diuron (98% pure, Sigma). A stock solution (10 mg L^{-1}), was made by dissolving diuron in acetone (2 ml), then diluting in 100 ml seawater, followed by gentle heating to volatilise the acetone (Schwarzschild *et al.* 1994). Seawater diuron concentrations were verified using high performance liquid chromatography interfaced via a high flow electrospray source to a triple stage mass spectrometer (LCMSMS) following extraction in dichloromethane and hexane. Dosing of the experimental aquaria was accurate, and reproducible, with less than 14% concentration differences between experimental replicates (Table 4.1). No diuron was detected in control aquaria water and the concentration of diuron maintained in aquaria during the 5 day exposure period remained stable, with less than 20% loss from the initial dose (Table 4.1).

Table 4.1. Concentration of diuron in aquaria water column at beginning (day 0) and at the end (day 5) of the experimental period.

Treatment	Replicate No.	Measured initial concentration ($\mu g\ L^{-1}$)	Measured final concentration ($\mu g\ L^{-1}$)
Control	a	< 0.1	< 0.1
Control	b	< 0.1	< 0.1
0.1 $\mu g\ L^{-1}$ diuron	a	0.1	0.1
0.1 $\mu g\ L^{-1}$ diuron	b	0.1	0.2
1.0 $\mu g\ L^{-1}$ diuron	a	0.9	0.9
1.0 $\mu g\ L^{-1}$ diuron	b	0.8	1.0
10 $\mu g\ L^{-1}$ diuron	a	8.1	7.4
10 $\mu g\ L^{-1}$ diuron	b	8.4	7.2
100 $\mu g\ L^{-1}$ diuron	a	86	74
100 $\mu g\ L^{-1}$ diuron	b	100	80

Table 4.2. Variation in aquaria water quality during diuron exposure and recovery periods.

Exposure period	Min. temp. (^oC)	Max. temp. (^oC)	Salinity (ppt)	pH
Day 1	20.0	35.0	37.2	8.42
Day 2	20.0	31.0	34.2	8.15
Day 3	22.5	32.0	38.5	8.21
Day 4	22.5	31.5	39.0	8.24
Day 5	22.0	31.0	39.4	8.26
Day 6	22.5	25.0	37.7	8.17
Day 7	23.0	31.0	38.2	8.13
Day 8	23.0	26.0	35.9	8.16
Day 9	23.0	25.0	32.6	8.18
Day 10	23.5	31.0	33.2	8.22

Aquaria salinity and pH were measured daily in both the flow-through and experimental aquaria with a water quality probe (Horiba U-10). Minimum and maximum temperatures were recorded daily from a min/max thermometer placed in one of the flow-through aquaria. Aquaria temperature ranged from 20-35^{o}C. Forty-eight hours of rainfall over the experimental period resulted in a slight decrease in salinity in the test aquaria, and this alteration was reflected in a change in seawater pH (Table 4. 2).

4.2.3. Fluorescence Measurements

The effect of diuron on seagrass photosynthesis was assessed by measuring change in chlorophyll fluorescence using a Pulse-Amplitude-Modulated fluorometer (Diving-PAM) (Walz, Germany) (Schreiber *et al.* 1994; Jones *et al.* 1999). Chlorophyll fluorescence analysis was performed underwater, and was measured instantaneously using special clips to ensure a constant distance between the instruments fibre optic head and the seagrass leaf surface. The fluorescence signal was sampled at a standard position on the leaf (approximately in the middle of the adaxial surface on the second leaf from the plant meristem) (Ralph 2000). Specimens were measured daily (1000 h).

4.2.4. Statistical Analysis

Seagrass fluorescence data were analysed using a repeated measures analysis of variance (ANOVA) model. Two effective quantum yield ($\Delta F/F_{m'}$) measurements were taken from separate leaves from two plants per experimental aquaria at each measurement interval. These values were averaged as the samples were contained within the same aquaria, and were not independent. The averaged values from two independent tanks were used in the repeated measures analysis of variance, where there were 3 seagrass species, 5 treatment levels (diuron concentration) and 12 sample times (day 0, at 2 hrs following diuron exposure, and then day number 1 to day number 10). Two-way ANOVA was used to compare effective quantum yield between seagrass species and diuron exposure concentrations at day 5 (the end of the diuron exposure period) and at day 10, (after 5 days recovery in uncontaminated seawater). The Tukey multiple comparison procedure with an experiment-wise Type I error probability of 0.05 was used to locate any significant differences in effective quantum yield between seagrass species and diuron concentrations (Ott 1993).

A significant interaction was present for the Day 5 analysis, and these data were re-analysed using a one-way ANOVA of effective quantum yield for each species separately. Dunnett's test was used to assess significance ($\alpha = 0.05$) of differences in effective quantum yield between control and diuron exposed plants for these analyses (Ott 1993). Data were assessed for gross deviations from normality and, where necessary, transformed (Log_{10}) prior to analysis. All statistical computations were carried out using the SYSTAT V7.0 software package (Wilkinson 1996).

4.3. Results

4.3.1. Photosynthetic Impact of Diuron

All three species of seagrass exhibited a rapid fluorescence response to diuron exposure (Figure. 4.2). Significant main effects as well as significant time x species and time x treatment (diuron concentration) interactions were recorded in the repeated-measures analysis of variance (Table 4.3) indicating the presence of significant variability in seagrass species response to diuron concentration over time. The effective quantum yield of all 3 seagrass species declined within 2 hours of exposure to the most concentrated diuron treatments (10 and 100 μg L^{-1} diuron). Effective quantum yield from *H. ovalis* declined over the first 24 hrs of the experiment in plants exposed to even lower diuron concentrations (0.1 and 1.0 μg L^{-1} diuron). Depression of effective quantum yield was maintained in *H. ovalis* over the rest of the 5 day exposure period. Effective quantum yield was also depressed in *Z. capricorni* at all diuron concentrations after 5 days of herbicide exposure (Fig. 4.2). Depressed effective quantum yield was only exhibited at the two highest diuron concentrations (10 and 100 μg L^{-1}) *in C. serrulata* after 5 days of herbicide exposure. Effective quantum yield at the end of the diuron exposure period (day 5) was significantly lower in plants exposed to highest diuron concentrations (10 and 100 μg L^{-1}) in all seagrass species (Dunnet's test, α=0.05) (Figure. 4.3; Tables 4.4 and 4.5). Effective quantum yield was still significantly depressed at the end of the recovery period (day 10) in all 3 seagrass species in plants that had been exposed to the highest (100 μg L^{-1}) diuron concentration (Figure. 4.4, Table 4.4).

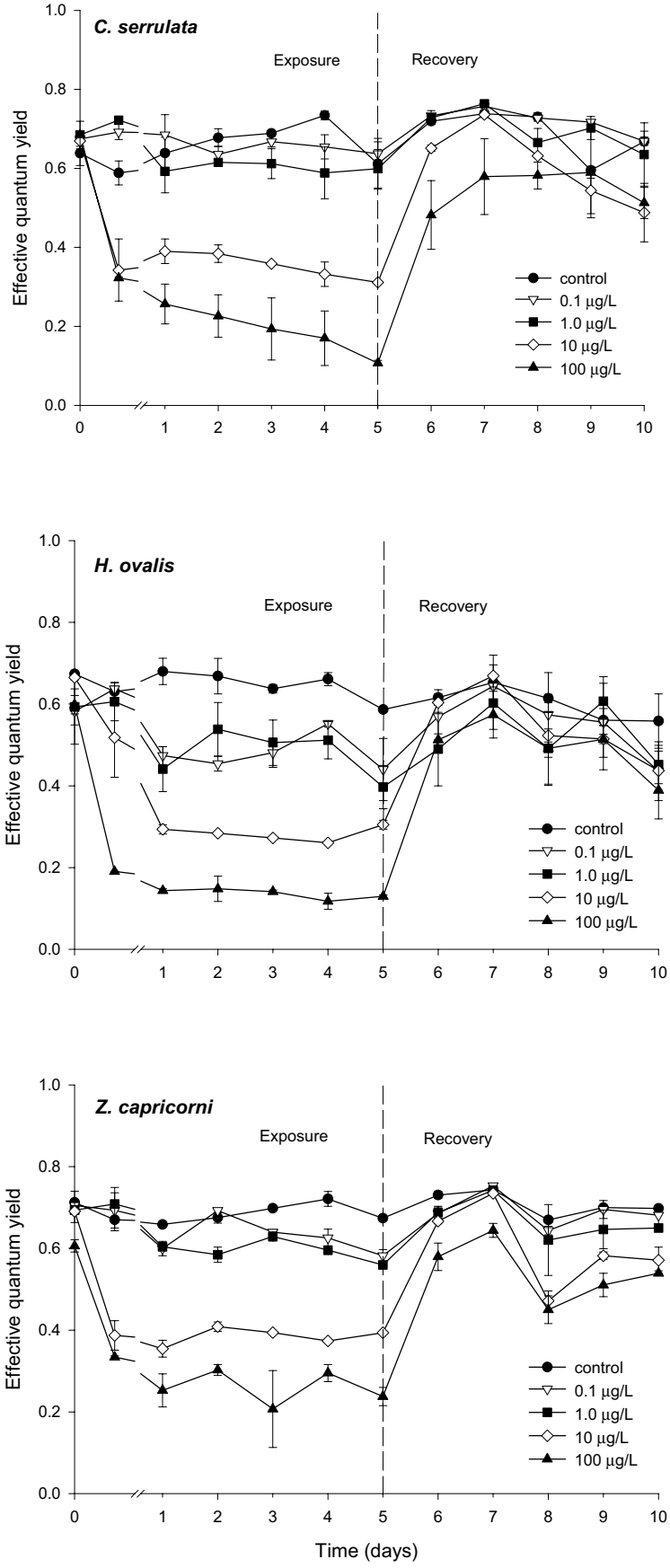


Figure 4.2. Seagrass fluorescence response over 5 day exposure and recovery periods.

Table 4.3. Summary of the repeated-measures ANOVA of seagrass effective quantum yield over the 10 day experimental period. (n =2).

Component	*F* value	*P*
Species	21.676	<0.001
Treatment	68.274	<0.001
Species x Treatment	1.232	0.346
Constant (Time only)	100.866	<0.001
Species x Time	3.080	<0.001
Treatment x Time	19.042	<0.001
Species x Treatment x Time	1.404	0.032

Table 4.4. Summary of two-way ANOVA of effective quantum yield, day 5 (end of diuron exposure) and day 10 (end of recovery period).

Time	Factor	*F* ratio	*Post hoc* comparison[a]
Day 5 (final exposure day)[L]	Species	24.171***	See Table 4.5
	Treatment	179.711***	
	Interaction	6.691**	
Day 10 (final recovery day)	Species	18.184***	*H.ovalis* *C.serrulata* *Z. capricorni*
	Treatment	5.923**	0 0.1 1.0 10 100
	Interaction	0.571	

[L]Log_{10} transformed prior to analysis

**0.001<*P*<0.01, ***P<0.001

[a]Concentrations or species joined by a horizontal line were not significantly different

Table 4.5. Summary of one-way ANOVAs of effective quantum yield, by species, Day 5.

Time	Species	ANOVA F ratio	Dunnet's test (α=0.05)
Day 5	*C. serrulata*	119.738 (p<0.001)	Control>>10, 100 µg l^{-1}
	H. ovalis	32.609 (0.001<p<0.01)	Control>>10, 100 µg l^{-1}
	Z. capricorni	89.844 (P<0.001)	Control>>10, 100 µg l^{-1}

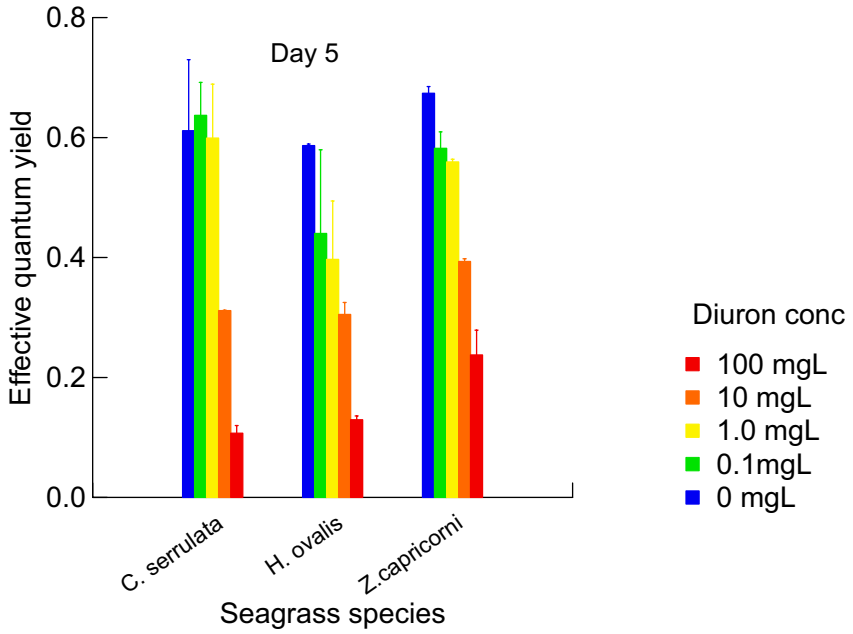


Figure 4.3. Seagrass fluorescence response, Day 5. (n=2, error bars = 1 SEM).

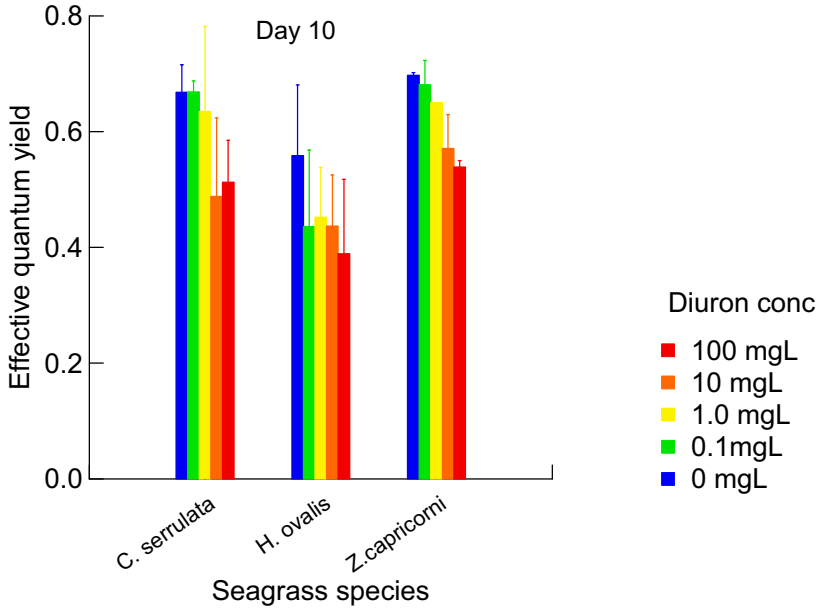


Figure 4.4. Seagrass fluorescence response, Day 10. (n=2, error bars = 1 SEM).

4.4. Discussion

All concentrations of diuron tested showed some degree of toxicity to one or more of the exposed seagrass species, as indicated by a decline in effective quantum yield over the exposure period. This is in agreement with an earlier study which demonstrated that exposure of *H. ovalis* to diuron concentrations of 10 and 100 μg L^{-1} for 72 hours depressed effective quantum yield by 25 and 50% respectively (Ralph 2000). Concentrations of 10 and 100 μg L^{-1} diuron reduced effective quantum yield in all three species of seagrass by 50 to 75% after a 5 day exposure period. Lower concentrations of diuron (0.1 and 1.0 μg L^{-1}) reduced effective quantum yield by 10 to 30% in *H. ovalis* and *Z. capricorni* respectively, whereas effective quantum yield was essentially unaffected in *C. serrulata* exposed to the lower diuron concentrations at the end of the 5 day exposure period.

Recovery of photosynthetic ability was initially rapid in all three tested seagrass species following return to clean seawater. However, recovery was not necessarily sustained, with all species exhibiting fluctuations in effective quantum yield over the 5 day recovery period. The overall decline in effective quantum yield in *H. ovalis* and to a lesser extent in *C. serrulata* at most diuron concentrations is of particular concern. *C. serrulata* and *Z. capricorni* are two of the four Queensland seagrass species which contribute most to seagrass abundance along the majority of the Queensland coast (Cape York and Hervey Bay) (Lee Long *et al.* 1993; Kirkman 1997). *H. ovalis* is also widely distributed over this region and *Cymodocea* and *Halophila* are also an important food resource for dugongs (Marsh *et al.* 1982). *Zostera* is also eaten incidentally, or in the absence of preferred seagrass species by dugongs (Preen 1995a; Preen 1995b).

Loss of seagrass food resources is a potentially threatening situation for dugongs. Widespread loss of seagrass in Hervey Bay following sustained flooding of the bay resulted in extensive dugong mortality and mass migration of surviving animals from the area (Preen and Marsh 1995). Other studies have linked reductions in dugong calving with reduced food resources (Marsh 1995). Dugong populations in southern Great Barrier Reef waters are critically endangered (Marsh *et al*. 1995), and any mortality or reduced reproductive capacity caused by reductions in their seagrass food resource has serious implications for the survival of local populations.

4.5. Conclusions

The immediate toxicity of diuron to seagrass and its potential ongoing impact is significant, as monitoring of diuron contamination in the nearshore environment along the Queensland coast has detected diuron at concentrations of 1-10 ug kg^{-1} (Chapter 3). Partitioning models indicate that overlying water concentrations of diuron may reach 1 µg L^{-1} at sediment concentrations of 10 ug kg^{-1} (Chapter 3), and this is within the range shown here to inhibit seagrass photosynthesis. The magnitude of temporal variation in the concentration of diuron in Great Barrier Reef marine sediments is presently unknown. Highest concentrations of diuron were detected in subtidal sediments from the wet tropics, adjacent to the mouth of the Herbert and Johnstone Rivers. Highest agricultural usage (sugar cane) of the herbicide occurs in these two river catchments (Hamilton and Haydon 1996). It is therefore likely that highest concentrations of the herbicide in the marine environment are likely to be adjacent to catchments with highest usage rates immediately after the first heavy rains of the wet season.

Terrigenous sediments are generally deposited in nearshore waters of the Great Barrier Reef (Larcombe *et al.* 1996), and consequently, it is unlikely that any herbicide contamination extends further than 10-15 km from the coast. Dugongs frequent coastal waters, with major concentrations of animals occurring in wide, shallow protected bays where seagrass beds grow (Marsh *et al.* 1999). If these inshore seagrass beds are compromised by herbicides, it is likely that local dugongs will be forced to migrate to locate alternative food resources. It has been postulated that “refugee” dugongs may be actively excluded from areas containing better quality seagrass by resident animals, resulting in reduced nutritional inputs and extended starvation (Preen and Marsh 1995). Starvation also results in the mobilisation of the animal's fat reserves and this mobilises any bioaccumulated lipophilic pollutants that may then exert a toxic effect on the animal (Chapter 5).

Chapter 5: Dugong pollutant concentrations: mermaids in distress?

GBRMPA

The Dugong (*Dugong dugon*)

CHAPTER FIVE: DUGONG ORGANOCHLORINE AND HEAVY METAL POLLUTANT CONCENTRATIONS: MERMAIDS IN DISTRESS?

5.1. Introduction

The global marine ecosystem is the ultimate repository for most well-known persistent contaminants including organochlorines and heavy metals (Wania *et al.* 1998), and it is well established that many of these contaminants are accumulated by marine mammals (O'Shea 1999; O'Shea *et al.* 1999). Accumulation of organochlorine pesticides and polychlorinated biphenyls (PCBs) has been implicated in reproductive and immunological abnormalities observed in terrestrial bird (Kubiak *et al.* 1989) and marine mammal populations in the northern hemisphere (Kuiken *et al.* 1994; Johnston *et al.* 1996). Examples include adrenocortical hyperplasia and disruption of steroid metabolism in seals attributed to DDE metabolites (Lund 1994), and reduced testosterone concentrations in Dall's porpoise attributed to DDE contamination (Subramanian *et al.* 1987).

Southern Great Barrier Reef dugong (*Dugong dugon*) populations have declined by an estimated 50 to 80% over the last 10 years (Marsh *et al*. 1993; Marsh *et al.* 1995). This is of particular concern as the animal has been endangered or exterminated over much of its worldwide range (Heinsohn and Marsh 1978; Marsh 1992; Marsh *et al.* 1999). Although large populations of dugongs still exist (Preen 1993), the species is considered to be vulnerable to extinction (IUCN 1996). Reasons for the reported decline in dugong numbers in southern Great Barrier Reef Marine Park waters are unclear, although a number of human influences threaten dugong populations. These include indigenous hunting and accidental capture in gill nets, as well as loss of seagrass habitat and water quality degradation caused by coastal and hinterland development (Anon 1993; Marsh *et al.* 1994; Preen *et al.* 1995; Marsh *et al.* 1999).

Little information is available about contaminant concentrations in herbivorous marine mammals such as the dugong (Heinsohn and Marsh 1978; Miyazaki *et al.* 1979; Denton *et al.* 1980; Denton and Breck 1981; Dight and Gladstone 1993; Gladstone 1996) or other sirenians (Forrester *et al.* 1975; O'Shea *et al.* 1984; Ames and Van Vleet 1996).

As a consequence, heavy metal and organochlorine residues present an almost completely unstudied risk to dugongs of tropical and sub-tropical Australia. This is important, as recent surveys (Chapter 3) of pollutant concentrations in nearshore Great Barrier Reef habitat have indicated that sediments contain a range of organochlorine pollutants including DDT (and its breakdown products) as well as dieldrin and lindane. This chapter provides the first contemporary data on concentrations of organochlorines and heavy metals present in Queensland dugongs, and compares these concentrations with those detected in sirenians and other marine mammals from Australia and elsewhere.

5.2. Materials and Methods

5.2.1. Tissue Sampling

Tissue samples were collected from thirty-one dugong carcasses stranded on Queensland beaches between Hervey Bay and Cairns between August 1996 and April 2000 (Figure 5.1). Eleven of the carcasses were in good condition (fresh) at the time of sampling. Fourteen animals were in fair condition (decomposing, organs intact), and six sampled animals were in poor condition (advanced decomposition) at the time of sampling. The cause of death was unable to be ascertained for fifteen stranded animals. Of the others, death resulted from net drownings (n=6), an underwater explosion (n=1), starvation (n=2) and infection following wounding (n=7). Eighteen animals were considered mature (>2.2m in length; 10 male, 7 female) and 13 animals were immature (<2.2 m in length; 10 male, 3 female, 1 unknown). Samples of blubber and/or liver were collected from each carcass using standard techniques (Figure 5.2) (Geraci and Lounsbury 1993; Eros *et al.* 2000). Blubber tissues were collected from the outermost layers of blubber and muscle, just to one side of the mid-ventral line. Samples of liver were collected from the left caudal tip of the organ. Samples were collected under Scientific Purposes Permit No. 0011221/96/SAB*, Queensland Nature Conservation Act (1992).* Basic anatomical data were also recorded for each carcass at the time of sampling (Table 5.1). Collected tissue was divided and stored frozen in acid washed plastic containers for metal analyses and in solvent washed glass containers for organochlorine analyses.

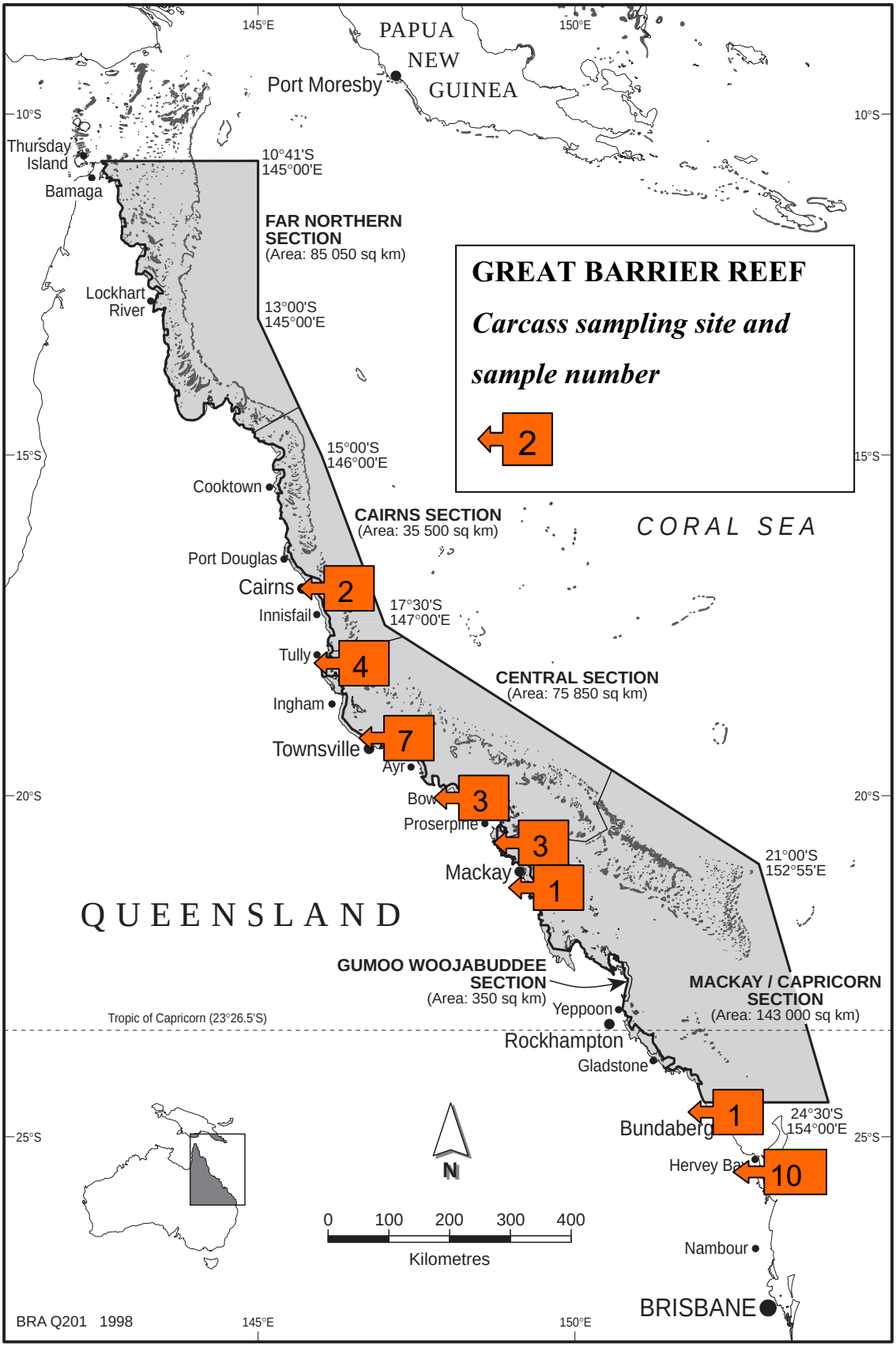
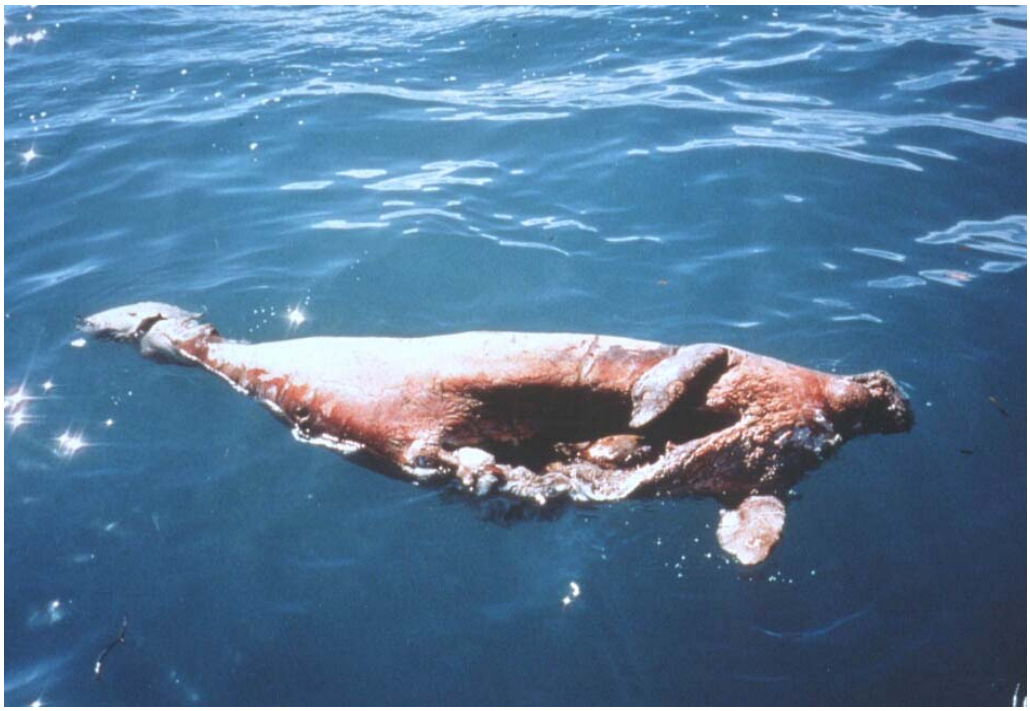


Figure 5.1. Recovery locationsand dugong stranding numbers Queensland, 1996-2000.



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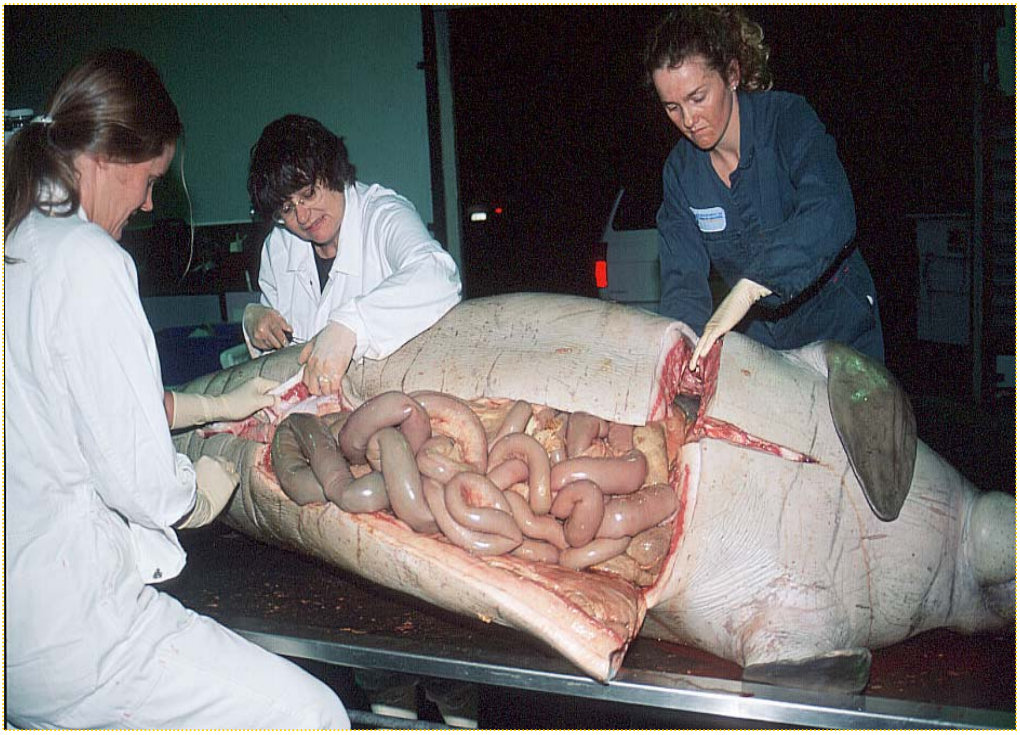

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Figure 5.2. Dugong carcass retrieval and tissue sampling, Townsville, April 1999.

Table 5.1. Queensland stranded dugong carcass characteristics, 1996-2000. (Locations are ordered north to south).

Ref No	Date	Location	Region	Sex	Length (cm)	Maturity[1]	Condition[2]	Suspected Cause of Death	Blubber	Liver
c046	10/10/1999	False Cape	Cairns	F	267	Mature	Fair	Unknown	Y	
c048	10/10/1999	False Cape	Cairns	M	120	Immature	Fair	Death of mother	Y	Y
c009	02/11/1996	Tully Heads	Hinchinbrook	M	110	Immature	Fair	Starvation	Y	Y
c019	25/08/1999	Cardwell	Hinchinbrook	M	235	Mature	Poor	Septisemia	Y	
c028	13/11/1999	Cardwell	Hinchinbrook	M	190	Immature	Fresh	Perforation of intestine	Y	Y
c036	08/04/2000	Lucinda	Hinchinbrook	M	152	Immature	Fresh	Unknown		Y
c004	20/09/1996	Horseshoe Bay	Townsville	F	282	Mature	Fresh	Net drowning	Y	Y
c013	27/04/1999	Cleveland Bay	Townsville	M	205	Immature	Fair	Net drowning	Y	Y
c016	15/05/1999	Cleveland Bay	Townsville	M	130	Immature	Fair	Explosion		Y
c017	13/08/1999	Nelly Bay	Townsville	F	196	Immature	Poor	Extensive oedema and haemorraging	Y	
c018	23/08/1999	Rowes Bay	Townsville	M	194	Immature	Fresh	Bacterial infection	Y	
c025	16/10/1999	Saunders Beach	Townsville	M	220	Mature	Fair	Net drowning	Y	Y
c035	03/03/2000	Cleveland Bay	Townsville	M	229	Mature	Fresh	Stingray wound	Y	Y
c003	02/09/1996	Kings Beach	Bowen	M	261	Mature	Fair	Net drowning	Y	Y
c047	12/09/1999	Rowes Bay	Bowen	M	237	Mature	Fresh	Stingray wound	Y	Y
c049	26/10/1999	Queens Beach	Bowen	F	u	Immature	Fresh	Unknown	Y	Y
c007	03/09/1998	Repulse Bay	Whitsundays	M	294	Mature	Fair	Unknown	Y	
c010	17/02/1999	Repulse Bay	Whitsundays	M	260	Mature	Fair	Net Drowning	Y	Y
c034	20/01/2000	Pioneer Bay	Whitsundays	F	240	Mature	Fresh	Unknown	Y	Y
c002	08/08/1996	Glendower Point	Mackay	M	266	Mature	Fresh	Net drowning	Y	Y
c050	27/10/1999	Main Beach	Mon Repos	F	300	Mature	Fresh	Unknown	Y	Y
c012	27/02/1999	Burrum Heads	Hervey Bay	F	213	Mature	Fair	Unknown	Y	Y
c037	02/03/1999	Burrum River	Hervey Bay	F	297	Mature	Poor	Unknown	Y	Y

c038	21/06/1999	Buxton	Hervey Bay	M	198	Immature	Fair	Unknown	Y	
c040	06/08/1999	Burrum Heads	Hervey Bay	M	155	Immature	Fair	Pneumonia	Y	Y
c042	27/08/1999	Great Sandy Strait	Hervey Bay	M	320	Mature	Poor	Unknown	Y	
c043	29/08/1999	Burrum Heads	Hervey Bay	u	173	Immature	Poor	Unknown	Y	
c044	01/09/1999	Fraser Island	Hervey Bay	F	240	Mature	Poor	Unknown	Y	
c045	09/09/1999	Great Sandy Strait	Hervey Bay	F	287	Mature	Fair	Unknown	Y	Y
c051	08/11/1999	Rainbow Beach	Hervey Bay	M	290	Mature	Fair	Unknown	Y	Y
c052	10/11/1999	Burrum River	Hervey Bay	M	160	Immature	Fresh	Pneumonia	Y	Y

[1]Animals longer than 2.2m classified as mature; <2.2m as immature (Marsh 1995); [2](Eros *et al.* 2000); u: unknown

5.2.2. Sample Analyses: Metals

The liver is a major repository for trace metals in marine mammals (Thompson 1990). Metal in tissues analyses were carried out by the Resources Sciences Laboratories, Department of Natural Resources, Indooroopilly, Brisbane. Liver samples for metals analyses were freeze-dried and ground to a fine powder. Approximately 100 mg of each dried sample was microwave digested for 16 minutes in double-distilled nitric acid. The sample was then cooled in an ice bath and the sample solution made up to 10 g with polished reverse-osmosis water. Three g of each solution was reserved for mercury analysis and the remainder (7 g) evaporated to near dryness on a hotplate. A further 2 mL of HNO_3 and 2 mL of H_2O_2 was then added drop-wise to each residue to complete tissue digestion. The digestion solutions were washed into separate polypropylene tubes with 1% HNO_3, and made up to 20 g. Inductively coupled mass spectrometry (ICP-MS) using a Perkin-Elmer Sciex ELAN 5000 was used to determine sample solution concentrations of all metals (aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn)).

5.2.3. Sample Analyses: Organochlorines

Blubber is the major repository for organochlorines in marine mammals (O'Shea 1999). Organochlorine concencentrations in blubber were determined by the Queensland Health and Scientific Services Laboratories, Brisbane. Between 2-5 g of blubber were extracted by macerating the sample in 100 mL of acetone in a blender. The samples were then centrifuged and the supernatant transferred into separating funnels. This was repeated twice and the extracts were combined. A 100 mL aliquot of dichloromethane (DCM) and 5 mL of saturated NaCl aqueous solution were added to the supernatant. Following phase separation, the non-polar fraction was concentrated, taken up in n-hexane and transferred to a column packed with Florisil. This was eluted with 6 % diethylether (DEE) in n-hexane which removed most organochlorines and PCBs. The individual fractions were reduced, transferred to DCM and then passed through a gel-permeation column (GPC) (Envirogel, Waters) using DCM as the mobile phase. Following the GPC step, the 6 % DEE fractions were transferred into n-hexane and concentrated to 1 mL.

The samples were then analysed for HCB (detection limit 0.1 μg kg^{-1}), lindane (detection limit 0.2 μg kg^{-1}), heptachlor (detection limit 0.2 μg kg^{-1}), heptachlor epoxide (detection limit 0.2 μg kg^{-1}), aldrin (detection limit 0.2 μg kg^{-1}), dieldrin (detection limit 0.2 μg kg^{-1}), DDT (detection limit 0.2 μg kg^{-1}), DDE (detection limit 0.1 μg kg^{-1}), DDD (detection limit 0.2 μg kg^{-1}) and PCBs (detection limit 0.2 μg kg^{-1}) on a gas chromatograph employing an electron capture detector (GC-ECD). The total lipid content of each sample was determined gravimetrically. Dugong fat samples were not analysed for diuron as the chemical has a relatively low Log K_{ow} value (2.8), minimising its potential for bioaccumulation (Connell 1990).

5.2.4. Quality Assurance and Statistical Analysis

Certified Standard Reference Material (National Research Council, Canada; DORM-2; dogfish muscle), reagent blanks and sample duplicates were analysed concurrently with dugong tissue to validate the metal analyses methods used (Table 5.2). Reagent blanks and spiked recovery samples for organochlorine compounds and PCBs were analysed concurrently with dugong tissue samples. Average recoveries of spikes ranged from 18-115 % (Table 5.3). No organochlorines were detected in reagent blanks.

One-way analysis of variance (ANOVA) was used to compare metal concentrations in livers of mature and immature dugongs. Data were plotted and visually assessed for gross deviations from normality and, where necessary, transformed (Log_{10}) prior to analysis. Where metal concentrations were less than detection limits, values were assigned at half the detection limit. An agglomerative hierarchical algorithm using complete clustering was used to classify liver metal data, and principal components analysis (PCA) was used to ordinate the liver metal data. Liver metal concentrations were standardised to *Z* scores prior to Principal Components Analysis. The presence of natural groupings in the data was defined by concurrence in both the classification and ordination analyses (Clarke and Warwick 1994). Two-way analysis of variance was also used to investigate the relationship between detectable blubber organochlorine concentrations (DDE and dieldrin) and animal maturity and gender (Ott 1993). Statistical analyses were carried out using the SYSTAT V7.0 statistical package (Wilkinson 1996).

Table 5.2. Average recoveries (%) of Standard Reference Material (DORM 2, Dogfish muscle, National Research Council, Canada).

Metal	Average recovery, samples c2-4	Average recovery, samples c7-16	Average recovery, samples c17-26	Average recovery, samples c27-52
Al	88.1	82.6	91.5	86
As	105.6	86.7	87.8	77
Cd	100.0	100.0	100.0	105
Cr	86.7	80.1	95.7	88
Cu	98.3	100.9	88.0	107
Fe	na	90.8	104.9	108
Pb	109.2	115.4	123.1	94
Mn	93.2	86.3	99.7	99
Hg	97.4	95.5	95.7	94
Ni	90.7	81.4	99.5	84
Se	108.6	86.4	81.4	91
Zn	94.9	85.9	96.5	104

na: not available

Table 5.3. Average recoveries (%) of organochlorine compounds in spiked samples.

Compound	Sample no c7-c13	Sample no c17-c19	Sample no c23-c26	Sample no c27-c52
HCB	64	18	35	71
Lindane	89	41	61	98
Heptachlor	91	32	56	72
Heptachlor epoxide	96	na	62	93
Dieldrin	101	34	48	102
Aldrin	84	22	31	87
DDT (pp)	115	52	80	98
DDE (pp)	102	44	67	98
DDD (pp)	104	46	78	93
PCBs	na	na	na	84

na: not available

5.3. Results

5.3.1. Metals

Twenty-two liver tissue samples were collected from stranded dugong carcasses and analysed for metal concentrations between 1996-2000 (Table 5.1). Detectable concentrations of all metals analysed were present in dugong liver (Table 5.4). Highest average concentrations of all metals except aluminium, chromium, manganese and nickel were found in mature animals (Table 5.4), although only concentrations of arsenic, cadmium, iron, mercury and zinc were significantly higher in older animals ($p<0.05$; Table 5.5). Tissue samples collected from five animals contained comparatively elevated concentrations of one or more metals (arsenic, chromium, manganese, nickel and lead) compared with concentrations typically present in marine mammals (Table 5.6). All of these animals were in relatively good condition at the time of death.

The first two components of a principal components analysis of liver metal concentrations accounted for 53% of the variance in the metal data (Table 5.7). Principal component I (33% of the variance) was associated with iron, mercury, cadmium, zinc, lead and manganese concentrations. Principal component II (19% of the variance) was associated with nickel and chromium concentrations. Principal component III (12% of the variance) was associated with aluminium, copper and arsenic concentrations. Principal component IV (11% of the variance) was associated with selenium concentrations. Classification and ordination analysis failed to group sampled animals by age, gender or sampling location (Figure 5.3).

Table 5.4. Summary statistics, dugong liver metal concentrations. (All concentrations mg kg^{-1} dry weight).

Immature animals (n=9)	Minimum	Maximum	Mean	SD
Length (cm)	110	205	153	34
% Wet Weight	69	80	77	3
Al	<5	264	39	85
As	0.2	4.6	1.4	1.5
Cd	<0.03	4.95	1.00	1.58
Cr	0.9	10.2	4.0	3.0
Cu	7	206	79	66
Fe	540	6570	2770	1790
Hg	0.04	0.37	0.11	0.11
Pb	<0.08	0.64	0.20	0.18
Mn	<1	17	12	5
Ni	<0.3	7.4	2.7	2.4
Se	<0.02	2.96	1.04	1.21
Zn	46	2463	812	686
Mature animals (n=13)				
Length (cm)	213	300	260	30
% Wet Weight	69	80	75	4
Al	<5	157	34	42
As	0.45	7.0	2.7	1.8
Cd	0.5	32.5	6.5	8.5
Cr	0.2	18	2.6	4.7
Cu	9.5	303	87	81
Fe	1660	137730	30380	39270
Hg	0.05	1.11	0.34	0.33
Pb	<0.08	2.78	0.46	0.74
Mn	<1	35	8.5	9.6
Ni	<0.3	14.36	2.11	3.8
Se	<0.02	3.6	1.5	1.0
Zn	457	5375	2521	1468

Table 5.5. Summary of one-way ANOVAs of liver metal concentrations between mature and immature dugongs. (All data dry wt and $\log_{10}$ transformed prior to analyses).

Metal	ANOVA *F* ratio (Animal age)	*p*
Al	0.339	0.567
As	**4.48**	**0.047**
Cd	**11.301**	**0.003**
Cr	3.336	0.083
Cu	0.055	0.817
Fe	**12.577**	**0.002**
Hg	**4.401**	**0.049**
Mn	2.607	0.122
Ni	0.984	0.333
Pb	1.003	0.328
Se	1.173	0.292
Zn	**13.052**	**0.002**

Table 5.6. Queensland dugong carcasses with elevated concentrations of one or metals in liver samples. (All metal concentrations mg kg^{-1} (dry weight)).

Sample no	Description	Cause of death	As	Cr	Mn	Ni	Pb
C002	Adult male	Drowning			34.9		
C010	Adult male	Drowning	7.0				
C025	Adult male	Drowning					2.78
C045	Adult female	Unknown		18.0		14.7	
C052	Juvenile male	Unknown		10.2		7.4	
Typical marine mammal tissue wet weight metal concentration (Thompson 1990)			<1	<1	7	<1	<1

Table 5.7. Summary of PCA analysis of metal concentrations in Queensland dugong liver.

Metal	Component I	Component II	Component III	Component IV
Fe	**0.916**	0.016	0.117	0.190
Hg	**0.902**	-0.216	0.066	0.103
Cd	**0.886**	-0.007	-0.011	0.268
Zn	**0.737**	0.164	0.081	0.495
Pb	**0.611**	0.219	0.154	-0.219
Mn	**-0.597**	0.357	0.111	0.204
Ni	0.028	**-0.975**	0.025	0.057
Cr	0.020	**-0.958**	0.133	-0.010
Al	0.082	0.086	**0.820**	-0.054
Cu	-0.243	0.235	**-0.584**	0.241
As	0.422	0.391	**-0.567**	-0.299
Se	0.223	-0.067	-0.162	**0.869**
Eigen Value	4.16	2.45	1.42	1.11
% variation explained	33.38	19.49	12.00	11.35

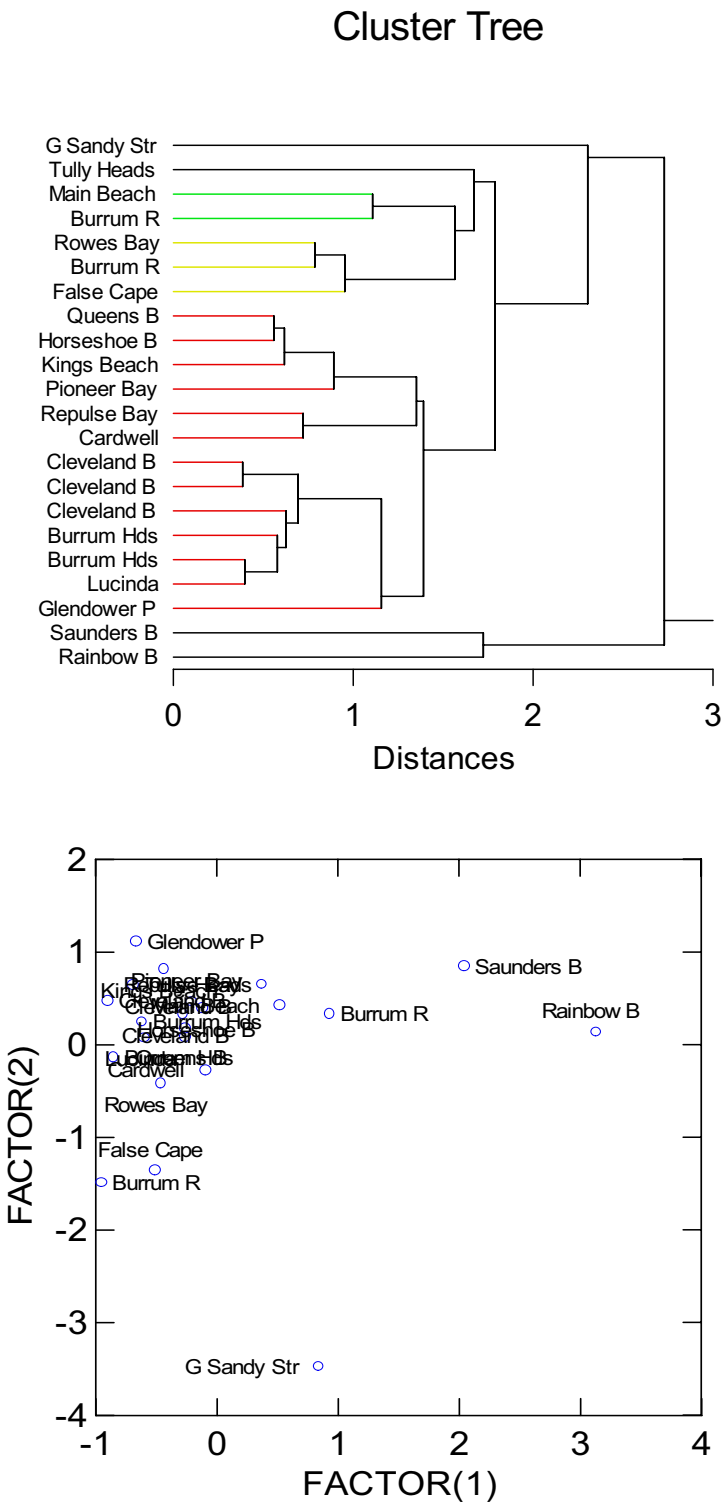

Figure 5.3. Classification and ordination of metal concentrations in dugong liver.

5.3.2. Organochlorines

Twenty-nine blubber samples were collected from dugong carcasses and analysed for organochlorine concentrations between 1996-2000 (Table 5.1). Twenty-three of these samples (72%) contained concentrations of one or more organochlorine compounds (dieldrin, DDT, DDD and/or DDE) (Table 5.8). When detected, dieldrin concentrations ranged from 0.4-9.0 μg kg^{-1} wet weight, DDT concentrations ranged from 0.5-59 μg kg^{-1} wet weight, and DDE concentrations ranged from 0.1-15.0 μg kg^{-1} wet weight. Lindane (detection limit 0.1 μg kg^{-1}), heptachlor (detection limit 1.0 μg kg^{-1}), heptachlor epoxide (detection limit 0.2 μg kg^{-1}), aldrin (detection limit 0.2 μg kg^{-1}), HCB (detection limit 0.1 μg kg^{-1}), and PCBs (detection limit 0.2 μg kg^{-1}) were not detected in sampled tissues.

Average wet weight concentrations of DDE were highest in mature male dugongs, and increased with increasing age in male animals (Figure 5.4). In contrast, average wet weight concentrations of DDE declined with maturity in female animals, although these differences were not statistically significant (Table 5.9). Concentrations of dieldrin in blubber also exhibited a similar pattern of accumulation, with male animals accumulating dieldrin with age and mature female animals having lower dieldrin concentrations than immature females.

Highest average concentrations of DDE were present in dugong blubber collected from mature animals stranded at northern sampling sites between Bowen and Townsville (Figure 5.5). Dieldrin concentrations were more uniformly distributed across stranding locations, with highest concentrations present in animals stranded at sites south of the Hinchinbrook region (18^{o} S)(Figure 5.5).

Table 5.8. Queensland dugong blubber organochlorine concentrations, 1996-2000.

(All data μg kg^{-1} wet weight).

Ref No	Length (cm)	Sex	Lipid (%)	DDT (ww)	DDD (ww)	DDE (ww)	Dieldrin (ww)
c002	266	M	74.2	.	.	0.9	0.9
c003	261	M	78.8	.	.	8.0	1.7
c004	282	F	74.9	.	.	3.0	2.1
c007	294	M	7.2	.	.	1.8	2.1
c009	110	M	3.7	.	.	.	.
c010	260	M	6.3	.	.	0.3	2.6
c012	213	F	76.2	.	.	0.7	5.3
c013	205	M	11.4	.	.	0.1	0.4
c017	196	F	57.4	.	.	0.5	0.8
c018	194	M	1.4	.	.	0.4	.
c019	235	M	4.4	.	.	1.0	0.5
c025	220	M	4.9	.	.	0.7	0.4
c028	190	M	6.0	.	.	.	.
c034	240	F	9.1	.	.	0.6	1.9
c035	229	M	89.1	59.0	6.0	15.0	7.0
c037	297	F	5.0	.	.	0.6	0.5
c038	198	M	8.5	.	.	.	.
c040	155	M	4.0	.	.	2.1	1.5
c042	320	M	4.8	.	.	trace	.
c043	173	U	7.3	.	.	.	.
c044	240	F	13.6	6.0	.	.	9.0
c045	287	F	11.0	.	.	.	.
c046	267	F	83.1	.	.	.	.
c047	237	M	7.6		.	.	.
c048	120	M	17.3	0.5	.	.	0.9
c049	?	F	6.3	.	.	.	.
c050	300	F	6.3	.	.	trace	.
c051	290	M	3.5	.	.	.	trace
c052	160	M	4.4	.	.	.	1.9

Table 5.9. Summary of two-factor ANOVA F *ratios of dugong DDE and dieldrin concentrations.*

(All p values >0.05). (Data Log_{10} transformed prior to analysis).

Compound	ANOVA *F* ratio (Animal maturity)	ANOVA *F* ratio (Animal gender)	ANOVA *F* Ratio (Interaction)
DDE (wet weight)	0.646	0.001	2.862
DDE (lipid weight)	0.950	0.814	0.568
Dieldrin (wet weight)	0.380	2.674	0.968
Dieldrin (lipid weight)	0.071	0.052	0.000

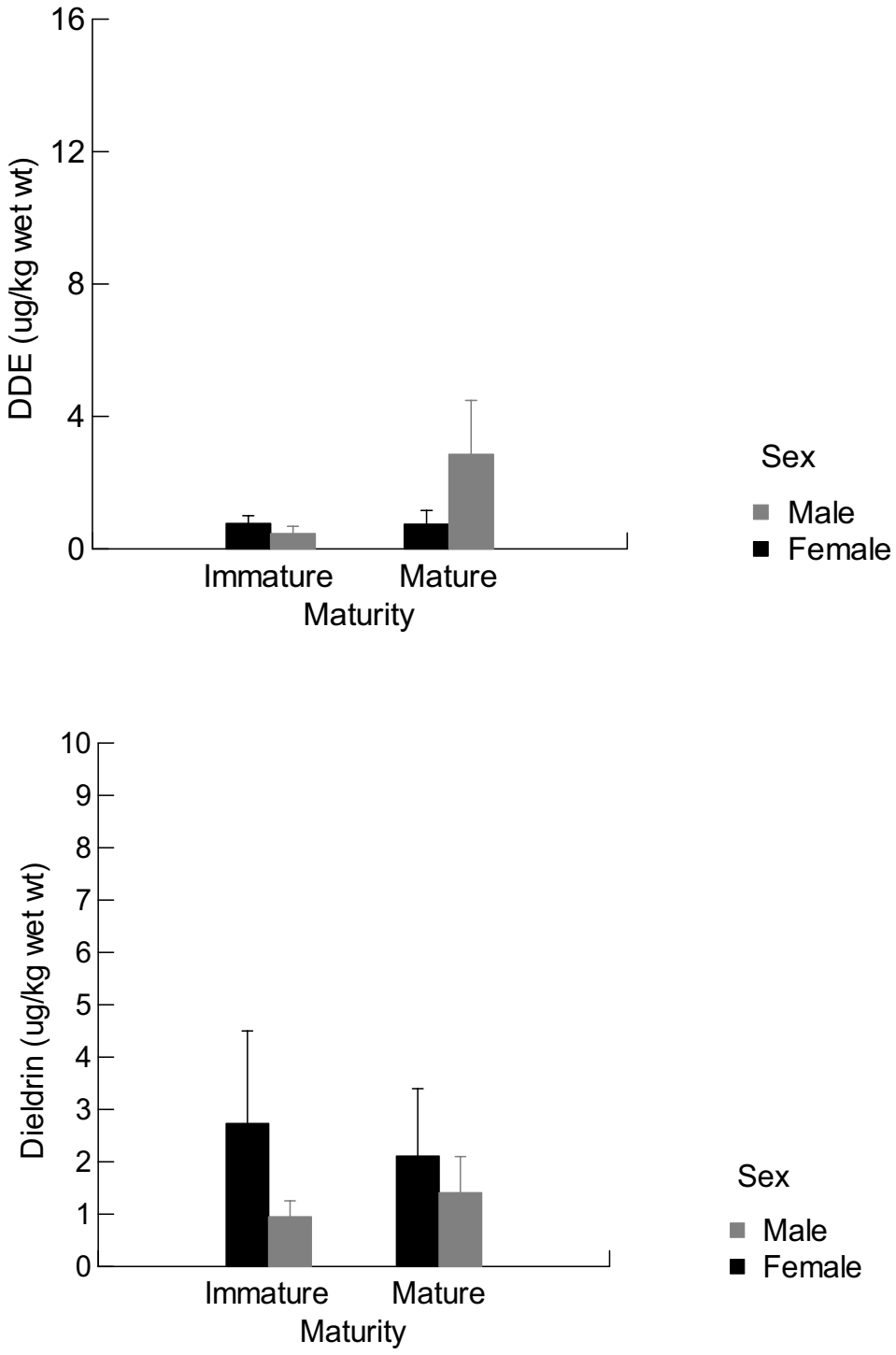

Figure 5.4. Concentrations of DDT and dieldrin in Queensland dugong blubber. (Error bars = 1 SEM).

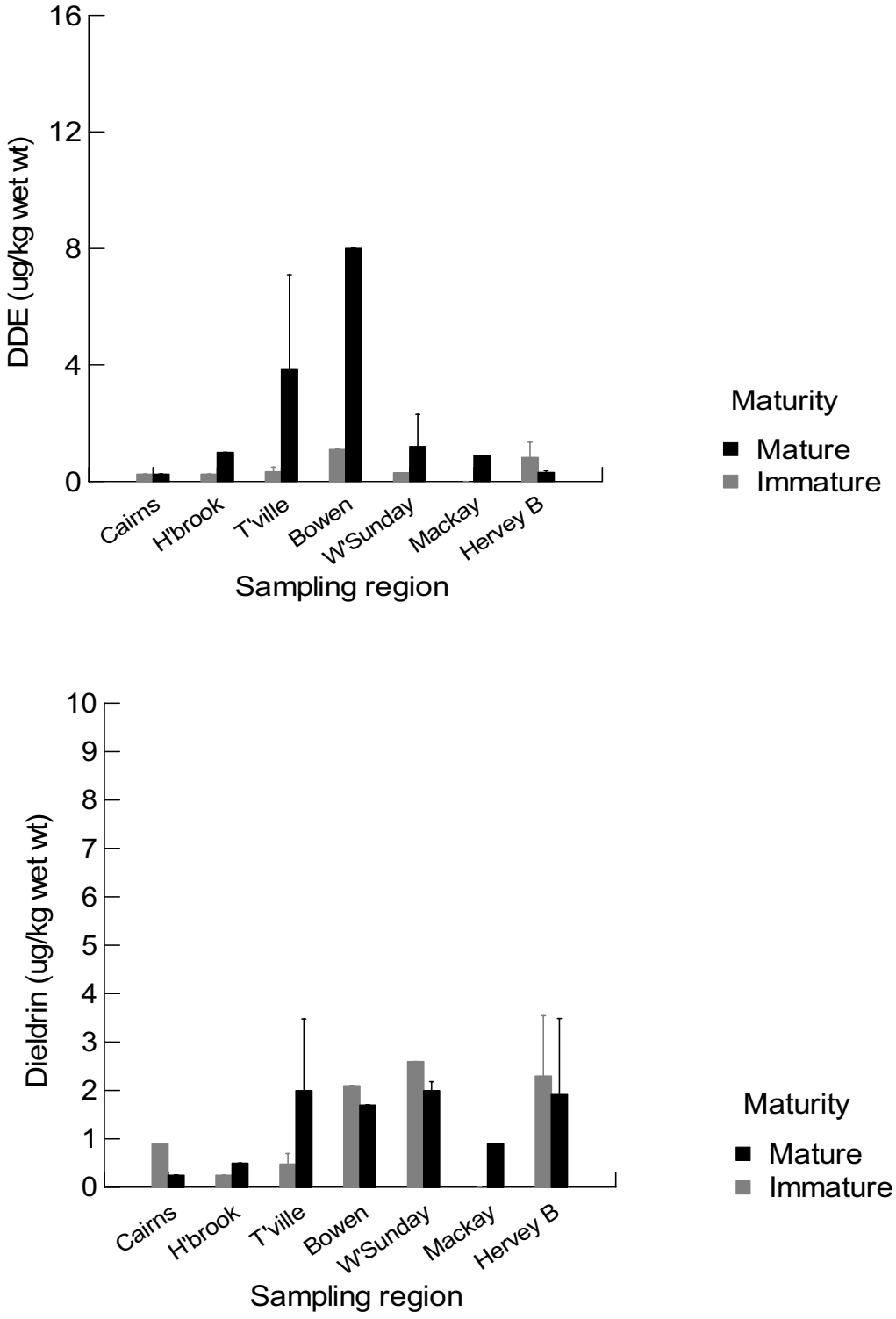

Figure 5.5. Concentrations of DDE and dieldrin in Queensland dugong carcass by salvage location. (Error bars = 1 SEM when n>1).

5.4. Discussion

A range of pollutants were detected in dugong tissues sampled along the Queensland coast between 1996 and 2000. Liver concentrations of metals were generally similar to, or lower than those reported previously in dugong collected along the northern Australian coast and in Torres Strait (Denton *et al*. 1980; Denton and Breck 1981; Marsh 1989; Parry and Munksgaard 1992; Parry and Munksgaard 1993; Dight and Gladstone 1993; Gladstone 1996). The general trend of higher average metal concentrations in mature dugong compared with younger animals found in these samples is typical of metal accumulation patterns present in marine mammals, and is associated with length of contaminant exposure (Aguilar *et al.* 1998; O'Shea 1999; O'Shea *et al.* 1999). Five of the twenty-two liver samples contained relatively elevated concentrations of one or more metals. The animals from which these tissue samples were obtained were in relatively good condition immediately prior to death and it is therefore unlikely that these metal body burdens contributed to the animals death.

Low concentrations of dieldrin and DDT and its metabolite DDE were detected in dugong blubber in this study. Dugong blubber dieldrin concentrations were similar to those reported in the liver of dugongs collected from the same region 20 years earlier (0.32-1.02 μg kg^{-1} wet weight) (Heinsohn and Marsh 1978). Dugong blubber dieldrin concentrations were also lower than concentrations detected in baleen whales (i.e. typically <100 μg kg^{-1} wet weight) (O'Shea and Brownell 1994) and were low compared with concentrations detected in blubber from toothed whales (70-3600 μg kg^{-1} wet weight) (Jarman *et al.* 1996; Law *et al.* 1997; Holsbeek *et al.* 1998).

Total DDT concentrations in dugong blubber were one to three orders of magnitude lower than those typically found in other marine mammals (<5-100 g kg^{-1}) including seals (Tanabe *et al.* 1994; Oehme *et al.* 1996), beluga whales (Muir *et al.* 1996); dolphins (Kannan *et al.* 1993) and baleen whales (deKock *et al.* 1994; O'Shea and Brownell 1994; de Guitart *et al.* 1996). Concentrations of ΣDDT in dugong blubber were also two orders of magnitude lower than concentrations detected in livers of Florida manatee (Ames and Van Vleet 1996).

Gender and age patterns of accumulation of DDE and dieldrin concentrations (on a wet weight basis) in dugongs followed the general trend of increased concentrations in mature males compared with immature males and a decline in concentrations in females with maturity associated with maternal contaminant transfer (Aguilar *et al.* 1998; O'Shea 1999; O'Shea *et al.* 1999).

5.5. Conclusions

Concerns about the conservation and protection of marine mammals inevitably extends to consideration of the impact of contaminants (O'Shea *et al.* 1999). Dugongs are coastal residents and it is these waters that tend to receive highest concentrations of metals and persistent organic pollutants from riverine inflows and direct emissions, as well as highest atmospheric rates of pollutant deposition due to their proximity to land-based sources (Wania *et al.* 1998). In Queensland, dieldrin and DDT are still a widely distributed in agricultural soils (Cavanagh *et al.* 1999; Müller *et al.* 2000) and this is reflected in their occurrence in nearshore subtidal sediments along the Queensland wet-tropics coastline (Chapter 3). Similarly, elevated concentrations of a number of heavy metals derived from igneous parent material are also present in nearshore coastal Queensland sediments.

Persistent contaminants are generally incorporated into the body of marine mammals through food intake (Aguilar *et al.* 1998). Dugongs feed by uprooting entire seagrass plants from the benthos (Spain and Heinsohn 1973; Preen 1995a; Preen 1995b), and as a consequence, most intra- and inter-specific variation in dugong metal body burdens can probably be associated with variable metal concentrations in seagrass and associated sediments and animal age. Variation in body burdens of organochlorine residues are also likely to be related to environmental concentrations as well as the reproductive history of female animals.

Potential toxicity of accumulated metals in marine mammals is related to cellular enzyme inactivation, however, with the exception of mercury, no experimental or field collected data has yet demonstrated a toxic impact of accumulated metals in marine mammals (Johnston *et al.* 1996; O'Shea 1999). Although cause of death has not been established conclusively for a majority of the Queensland dugong carcasses with

elevated metal concentrations, a majority were suspected net drownings. It is therefore unlikely that heavy metal accumulation has played a significant part in dugong mortalities along the coast. Accumulation of dieldrin and DDT in marine mammals has demonstrated reproductive and endocrine disruptive effects (Fossi *et al.* 1999). However, the concentrations of these pollutants accumulated by Queensland dugongs are relatively low compared with those present in marine mammals elsewhere. It is therefore also unlikely that these compounds present a direct risk to local dugong populations.

A greater, indirect risk to Queensland dugong populations is likely to be presented by the impact of herbicide residues on their nearshore seagrass food resource (Chapter 4), and the relatively high concentrations of dioxins, (especially the hepta- and octa-chlorinated dibenzodioxins), which have been detected in the blubber of these animals (Chapter 6).

Chapter 6: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the Great Barrier Reef environment.

GBRMPA

Intertidal habitat, Hinchinbrook Channel, Northern Great Barrier Reef

CHAPTER SIX: POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN THE GREAT BARRIER REEF ENVIRONMENT.

6.1. Introduction

Dioxins are a group of 210 chlorinated compounds consisting of chlorinated dibenzo-para-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs). They are formed during various chemical and industrial manufacturing processes and by combustion of organic material (Kjeller *et al.* 1991), and also via lesser known natural processes (Hashimoto *et al.* 1995; Alcock *et al.* 1998). Dioxins are known to display a diverse and complex array of toxicological properties (Buckland *et al.* 1990) and have been detected in a variety of environmental compartments including freshwater and marine sediments (Czuzwa and Hites 1984; Rappe *et al*. 1987; Jonsson *et al*. 1993; Mosse and Haynes 1993) and the tissue of marine mammals (Buckland *et al.* 1990; Norstrom *et al.* 1990; Oehme *et al.* 1995; Jarman *et al.* 1996; Muir *et al.* 1996; Tarasova *et al.* 1997).

Australia's north-east is in a subtropical to tropical region and has a low population density with relatively little industrial activity. Although little information on the occurance of PCDD/Fs in tropical Australia is available, it has been assumed that no significant sources of PCDDs and PCDFs exist in this region. However, in an earlier terrestrial study, high concentrations of octachlorinated dibenzodioxin (OCDD) and a relatively unusual PCDD/F congener profile were found in topsoil samples collected from a sugar cane field in northern Queensland (Müller *et al.* 1996a; Müller *et al.* 1996b).

In the light of these results, a pilot study was initiated concurrently with the study of the distribution of other marine pollutants (Chapters 2 and 3) to investigate concentrations of PCDDD/Fs in selected local marine sediment and seagrass samples collected along the Queensland coast with the goal of identifying contaminated areas. Dioxin concentrations present in dugong tissue collected opportunistically from stranded animals were also assessed.

6.2. Materials and Methods

6.2.1. Sediment and Seagrass Sampling

Sediment and seagrass samples were collected at five sampling sites along the northern Queensland coast (Figure 6.1). Samples were collected between February and May 1997. All sampling locations were in the vicinity of important dugong habitat (Marsh and Corkeron 1997). At each location, three replicate sediment samples were collected into 1 L solvent-washed glass jars. Each sediment sample was a composite of multiple surficial sediment samples scooped directly into the sampling jar. Sediments were collected randomly over an area of approximately 400 m^2 at each location. Three random samples of the dominant seagrass (*Halodule uninervis* or *Zostera capricorni*) were also collected over the same area at each of the five northern Queensland sampling sites. Entire plants (leaves, roots and rhizomes) were sampled and vigorously rinsed in seawater at the time of collection to simulate dugong feeding, which appears to efficiently remove course sediments associated with seagrass leaves and rhizomes prior to ingestion of plant material (Heinsohn and Birch 1972; Preen 1995a; Preen 1995b).

6.2.2. Dugong Tissue Sampling

Tissue samples were collected opportunistically from 3 dugong carcasses washed onto Queensland beaches between Mackay and Townsville (Glendower Point, Kings Beach and Horseshoe Bay) in 1996 (Figure 6.1). Basic anatomical data were recorded for each carcass (Table 6.2). All carcasses were in good condition at the time of sampling, and all animal deaths were confirmed or suspected net drownings. From each animal, samples of fat tissue were collected from the outermost layer of fat, just to one side of the mid-ventral line (Geraci and Lounsbury 1993). Tissue samples were stored frozen in plastic zip-top bags. Samples were transported to the analytical laboratory at Bayreuth, Germany on dry ice. (Tissue samples were collected under Scientific Purposes Permit No. 0011221/96/SAB – *Queensland Nature Conservation Act 1992*).

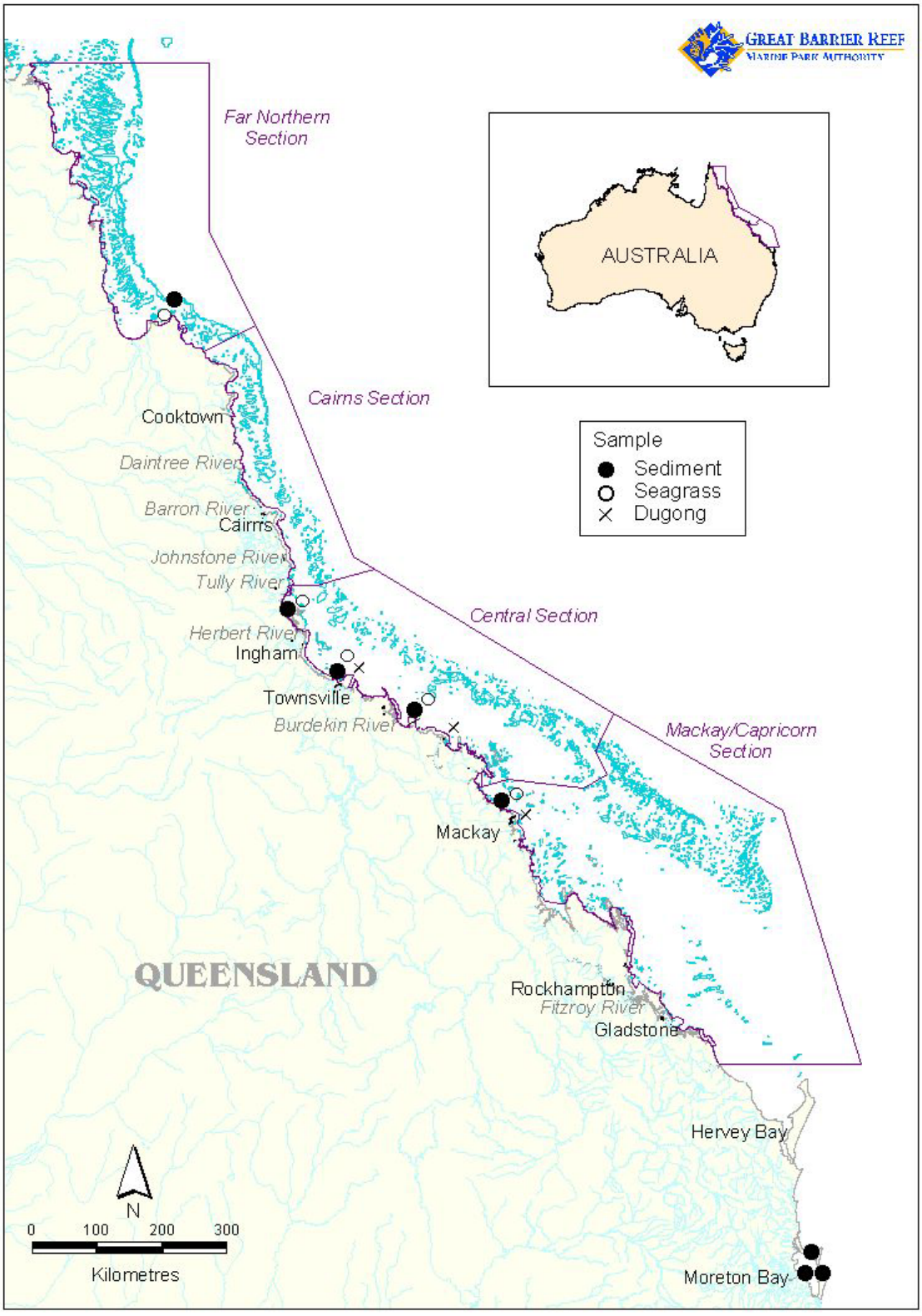

Figure 6.1. Queensland sediment, seagrass and dugong sampling locations,1996-1997.

Table 6.1. Details and description of sediment and seagrass sampling areas, 1997.

Sampling area	Description of sampling area
Newry Bay	Sediments collected from the intertidal zone. Adjacent area under intensive agriculture (sugar cane).
Upstart Bay	Site located in SE corner of Upstart Bay. Local intensive agriculture (vegetable growing). Sediments collected from the intertidal zone.
Pallarenda	Site adjacent to the largest north Queensland urban center (Townsville), population 120,000. Sediments collected from the intertidal zone.
Cardwell	Samples collected adjacent to a small rural center. Surrounding area under intensive agriculture (sugar cane). Sediments collected from the intertidal zone.
Flinders Island	Samples collected in the remote far northern section of the Great Barrier Reef Marine Park. Sediments collected from the intertidal zone.

Table 6.2. Characteristics of dugong carcasses sampled for dioxin analyses, Queensland 1996.

Sampling date	Sampling location	Cause of death	Length (cm)	Sex	Age	Carcass condition
8/8/96	Glendower Point, Mackay, Qld.	Net drowning	266	Male	Mature	Good
2/9/96	Kings Beach, Bowen, Qld.	Unconfirmed net drowning	261	Male	Mature	Good
20/9/96	Horseshoe Bay, Magnetic Is. Qld.	Net drowning	282	Female	Mature	Good

6.2.3. Sediment Sample Analysis

One sediment replicate collected from each sampling site was selected at random for analysis. The selected sediment samples and a blank consisting of 100 g anhydrous Na_2SO_4 were freeze dried at the Queensland Health and Scientific Services laboratory in Brisbane, and samples were subsequently transported in sealed containers to the University of Bayreuth, Germany, for dioxin analysis.

Before extraction, mixtures of 12 $^{13}C_{12}$-labeled 2,3,7,8-substituted PCDD/PCDF congeners were added to the extraction solvent (toluene). All samples including blanks were soxhlet extracted for 24 h. The clean-up procedure for the PCDDs/PCDFs was based on published methodologies (Hagenmaier *et al.* 1986). After extraction the sample was concentrated and applied to an acid/base column (filled from the bottom with silica gel / 1 N NaOH (33 %), activated silica, silica gel / concentrated H_2SO_4 (44 %), and silica gel / concentrated H_2SO_4 (22 %)). The PCDDs/PCDFs were eluted with n-hexane and the purified extract was then fractionated on a basic alumina column. The PCDDs/PCDFs were eluted with a mixture of dichloromethane/n-hexane (50/50, V/V). The PCDD/PCDF fractions were concentrated and a $^{37}Cl_4$-2,3,7,8-TeCDD recovery standard was added. The extract was then transferred into 100 µl vials and reduced to 25 µl. All samples were analysed using HRGC/HRMS on a Hewlett Packard 5890/II GC (splitless) coupled to a VG Autospec Ultima mass spectrometer. The 2,3,7,8 substituted PCDD/PCDF congeners were separated on a RTX-2330 capillary column (60 m; 0.25 mm ID; 0.1 µm film thickness). The mass spectrometer was operated at a resolution of 9000–10000.

For total organic carbon content (TOC) quantification, inorganic carbonates were first removed using an acid catalysed digestion (10% HCl, 1% $FeCl_2$ at 70^{o}C). The remaining material was dried and subjected to a combustion procedure (LECO induction furnace) with subsequent detection of CO_2 (LECO WR12 CO_2 detector).

6.2.4. Seagrass Sample Analysis

One replicate seagrass sample collected at each northern Queensland sampling site was also selected at random for dioxin analysis. Selected samples were transported on ice to Bayreuth, Germany for analysis. The seagrass samples were homogenised in a blender and aliquots of approximately 40 g were soxhlet extracted in toluene for 16 h following addition of a mixture of 12 $^{13}C_{12}$ labelled 2,3,7,8-substituted PCDD/F congeners to the extraction solvent. The extracts were cleaned up using a H_2SO_4/silica gel + NaOH/silica gel mixed column and an alox column (Horstmann *et al.* 1992). Purified extracts were concentrated to 10 µL, a recovery standard was added, and the samples were analysed for the 2,3,7,8-substituted PCDD/F congeners using HRGC/HRMS on a VG Autospec Ultima at a resolution of ~10,000 (Horstmann and McLachlan 1995).

6.2.5. Dugong Tissue Analysis

Approximately 1 g of blubber from each dugong sample was mixed with 10 g of anhydrous sodium sulphate. The mixture was poured into a glass column. Mixing beakers and utensils were rinsed with 35 ml of a 1:1 (v/v) mixture of n-hexane/dichloromethane and this was also transferred to the glass column. Hexane/dichloromethane completed the extraction. The extract was evaporated to ca. 1 ml on a rotary evaporator and then transferred to a glass column containing (from the bottom) NaOH/silica gel, silica gel and H_2SO_4/silica gel. PCDD/Fs were eluted with n-hexane. The eluate directly flowed onto a second column containing 7.5 g Al_2O_3 (ICN b super 1) and 5 g Na_2SO_4. A pre-eluate from the Al_2O_3 with 80 ml of n-hexane/dichloromethane 98:2 (v/v) was discarded. PCDDs and PCDFs were then eluted from the Al_2O_3 column with 80 ml of n-hexane/dichloromethane 1:1 (v/v). A $4Cl_{37}$ labeled 2,3,7,8-TCDD standard was added to estimate recovery. Extracts were transferred to a vial, evaporated almost to dryness, and taken up in 30µl of toluene. The HRGC/HRMS analyses were conducted using a HP-5890 gas chromatograph coupled to a VG-autospec Ultima mass spectrometer operating in El mode at 34 ev and a resolution of approximately 10,000. A 60m x 0.25mm i.d. RTX 2330 (ResTek) column with a film thickness of 0.10 µm was employed.

6.2.6. Quality Control and Statistical Analysis

Analytical data were required to fulfil a set of criteria including conformation of the analyte retention time to the retention time of an external standard and, after correcting for isotope shift, with the retention time of an internal standard. Chlorine isotope ratios were not allowed to differ more than 10 % from the theoretical values. The mass fragment with the highest intensity was used for quantification. Detection limits are specific for a given compound in a given sample, and varied depending on the injection volume, analytical conditions, initial and final sample volumes and observed contamination concentrations in the blank. Sample detection limit for an individual compound was defined by a signal of greater than 3 times the average baseline noise in the retention window or 3 times the concentrations in the respective matrix and solvent blanks. In all samples, the recoveries of the tetra- to octachlorinated $^{13}C_{12}$ labeled internal standards determined using the recovery standard $^{37}Cl_4$-2,3,7,8-TeCDD were greater than 70 %. PCDD/PCDF sediment and seagrass data were transformed (Log_{10}) prior to principal components analysis (PCA). Values which were below the detection limit criteria were set at half the detection limit for this analysis. Additional data from previous studies (Müller *et al.* 1996a; 1996b; 1999) on PCDD/Fs concentrations in top-soil collected from a sugar cane area at Cardwell, adjacent to northern marine sampling sites, and from Moreton Bay, Southern Queensland, were incorporated into the analysis to explore any similarities in PCDD/F contamination. An agglomerative hierarchical algorithm using complete clustering was used to classify the PCDD/F sediment data (dry weight). PCA was used to ordinate the data. Euclidean distances were utilized to calculate dissimilarities. The presence of natural groupings in the data was defined by concurrence in both the classification and the ordination analyses (Clarke and Warwick 1994). All statistical calculations were carried out with the SYSTAT V7.0 software package (Wilkinson 1996).

6.3. Results

6.3.1. Sediment Dioxin Concentrations

A series of 2,3,7,8-substituted PCDDs were detectable in all sediment samples, whereas PCDFs were below the limit of quantification at most sites (Table 6.3).

OCDD was the dominant PCDD/F in all sediments analysed, and its concentration ranged from 17,500 pg g^{-1} OC at the Upstart Bay site to 190,000 pg g^{-1} OC in sediment samples collected from Newry Bay (Table 6.4). 2,3,7,8-TCDD was detectable only in samples collected from Newry Bay, while 1,2,3,7,8-PeCDD was found in all sediment samples except that from Upstart Bay. In contrast to the higher chlorinated PCDDs which were detected in all sediment samples, the PCDF concentrations were relatively low and the 2,3,7,8-substituted tetra- to hexachlorinated dibenzofurans were, with few exceptions, only detected in the samples from Cardwell and Newry Bay.

Expressed on an organic carbon basis, the total toxicity equivalents (TE), (using the pre 1997 NATO-CCMS toxicity equivalency factors) ranged from less than 100 pg TE g^{-1} OC in sediments from the Flinders Island and Upstart Bay sites to 420 pg g^{-1} OC in sediments collected from Newry Bay. Similarly, if expressed as the sum of all 2,3,7,8-substituted PCDD/Fs, concentrations were significantly higher in sediments from Newry Bay compared to the other sites sampled in northern Queensland (Table 6.4).

Table 6.3. Concentrations of total organic carbon (%) and 2,3,7,8 substituted PCDD/PCDF congeners in Queensland sediments. (All data in pg g^{-1}).

Congener	Newry Bay	Upstart Bay	Pallarenda	Cardwell	Flinders Is
2,3,7,8-TCDD	0.09	<0.01	<0.02	<0.06	<0.03
1,2,3,7,8-PeCDD	0.4	<0.01	0.07	0.39	0.15
1,2,3,4,7,8-HxCDD	0.95	<0.02	0.09	1.2	0.32
1,2,3,6,7,8-HxCDD	1.5	<0.02	0.21	1.8	0.48
1,2,3,7,8,9-HxCDD	2.7	0.04	0.29	3.7	1.2
1,2,3,4,6,7,8-HpCDD	57	0.67	6.2	77	12
OCDD	1200	14	130	2900	190
2,3,7,8-TCDF	<0.03	<0.01	<0.01	0.05	<0.01
1,2,3,7,8-PeCDF	<0.08	<0.01	<0.02	<0.04	<0.03
2,3,4,7,8-PeCDF	<0.02	<0.004	<0.01	<0.02	<0.01
1,2,3,4,7,8-HxCDF	<0.02	<0.01	<0.02	<0.04	<0.01
1,2,3,6,7,8-HxCDF	<0.03	<0.001	<0.02	<0.04	<0.01
1,2,3,7,8,9-HxCDF	<0.03	<0.005	<0.02	<0.02	<0.01
2,3,4,6,7,8-HxCDF	<0.04	<0.01	<0.02	<0.05	<0.03
1,2,3,4,6,7,8-HpCDF	0.09	<0.01	0.11	0.3	<0.02
1,2,3,4,7,8,9-HpCDF	<0.01	<0.004	<0.01	0.02	<0.01
OCDF	0.18	<0.01	0.26	1.2	0.05
TOC	0.68	0.08	0.15	2.2	0.72

Table 6.4. Concentrations of 2,3,7,8 substituted PCDD/PCDF congeners in Queensland sediments. (All data in pg g^{-1} TOC).

Congener	Newry Bay	Upstart Bay	Pallarenda	Cardwell	Flinders Is
2,3,7,8-TCDD	15	<13	<13	<2.7	<4.2
1,2,3,7,8-PeCDD	66	<13	47	18	21
1,2,3,4,7,8-HxCDD	150	<25	60	55	44
1,2,3,6,7,8-HxCDD	240	<25	140	82	67
1,2,3,7,8,9-HxCDD	440	50	190	170	170
1,2,3,4,6,7,8-HpCDD	9 100	840	4 100	3 500	1 700
OCDD	190 000	17 500	87 000	130 000	26 000
2,3,7,8-TCDF	4.8	<13	<6.7	2.3	<1.4
1,2,3,7,8-PeCDF	<13	<13	<13	<1.8	<4.2
2,3,4,7,8-PeCDF	<3.2	<5.0	<6.7	<0.9	<1.4
1,2,3,4,7,8-HxCDF	<3.2	<13	<13	<1.8	<1.4
1,2,3,6,7,8-HxCDF	<4.8	<1.3	<13	<1.8	<1.4
1,2,3,7,8,9-HxCDF	<4.8	<6.3	<13	<0.9	<1.4
2,3,4,6,7,8-HxCDF	<6.5	<13	<13	<1.8	<4.2
1,2,3,4,6,7,8-HpCDF	15	<13	73	14	<2.8
1,2,3,4,7,8,9-HpCDF	<1.6	<5.0	<6.7	0.9	<1.4
OCDF	29	<13	170	55	6.9
TEq (pre 1997)	420	63	210	210	88
Σ PCDDs/PCDFs	210 000	18 000	91 000	140 000	28 000

Table 6.5. Concentrations of 2,3,7,8 substituted PCDD/PCDF congeners in Great Barrier Reef seagrass. (All data in pg g^{-1}).

congener	Newry Bay	Upstart Bay	Pallarenda	Cardwell	Flinders Island
2,3,7,8-TCDD	0.07	<0.01	0.02	0.04	0.03
1,2,3,7,8-PeCDD	0.44	0.03	0.14	0.38	0.26
1,2,3,4,7,8-HxCDD	1.1	0.08	0.29	1.1	0.43
1,2,3,6,7,8-HxCDD	1.5	0.11	0.4	1.5	0.66
1,2,3,7,8,9-HxCDD	2.5	0.18	0.52	2.4	1.5
1,2,3,4,6,7,8-HpCDD	47	2.5	8.2	44	15
OCDD	890	49	90	1300	200
2,3,7,8-TCDF	0.1	<0.01	0.08	0.05	0.13
1,2,3,7,8-PeCDF	0.21	0.02	0.11	0.07	0.41
2,3,4,7,8-PeCDF	0.02	<0.01	0.03	0.02	0.02
1,2,3,4,7,8-HxCDF	0.01	<0.01	0.01	0.01	0.01
1,2,3,6,7,8-HxCDF	0.02	<0.01	0.01	0.02	0.01
1,2,3,7,8,9-HxCDF	<0.01	<0.01	0.01	0.02	0.01
2,3,4,6,7,8-HxCDF	<0.02	<0.01	<0.02	<0.02	<0.02
1,2,3,4,6,7,8-HpCDF	0.1	<0.01	0.2	0.13	0.04
1,2,3,4,7,8,9-HpCDF	<0.01	<0.02	<0.01	0.01	<0.002
OCDF	<0.09	<0.04	0.21	0.32	<0.02

6.3.2. Seagrass Dioxin Concentrations

A series of 2,3,7,8-substituted PCDDs and PCDFs were detectable in all seagrass samples (Table 6.5). 2,3,7,8-TCDD was detectable in all seagrass samples except those collected at Upstart Bay (Table 6.5). As for sediments samples, OCDD was the dominant PCDD/PCDF congener in all seagrass analysed, where its concentration ranged from 49 pg g^{-1} at the Upstart Bay site to 1300 pg g^{-1} in the sample collected from the Cardwell site. A good correlation was observed between the concentrations of hepta- and octa-chlorinated dioxins in sediment and seagrass from the same sampling site, as illustrated for Cl_7DD (r^2=0.926; Figure 6.2) and Cl_8DD (r^2=0.935; Figure 6.2).

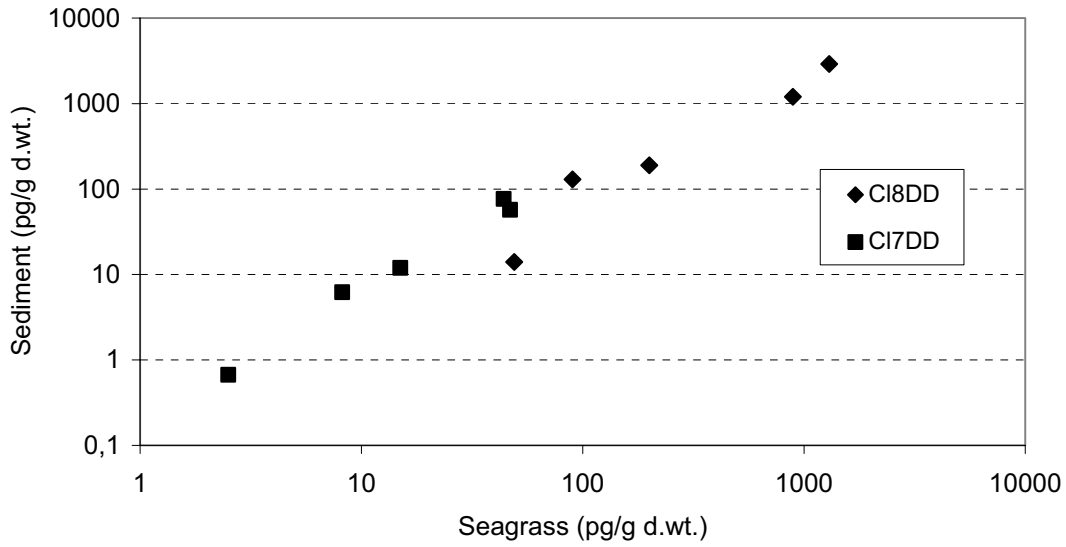

Figure 6.2. Plot of sediment vs. seagrass concentrations of 1,2,3,4,6,7,8-Cl_7DD and Cl_8DD at the 5 Great Barrier Reef sampling sites.

6.3.3. Dioxin and Furan PCA anlysis

Data on concentrations of PCDD/Fs in soil collected from a north Queensland sugar cane property in 1996 and Moreton Bay in 1997 (Table 6.6) were incorporated into the data-set described in this chapter and included in a principal components analysis of marine (sediment and seagrass) dioxin concentrations.

Table 6.6. Concentrations (in pg g^{-1} dry weight) of 2,3,7,8 substituted PCDD/PCDF congeners in topsoils from a sugarcane farm in North Queensland and Moreton Bay sediments used in the PCA analysis (Müller et al. *1996a; Müller* et al. *1996b; Müller* et al. *1999).*

Congener	Brisbane River.	Northern Moreton Bay	Eastern Moreton Bay	Cane soil, trash burnt	Cane soil trash unburnt
2,3,7,8-TCDD	0.63	0.25	<0.04	<0.04	0.13
1,2,3,7,8-PeCDD	0.51	0.73	0.15	0.09	0.39
1,2,3,4,7,8-HxCDD	1.2	1.4	0.29	0.52	1.0
1,2,3,6,7,8-HxCDD	4.2	2.6	0.43	0.46	1.1
1,2,3,7,8,9-HxCDD	6.4	5	0.91	1.2	2.2
1,2,3,4,6,7,8-HpCDD	150	100	15	51	91
OCDD	5400	2600	490	5 200	9 000
2,3,7,8-TCDF	1.3	0.61	<0.03	<0.03	0.80
1,2,3,7,8-PeCDF	0.51	0.26	<0.02	0.08	0.14
2,3,4,7,8-PeCDF	0.5	0.26	<0.01	0.03	0.05
1,2,3,4,7,8-HxCDF	0.63	0.24	<0.01	<0.02	0.04
1,2,3,6,7,8-HxCDF	2.3	0.4	<0.01	<0.03	0.05
1,2,3,7,8,9-HxCDF	0.25	0.11	<0.01	<0.23	<0.26
2,3,4,6,7,8-HxCDF	0.51	0.17	<0.04	<0.04	<0.03
1,2,3,4,6,7,8-HpCDF	11	1.7	<0.09	<0.08	0.13
1,2,3,4,7,8,9-HpCDF	1.1	0.16	<0.01	<0.02	<0.02
OCDF	40	3.9	0.18	2.0	3.3

Table 6.7. Results of PCA analysis of sediment and seagrass PCDD/F concentrations

Congener	Component I	Component II
1,2,3,4,7,8-HxCDF	**0.943**	0.168
1,2,3,4,7,8-HpCDF	**0.942**	0.243
2,3,4,6,7,8-HxCDF	**0.852**	0.400
1,2,3,6,7,8-HxCDF	**0.843**	0.497
OCDF	**0.839**	0.424
2,3,4,7,8-PeCDF	**0.832**	0.486
1,2,3,4,6,7,8-HpCDF	**0.808**	0.471
1,2,3,7,8,9-HxCDF	**0.748**	0.373
2,3,7,8-TCDD	**0.717**	0.646
2,3,7,8-TCDF	**0.624**	0.590
1,2,3,4,7,8-HxCDD	0.267	**0.953**
1,2,3,7,8-PeCDD	0.263	**0.942**
1,2,3,7,8,9-HxCDD	0.356	**0.918**
1,2,3,6,7,8-HxCDD	0.387	**0.903**
1,2,3,4,6,7,8-HpCDD	0.442	**0.873**
OCDD	0.479	**0.760**
1,2,3,7,8-PeCDF	0.390	**0.712**
Eigenvalue	14.195	1.492
% variance explained	45.39	43.16

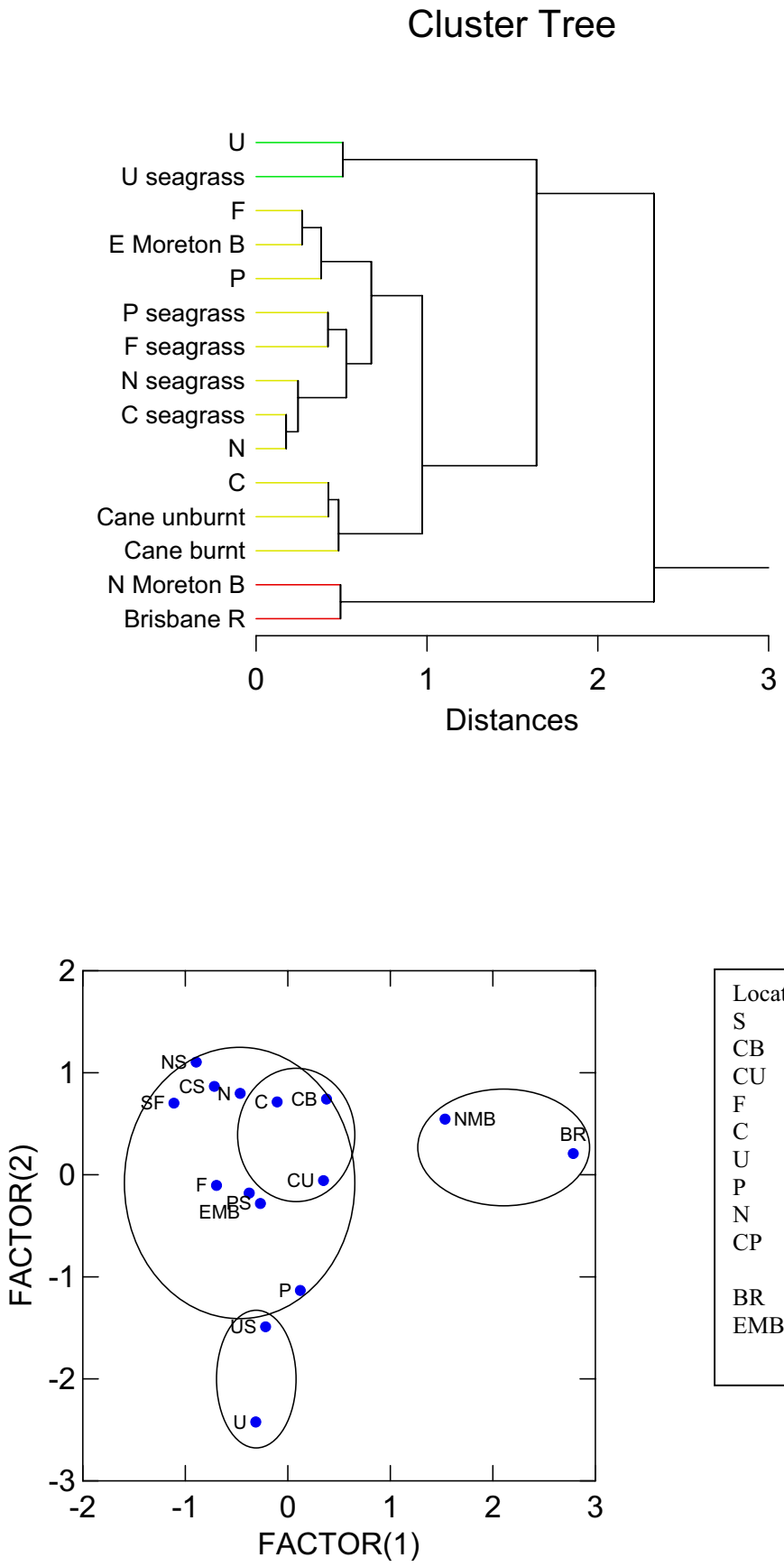

Figure 6.3. Classification and ordination of PCDD/F congener concentrations.

The first two components of the principal components analysis accounted for 88 % of the variance in the data (Table 6.7). Principal component I (45% of the variance) was correlated with sediment PCDF and 2,3,7,8-TCDD concentrations. Principal component II (43 % of the variance) was correlated with sediment PCDD and 12378 PeCDF concentrations. Classification and ordination of the data revealed five broad groups of samples based on PCDD/F congener concentration (Figure 6.3). These were samples collected from the western side of Moreton Bay (Brisbane River and Coffee Pots), samples collected from areas associated with sugarcane production (Cardwell, and burnt, and raked and unburnt trash blanketed cane field samples). Samples remote from cane production (Flinders Island, Pallarenda, and eastern Moreton Bay) formed a third distinct cluster. A fourth cluster was comprised of seagrass samples and the sediment sample collected from Newry Bay, and a fifth group was derived from seagrass and sediment samples collected from Upstart Bay.

6.3.4. Dugong Dioxin Concentrations

Concentrations of 2,3,7,8-substituted PCDD/F congeners detected in dugong blubber samples are presented in Table 6.8. With the exception of hepta- and octa-substituted PCDFs, detection of 2,3,7,8-substituted isomers in dugong fat was confined almost exclusively to PCDD congeners. OCDD and 1,2,3,4,6,7,8-HpCDD were the dominant congeners present with a mean (standard deviation) concentration in the dugong fat of 210 (±40) and 59 (±14) pg g^{-1} lipid respectively. A trend of increasing congener concentration with increasing degree of chlorine substitution in fat samples was present (Table 4.8) and total toxicity of detectable PCDD/Fs present in samples (expressed as 2,3,7,8-TCDD TE) ranged from 13 to 22 pg TE g^{-1} lipid.

Table 6.8. PCDD and PCDF concentrations in dugong fat samples. (Concentration in pg g^{-1} fat).

Congener	Mackay	Bowen	Townsville
2,3,7,8-TCDD	2.3	2.8	6.0
1,2,3,7,8-PeCDD	9.5	5.8	10
1,2,3,4,7,8-HxCDD	11	7.6	11
1,2,3,6,7,8-HxCDD	14	8.7	14
1,2,3,7,8,9-HxCDD	13	7.9	13
1,2,3,4,6,7,8-HpCDD	62	44	72
OCDD	200	170	250
2,3,7,8-TCDF	< 0.37	< 1.1	< 1.7
1,2,3,7,8-PeCDF	< 0.19	< 0.41	< 0.92
2,3,4,7,8-PeCDF	< 0.51	< 1.3	< 1.1
1,2,3,4,7,8-HxCDF	< 0.47	< 0.84	< 0.97
1,2,3,6,7,8-HxCDF	< 0.20	< 0.46	< 0.48
1,2,3,7,8,9-HxCDF	< 0.19	< 0.14	< 0.63
2,3,4,6,7,8-HxCDF	< 0.40	< 1.3	< 1.2
1,2,3,4,6,7,8-HpCDF	2.5	6.5	6.7
1,2,3,4,7,8,9-HpCDF	< 0.15	< 0.62	< 0.41
OCDF	3.5	7.3	9.5
ΣPCDD/Fs	310	260	390
2,3,7,8-Teq* (humans/mammals)	17	13	22

*Calculated using the WHO-TEFs (Anon 1998)

6.4. Discussion

6.4.1. Sediment and Seagrass Dioxin Concentrations

Concentrations of OCDD in marine sediment samples from Queensland exceeded the concentrations observed in marine sediments from Bass Strait (southern Australia) by a factor of 5 – 1000 on a dry weight basis (Mosse and Haynes 1993)**.** Furthermore, the concentrations of higher chlorinated PCDDs, and in particular OCDD in the samples from the Brisbane River and Moreton Bay area as well as those from Newry Bay and Cardwell were similar to the concentrations in areas which are usually regarded as polluted. For example, the OCDD concentrations in these samples were higher than in sediment samples collected in 1993 from the River Elbe, a highly polluted European river (Schramm *et al.* 1995) or in the majority of sediment samples collected from the Housatic River which has its watershed downwind from the New York metropolitan area (Eitzer 1993). Also, the concentrations of sediment PCDDs detected in this study exceed concentrations determined in sediments collected from the Baltic (Witt *et al.* 1997), the North Sea and the Arctic Sea (Koistinen *et al.* 1997).

In contrast to HpCDD and OCDD, the concentration of PCDFs in sediment samples other than those from the Brisbane River area were very low compared to concentrations recorded in other studies (Eitzer 1993; Schramm *et al.* 1995; Witt *et al.* 1997). This indicates that within the study area, elevated PCDF concentrations in sediments are likely to be associated with urban sources. In contrast, other sources have contributed significantly to PCDD concentrations at all sites except the urban Brisbane River and northern Moreton Bay locations. The grouping of sediment and seagrass sampling sites derived using a PCA of dioxin concentrations (supported by the data from soils from the sugarcane farm) suggest a potent PCDD source is present in areas where sugarcane is the dominant crop. The source of dioxin contamination has not yet been identified (Müller *et al.* 2000).

6.4.2. Dugong Dioxin Concentrations

On a Toxicity Equivalency (TE) basis, dioxin concentrations in dugong samples collected along the Queensland coast were similar to those determined in samples from Hector dolphins (*Cephalorhynchus hectori*) stranded on the New Zealand coast (Buckland *et al.* 1990), and slightly lower than those present in many northern hemisphere marine mammals (Beck *et al.* 1990; Oehme *et al.* 1995; Jarman *et al.* 1996; Koistinen *et al.* 1997b). However, if the data are discussed on the basis of the total PCDD/Fs concentrations, the concentrations detected in dugongs are comparatively high. Total PCDD/F in dugongs ranged between 260 and 390 pg g^{-1}, whilst total PCDD/F concentrations determined in most marine mammal samples collected from both the northern and southern hemispheres are usually less than 200 pg g^{-1} (Buckland *et al.* 1990; Jarman *et al.* 1996; Tarasova *et al.* 1997)**.** The PCDD/F accumulation pattern in dugongs are also in contrast with results from other studies of PCDD/F accumulation in marine mammals where concentrations of OCDDs are usually an order of magnitude lower (Buckland *et al.* 1990; Oehme *et al.* 1995; Tarasova *et al.* 1997), and where tetra- and penta-CDD/Fs are the dominant PCDD/F congeners detected (Buckland *et al.* 1990; Oehme *et al.* 1995; Tarasova *et al.* 1997).

There are several hypotheses to account for the significant differences in the congener profile in dugongs compared with other marine mammals. The PCDD/F congeners present in dugong fat may have resulted from a bio-transformation of precursors of PCDD/Fs. Biochemical formation of PCDD/Fs from precursors has been emphasised as a potential source of PCDD/Fs (Oeberg and Rappe 1992; Fries *et al.* 1997). This may be of particular importance as dugongs are hindgut fermentors with ingested seagrasses (and sediments) undergoing digestion over an extended time period (140-160 hrs) in the digestive tract (Lanyon and Marsh 1995). The unusual congener profile may also be the result of selective degradation of certain PCDD/Fs. In cetaceans, the absence of PCDDs, is suspected to be the consequence of a selective degradation capacity (Muir *et al.* 1996). Dugongs may be able to eliminate PCDFs in a similar fashion. Alternatively, PCDD/Fs present in dugongs may be the result of direct accumulation of sediment and/or seagrass associated PCDD/Fs during feeding.

6.5. Conclusions

Unexpectedly high concentrations of 2,3,7,8 substituted dibenzo-*p*-dioxin congeners have been detected in sediments, seagrass and dugongs collected along the northern Queensland coast. The origin(s) of the dioxins is presently undefined, and it may be related to areas under intensive agricultural production. If this is the case, it is likely that movement of dioxins from agricultural lands to the marine environment is a consequence of the movement of eroded soil during high intensity rainfalls in the monsoon season. Once in the marine environment, dioxins are available for accumulation in marine fauna, including dugongs. Although the consequences of the presence of 2,3,7,8 substituted dioxin congeners in the Great Barrier Reef environment are unknown, every attempt should be made to reduce their transfer to the marine environment. Clearly, minimisation of soil loss from agricultural areas through the adoption of improved agricultural practices such as trash blanketing, and retention of riparian vegetation will potentially reduce the quantities of these pollutants lost to the coastal zone.

Chapter 7: Great Barrier Reef pollutants: current issues and new research directions

GBRMPA

Water quality data logger deployment, Kelso Reef

CHAPTER SEVEN: GREAT BARRIER REEF POLLUTANTS: CURRENT ISSUES AND NEW RESEARCH DIRECTIONS

7.1. Historical Risk Evaluation of Pollutants on the Great Barrier Reef

Some 25 major river catchments discharge directly into the Great Barrier Reef World Heritage Area (Moss *et al.* 1992b) and the bulk of their terrigenous inputs are deposited within 10 km of the Queensland coast (Larcombe *et al.* 1996). As a consequence, this nearshore deposition zone containing mangrove, soft-bottom communities, seagrass and fringing reef environments is most at risk from contaminants (sediments, nutrients, heavy metals and pesticides) sourced from anthropogenic activity in Queensland coastal catchments. Elevated sediment and nutrient concentrations have long been regarded as the major contaminant threats to these Great Barrier Reef environments (Wolanski and Jones 1981; Baldwin 1990; Bell 1991; Bell and Elmetri 1995), and there is recent evidence that eutrophication has occurred in some inshore areas of the Great Barrier Reef World Heritage Area. These data suggest that increases in local and/or regional nutrient concentrations have led to increased seagrass biomass and distribution at Green Island (Udy *et al.* 1999) and around Palm Island (Klumpp *et al*. 1997). Reductions in coral growth and the relative abundance and composition of coral communities of nearshore fringing reefs in the Whitsunday region has been linked to elevations in nutrient concentrations associated with river runoff (van Woesik *et al.* 1999). The potential risk to the Great Barrier Reef posed by other pollutants such as heavy metals, persistent organochlorines, polychlorinated biphenyls (PCBs) and petroleum related compounds has been considered to be of lesser consequence (Dutton 1985; Brodie 1997). This risk assessment was based on the low reported concentrations of these pollutants in the Great Barrier Reef World Heritage Area compared with locations elsewhere in the world. The only exceptions were sites adjacent to urban and industrial development such as commercial harbours, which were considered to be moderately contaminated by a range of pollutants (Dutton 1985).

7.2. Contemporary Risk Evaluation of Pollutants on the Great Barrier Reef

Although eutrophication is still considered the major threat to the sustainability of the Great Barrier Reef, the management focus on pollutants has shifted over the last five years as new research has been completed on concentrations of pesticides and heavy metals in the Great Barrier Reef region.

7.2.1. Contemporary Heavy Metal Concentrations

Recent work by Brunskill *et al*. (1999) concluded that mercury concentrations in surface sediments in Bowling Green Bay in the northern section of the Great Barrier Reef World Heritage Area are three times higher than pre-1850 background concentrations. The majority of this trace metal contamination has been attributed to the downstream transport of mercury used as an amalgam in the gold mining industry of northern Queensland at the turn of the century, and through the more recent use by the sugar cane industry of methoxyethylmercuric chloride as a fungicide (Walker and Brunskill 1997; Brunskill *et al*. 1999). Similarly, increases in cadmium and arsenic concentrations in marine sediments in the Hinchinbrook region have been noted adjacent to areas with intensive cropping. This is believed to be a consequence of the use by the sugar cane industry of phosphatic fertilisers naturally enriched in these elements (Tesiram 1995; Ridd 1999). Recently collected data also confirms that marine sediments collected along the Queensland coast and in the vicinity of urban areas are often enriched with a range of metals (Chapter 3; Doherty *et al* 2000). This is of significance, as it is now recognised that disturbed acid-sulphate soils along the Great Barrier Reef World Heritage Area coast can lower pH levels and subsequently enhance metal mobilisation rates (Cook *et al.* 2000).

7.2.2. Contemporary Organochlorine Concentrations

Recent information including data presented in this thesis (Chapters 2 and 3) also indicates that pesticide residues (including organochlorine residues) present a greater risk to the Great Barrier Reef and to the Queensland marine environment in general, than previously expected. A range of contaminants, including polychlorinated-*p*-dioxins, dieldrin, DDT (and its metabolites) and the herbicides diuron and atrazine have

all been detected in nearshore sediments and/or seagrass collected along the Great Barrier Reef World Heritage Area coast (Chapters 2 and 3; Müller *et al.* 1999; Gaus *et al.* in press). In particular, the concentrations of diuron found in sediments between Ingham and Port Douglas were determined to be high enough to depress seagrass photosynthesis (Ralph 2000; Chapter 4). Dieldrin has also been reported to be a ubiquitous contaminant of crabs (*Australoplax tridentata* and *Scylla serrata*) collected between Cairns and Brisbane (Mortimer 2000), as well as a contaminant present in dugongs (Chapter 5). Necropsy sampling of dugongs has also determined that octachlorinated dibenzo-dioxin (OCDD) congeners are accumulating in Great Barrier Reef dugongs to concentrations previously unseen in marine mammals elsewhere in the world (Haynes *et al.* 1999; Chapter 6).

7.3. Great Barrier Reef Catchment Modification

Although population growth and urban expansion in Queensland has been rapid (a 27% increase between 1986-1996), the northern Queensland coast still remains relatively sparsely populated (Anon 1999). Only 700,000 of the State's 2.9 million residents live in the coastal areas adjacent to the Great Barrier Reef World Heritage Area. Despite this low population pressure, extensive land modification has occurred over the last 200 years since European settlement (Anon 1993). Today, 80% of the land area of catchments adjacent to the Great Barrier Reef World Heritage Area support some form of agricultural production (Wachenfeld *et al*. 1998; Gilbert in press). To place Queensland land-use and vegetation clearing activities into perspective, more than 50 % of the State's original 117 million hectares of woody vegetation has been cleared primarily for agricultural purposes since European settlement (Anon 1999). As a consequence, run-off resulting from land-based agricultural activities (cattle grazing, vegetation clearance and intensive cropping) is the primary influence on water quality in the Great Barrier Reef World Heritage Area (Bell 1991; Moss *et al.* 1992b; Anon 1993; Brodie 1997). Increased soil erosion is estimated to have resulted in a 3-4 fold increase in the export of sediment loads into the Great Barrier Reef environment over the last 140 years (Moss *et al.* 1992b; Neil 1997). It is estimated that the total nutrient influx to reef waters (principally nitrogen and phosphorus) has increased by 30% during this time (Brodie 1997). Most of this increase in nutrient export has occurred during the last 40

years, a consequence of agricultural expansion, and the more than three-fold increase in fertiliser usage by the agricultural industry over this time (Pulsford 1996).

7.4. The Consequences of Substandard Catchment Management

Diffuse source pollutants originating from agricultural land clearly constitute the greatest chronic pollutant source influencing the Great Barrier Reef World Heritage Area. Increased water sediment concentrations and turbidity have been demonstrated to have a range of effects on coral communities (Tomascik and Sander 1985; Muller-Parker *et al*. 1994; Ward and Harrison 1996) and under extreme situations, can result in coral reef community collapse (Smith *et al*. 1981; Lapointe and O'Connell 1989). Chronic nutrient stress may also inhibit coral recovery after natural destructive events such as cyclones (Kinsey 1988). Increased nutrient concentrations and turbidity can also adversely affect seagrass by causing a shading induced reduction in photosynthesis (Walker and McComb 1992; Abal and Dennison 1996). In addition to nutrient stress, chronic herbicide exposure from agricultural run-off has the potential to impact seagrasses and other photo-autotrophic reef organisms (Vandermeulen *et al*. 1972). This includes shallow-water reef-building corals that rely on their symbiotic zooxanthellae for nutrition (Davies 1991). While the impact of organochlorines such as pesticides and dioxins are still unclear for lower invertebrates such as corals, their potential toxicity to immune systems and reproductive processes is of concern. Clearly, management of diffuse sources of pollutants is essential if the Great Barrier Reef is to be protected.

7.5. Great Barrier Reef Catchment Management and Monitoring Strategies

A number of land management strategies have been initiated in Queensland over the last 10 years. These include an Integrated Catchment Management (ICM) program, which is based on the premise that decision making processes in management of land and water resources must be coordinated to achieve sustainability (Johnson and Bramley 1996). The recognition of economically sustainable development principals at the farm level through the use of property management plans and development of industry codes of practice is now also emerging (Johnson *et al.* 1998). Whilst some notable achievements have been made by Queensland agricultural industries and communities (eg. widespread adoption of sugar cane trash blanketing to minimise exposure of un-vegetated soil to

rainfall), the fact remains that appropriate land management in Queensland remains a great challenge (ANAO 1997; Boully 1999). Early approaches to catchment management involved a large number of independent projects under the federally funded Landcare program. Today there is a growing realisation that a more strategic approach on a larger scale, backed by adequate resources, is required to achieve effective catchment management (ANAO 1997; Bellamy *et al*. 1999; Boully 1999). Key land management priorities clearly include the contol of sediment, nutrient, heavy metal and pesticide loss from catchments adjacent to the Great Barrier Reef (Table 7.1).

7.5.1. Sediment

Vegetation clearing on Queensland agricultural lands is still being carried out at rates that are up to an order of magnitude higher than any other Australian State, and soil erosion and associated nutrient and agricultural pollutant losses continue to be significant problems on Queensland agricultural properties (Anon 1999; Müller *et al*. 2000). Minimisation of sediment loss from agricultural lands is essential if water quality in the Great Barrier Reef is to be protected. This can be achieved, in part, through a minimisation of vegetation clearing, as well as implementation of effective sheet erosion management strategies and effective waterway and bank erosion management strategies.

7.5.2. Fertilisers (Nutrients)

Fertiliser usage on most of the Great Barrier Reef catchments has increased greatly in recent decades (Pulsford 1996) and modern agricultural practices have been strongly linked with elevated nutrient concentrations in the aquatic environment (Neil 1997). Reduction in nutrient loss from Great Barrier Reef catchments is essential if water quality in the Great Barrier Reef is to be protected. Introduction of farm soil nutrient analyses to enable optimal farm fertiliser application rates is one way of reducing the amount of fertiliser applied to agricultural lands and ultimately eroded from catchments. It is also essential that long term monitoring of the nutrient status of the Great Barrier Reef Marine Park is continued to provide early warning of increasing inshore water column nutrient concentrations and coastal eutrophication.

Table 7.1. Key pollutant management, monitoring and research strategies to control pollutant loss to the Great Barrier Reef.

Key Research Finding	Management Issue	Catchment Management Strategy	Research Strategy	Monitoring Strategy
Not assessed	Reduction in sediment loss	Trash blanketing and variable cattle stocking rates, retention of riparian and catchment vegetation	Investigation of GBR nearshore sediment resuspension dynamics and concentrations	Routine monitoring of spatial and temporal dynamics of flood plumes in the Great Barrier Reef
Not assessed	Reduction in nutrient loss	Soil nutrient analyses to optimise fertiliser application rates, reduction in percentage of un-vegetated areas	Investigation of impact of chronic nutrient impacts on nearshore GBR seagrass and coral species	Routine monitoring of Great Barrier Reef water column nutrient concentrations using DGTs
Diuron and dieldrin in subtidal GBR sediments	Reduction in pesticide loss	Regulation of pesticide application on agricultural properties, removal and safe disposal of unwanted organochlorine compounds	Investigation of GBR nearshore sediment pollutant resuspension and mobilisation dynamics and bioaccumulation	Routine and flood plume monitoring of Great Barrier Reef water column pesticide concentrations using SPMDs
Diuron inhibits GBR seagrass photosynthesis	Reduction in herbicide loss	Regulation and minimisation of diuron use in catchments	Investigation of chronic impact of pesticides on nearshore seagrass and coral species using PAM	Routine monitoring of inshore Great Barrier Reef seagrass distribution and coral health
Elevated metal concentrations in GBR sediments	Reduction in heavy metal loss	Regulation and minimisation of fertiliser application rates and minimisation of the use of mercury based anti-fungal preparations	Investigation of the impact of Hg, Cu and Zn on nearshore coral species using PAM	Routine monitoring of metals (copper, mercury and cadmium) in inshore Great Barrier Reef water using DGTs
Dieldrin and metals in dugongs	Reduction in pesticide and heavy metal loss	Minimisation of fertiliser and pesticide usage in agriculture, minimisation of soil loss from catchments	Comparison of pollutant body burdens in Queensland dugongs with Torres Strait, Northern Territory and Western Australian dugongs	Assessment of dugong pollutant body burdens every 5 years to monitor long term trends
Dioxin in GBR sediments and in dugongs	Reduction in formation of, and loss of dioxins	Maintenance of farm and riparian vegetation to minimise soil erosion. Use of agricultural practices that minimise chance of dioxin formation	Investigation of dioxin formation mechanisms, comparison of dioxin concentrations in dugong tissue collected from animals stranded along the Great Barrier Reef coast and in the Northern Territory and Western Australia	Routine monitoring of dioxin concentrations in Great Barrier Reef marine mammals and sediments

7.5.3. Pesticides

Atrazine and diuron are currently the two most widely used herbicides for the pre- and post-emergence control of weeds in Queensland catchments. An estimated 331 tonnes of atrazine and 197 tonnes of diuron are applied annually to Queensland cane fields (Hamilton and Haydon 1996). Regulation of diuron use and its replacement with a more environmentally benign herbicide along with regular auditing of farm soil pesticide concentrations would help reduce the runoff of pesticides to the Great Barrier Reef Marine Park. In addition. large quantities of farm chemicals including organochlorines in liquid formulation are still held on farming properties in Queensland (McGuffog *et al*. 1996). Over 50% of these are located in catchments adjacent to the Great Barrier Reef. Accidental loss or illegal application of banned pesticides together with the persistence of organochlorine residues in farming soils will lead to their eventual transport to the marine environment on soil particles. As a consequence, estuarine and nearshore environments along the Queensland coast are likely to continue to be contaminated with these compounds. Regular monitoring of pesticides and their impacts is important to assess long-term impacts on Great Barrier Reef biota.

7.5.4. Dioxins

Dioxin contamination is widespread in northern Queensland agricultural soils and adjacent marine sediments (Müller *et al.* 1999; Gaus *et al*. in press). Dioxins are also ubiquitous contaminants of Great Barrier Reef dugongs (Haynes *et al.* 1999; Gaus unpublished data). At present, the sources and/or formation mechanisms and environmental cycling of dioxins are unknown. However, a strong positive correlation between their occurrence in marine sediments and agricultural areas in the northern Queensland wet tropics has been reported (Müller *et al.* 1999). Dioxins are generally strongly adsorbed to sediment particulates. As a consequence, adoption of soil management practices in Great Barrier Reef catchments (eg trash-blanketing and vegetation retention) will help minimise the loss of dioxins from agricultural areas and their ultimate transfer to the marine environment. Monitoring of the distribution of dioxins as well as research on their formation mechanisms in the Queensland terrestrial and marine environments will help minimise their movement and potential impact to the Great Barrier Reef environment into the future.

7.5.5. Heavy Metals

With the exception of sites associated with urban and industrial activity, and metals associated with shipping antifoulants (Cu) and farming application (Cd, Hg), metal contamination in the Great Barrier Reef World Heritage Area remains a relatively minor concern. Adoption of optimal fertiliser application rates and minimisation of soil loss from catchments will help minimise future loss of metals from farming properties to the Great Barrier Ref World Heritage Area. However, given the toxicological relationships between methyl-mercury and copper exposure to target organisms, on-going monitoring of sediment concentrations of these metals is still warranted (Goldring 1992).

7.6. Future Monitoring Directions

In general, the highest concentrations (and loads) of catchment-sourced pollutants such as sediments (and their associated herbicides and insecticides) are transported from agricultural lands to the nearshore marine environment following the first major rainfalls of the wet season (Cooper and Riley 1996; Taylor and Devlin 1997). Apart from nutrient and sediments, no data is available about the concentrations and potential impact of these first-flush loads of pollutants on nearshore Great Barrier Reef biota. Acquisition of these data is particularly important given the potential synergistic impacts of pollutants (particularly herbicides) on corals and seagrass. These are created by a combination of reduced water salinities and high water temperatures often experienced by nearshore seagrass beds and reefs during the summer monsoon months (Fabricius 1999; Berkelmans and Oliver 1999). The capacity of monsoon river flood plumes to transport entrained nutrients to mid and outer-shelf reefs during calm conditions is documented (Devlin *et al.* in press), yet no information is available about the offshore transport of other contaminants in the Great Barrier Reef World Heritage Area.

7.7. Future Research Directions

Eco-toxicological research on early indicators of ecosystem stress resulting from exposure to pollutants is well established for temperate waters. For example, the induction of biomarkers such as the cytochrome P450 mono-oxygenases (Stegeman *et*

al. 1990; Goksøyr and Forlin 1992) or the expression of metallothioneins (Price-Haughey *et al*. 1987; Olsson and Kille 1997) have been used as time-integrated analyses tools to assess the exposure of organisms to contaminants for decades. Similarly, the formation of DNA-adducts in the presence of carcinogenic compounds (Ericson *et al.* 1998; Wirgin and Waldman 1998), and bioassays using cell lines (Tillitt *et al*. 1991; Michalek 1994) have also been recognised as important tools in the detection of various stresses impacting on aquatic organisms at biochemical, physiological whole organism and ecosystem levels. In tropical regions however, and the Great Barrier Reef region in particular, there is a critical information gap with respect to biomarkers and bioassay research.

Low-concentrations of dioxin contamination is widespread in northern Queensland agricultural soils (Müller *et al*. 2000) and adjacent marine sediments (Müller *et al*. 1999; Gaus *et al.* in press; Chapter 6). At present, the sources and/or formation mechanisms and environmental cycling of dioxins are unknown. However, a strong positive correlation between their occurrence in marine sediments and agricultural areas in the northern Queensland wet tropics has been reported (Müller *et al*. 1999). Given the teratogenic nature of dioxins and their ubiquitous distribution in wet tropics marine sediments and accumulation in dugongs (Chapter 6), there is an urgent need to assess their role (if any) in Great Barrier Reef ecosystem functioning and in local dugong population decline.

To date, only a limited number of tropical test organisms that relate to keystone species and appropriate test conditions are known (reviewed in Peters *et al.* 1997). Some of the few exceptions are bioassays based on quantification of coral bleaching (as loss of zooxanthellae) (Jones 1997) or the reduction in reproductive output in hard corals in response to trace metal exposure (Reichelt-Brushett 1998). Another promising tool for the assessment of sublethal stress in marine organism is the submersible Pulse-Amplitude-Modulated fluorometer (Diving PAM) (Chapter 6). Progress has also been made with the introduction of semi-permeable membrane devices (SPMDs) and diffusive gradients in thin films (DGT) techniques for the analysis of water column lipophilic contaminants as well as heavy metals and nutrient species (Figure 7.1). SPMDs are devices that consist of a thin film of triolein sealed in a polyethylene tube (Prest *et al.* 1995). Lipophilic compounds permeate the membrane and partition into the

lipid layer where they are concentrated and sequestered according to physico-chemical principals (Huckins *et al*. 1993). SPMDs have been shown to accurately reflect concentrations of pollutants present in local bivalves (Prest *et al.* 1992; 1995; Rantalainen *et al.* 1998).

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Figure 7.1. Deployment of DGT samplers, Osprey Reef, September 2000.

Similarly, DGT techniques are based on a simple device that accumulates solutes on a binding agent after passage through a hydrogel which acts as a well defined diffusion layer (Davison and Zhang 1994; Zhang *et al*. 1998). The use of these techniques reduce some of the problems inherent in the analyses of water, sediment and biota samples for pollutants (Huckins *et al*. 1993; Prest *et al.* 1995; Zhang *et al*. 1998).

7.8. Final Conclusions

Chemical data derived using innovative techniques can play an early warning role in the assessment of impacts of contaminants on mangrove, seagrass and coral reef organisms

of the Great Barrier Reef World Heritage Area. Moreover, the methods could contribute to the understanding of interactions of contaminants with high light and temperature conditions. Without consideration of the subtle impacts of chemical contaminants, managers will fail to fully understand the status of tropical marine ecosystems and the risks associated with anthropogenic impacts. However, if fundamental changes in land-management do not occur, even the most advanced research techniques cannot help in the ultimate protection of the Great Barrier Reef.

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Appendices

APPENDICES

Appendix 5: Dugong Liver Heavy Metal Concentrations, Queensland 1996-2000. (All concentrations mg kg^{-1})

Ref No	DW/WW	As	Se	Cd	Cr	Cu	Ni	Pb	Al	Fe	Mn	Zn	Hg	Moisture
c002	DW	2.2	1.3	3.6	0.62	77.3	0.29	0.49	10.8	19800	34.9	2010	0.078	69
c003	DW	2.65	1.6	5.9	0.685	168	0.285	0.195	12.35	10200	19.7	2220	0.069	69
c004	DW	3.1	2.4	3.9	0.93	138	2.1	0.15	27.4	2360	8.7	3470	0.1	69
c009	DW	0.21	<0.02	0.03	3.6	56.7	0.8	0.64	264	1196	15	486	0.06	69.3
c010	DW	7.01	<0.02	2.45	0.2	89.3	<0.3	0.16	<5	11080	6	1079	0.21	73.4
c012	DW	0.66	<0.02	0.5	0.5	9.5	0.9	<0.08	15.8	1663	14	457	0.19	73.4
c013	DW	1.99	<0.02	1.59	1.2	110	0.4	0.25	13.3	3513	9	938	0.22	75.8
c016	DW	0.43	<0.02	0.06	0.9	144	<0.3	0.18	7.1	2900	16	426	0.04	74.9
c025	DW	3.81	1.43	10.7	0.7	56	0.4	2.78	39	55080	<1	3164	0.63	71.4
c028	WW	0.99	0.17	0.25	1.11	5.1	0.7	0.05	4	1413	2.3	221	0.02	78.5
c034	WW	0.97	0.25	0.23	0.28	70.9	0.2	0.04	<2	1498	1.8	341	0.06	76.6
c035	WW	0.57	0.14	0.39	0.49	24.8	0.3	<0.04	12	739	1.1	404	0.02	76.6
c036	WW	0.53	0.04	0.1	0.69	4.49	0.5	0.04	3	591	4	153	0.01	76.6
c037	WW	0.28	0.41	1.99	0.18	3.85	<0.16	0.15	3	14860	<0.6	510	0.06	79.8
c040	WW	0.04	0.35	0.02	0.5	10.5	0.4	<0.04	<2	384	2.5	99	0.01	79.8
c045	WW	0.09	0.1	1.75	3.64	9.9	2.9	0.08	11	7566	<0.6	421	0.16	79.8
c047	WW	0.24	0.73	0.42	0.65	14.2	0.7	<0.04	<2	1039	1.1	396	0.01	79.8
c048	WW	0.14	0.16	<0.005	1.55	1.48	1.2	<0.04	<2	116	<0.6	10	0.01	78.4
c049	WW	0.36	0.64	1.07	0.54	44.6	0.5	0.05	2	857	2.8	532	0.08	78.4
c050	WW	0.38	0.36	0.34	0.49	4.04	0.3	<0.04	34	6755	1.3	1134	0.11	78.4
c051	WW	0.82	0.59	7.02	0.57	5.09	0.4	0.15	10	29750	<0.6	1161	0.24	78.4
c052	WW	0.09	0.63	0.12	2.2	19.3	1.6	<0.04	4	394	3.4	167	0.01	78.4

Appendix 4: Subtidal sediment metal concentrations, December 1999. (All concentrations mg kg^{-1} dry weight, Fe, Si and $CaCO_3$ %).

Location	Site	$CaCO_3$	Al	Ca	Co	Cr	Cu	Fe	Mn	Ni	Pb	Si	Zn	Cd	Hg	As
C Bowling Green	23	4.8	9.86	1.33	16	79	22	4.93	512	39	23	23	88	0.02	0.05	14.5
C Bowling Green	23	4.5	10.2	1.24	17	78	23	4.84	542	40	22	23.3	89	0.02	0.05	16
North Upstart Bay	24	9.7	8.98	3.66	12	64	21	4.35	595	28	20	21.6	80	0.02	0.04	14.3
North Upstart Bay	24	10.9	9.04	4.25	9	65	19	4.43	621	31	26	22.2	81	0.02	0.04	14.5
Central Upstart Bay	25	21.5	6.7	9.53	<6	50	12	2.95	480	21	15	18.9	52	0.02	0.03	11.2
Central Upstart Bay	25	24.6	6.43	10.9	<6	47	9	2.85	463	20	16	18.9	51	0.01	0.02	10
South Upstart Bay	26	23.1	6.46	9.73	<6	46	10	2.7	466	16	15	19.9	48	0.02	0.03	8.6
South Upstart Bay	26	22.2	6.61	10.5	<6	44	9	2.69	482	20	14	19.7	49	0.01	0.03	8.6
N Edgecombe Bay	27	22.6	5.95	9.4	<6	48	<8	2.69	379	13	11	20.7	46	0.02	0.02	11.5
N Edgecombe Bay	27	19.2	6.41	8.4	<6	48	<8	2.9	400	17	14	20.5	49	0.01	0.02	11.8
S Edgecombe Bay	28	43.2	3.5	17.9	<6	34	<8	1.18	240	<10	9	15.7	24	<0.01	0.01	4.9
S Edgecombe Bay	28	40.6	3.6	18.1	<6	31	<8	1.19	246	<10	7	15.8	20	0.01	<0.01	5.4
Pioneer Bay	29	44.7	4.46	15.4	<6	42	<8	1.84	299	12	10	17.1	36	0.01	0.01	5.6
Pioneer Bay	29	49.6	4.34	16.2	<6	37	<8	1.77	301	<10	10	16.9	32	0.02	0.01	6.2
North Repulse Bay	30	25.2	5.19	9.75	<6	37	<8	2.18	373	11	12	20.5	39	0.01	0.02	6.4
North Repulse Bay	30	27.4	5.31	10.7	<6	42	<8	2.29	408	13	12	21.6	40	0.02	0.01	6.7
South Repulse Bay	31	17.4	5.47	7.58	<6	48	<8	2.26	407	<10	14	24.4	39	0.01	0.02	7.3
South Repulse Bay	31	17	5.37	7.58	<6	46	<8	2.26	427	11	13	25	37	0.02	0.02	7.5
St Helens Bay	32	12.7	4.67	5.36	<6	22	<8	2.16	465	<10	13	29	35	<0.01	0.02	11.1
St Helens Bay	32	9.7	5.16	3.9	<6	25	<8	2.14	458	<10	13	30.9	30	0.01	0.01	11.5
Sand Bay	33	6.4	5.9	3.24	<6	26	<8	1.86	466	<10	14	30.6	29	0.01	0.01	5.8
Sand Bay	33	6	6.02	3.33	<6	24	<8	1.95	465	<10	13	30.7	30	0.01	<0.01	6.7
Sandringham Bay	34	4.9	3.69	2.3	<6	<9	<8	0.7	352	<10	11	36.3	<12	<0.01	<0.01	8.7
Sandringham Bay	34	5	3.65	2.06	<6	<9	<8	0.69	309	<10	11	37	<12	<0.01	<0.01	14.1
Sarina Inlet	35	11	3.03	4.77	<6	31	<8	1.78	347	<10	12	32.1	20	0.02	<0.01	9.2
Sarina Inlet	35	11.4	2.92	4.49	<6	27	<8	1.73	347	<10	11	33.3	20	0.01	<0.01	8.7
Llewellyn Bay	36	8.6	0.77	3.4	<6	18	<8	0.4	200	<10	8	38.5	<12	<0.01	<0.01	2.7
Llewellyn Bay	36	7.8	0.76	3.25	<6	15	<8	0.42	207	<10	<4	39.2	<12	<0.01	<0.01	6.1
Ince Bay	37	29.4	1.78	13.2	<6	24	<8	1.49	384	<10	7	24.1	<12	0.01	<0.01	11.3

Ince Bay	37	28.8	1.48	12.4	<6	18	<8	1.12	352	<10	5	25.9	<12	0.01	<0.01	10.7
Three Mile Beach	38	26.9	2.07	11.9	<6	28	<8	1.27	467	<10	10	25.6	<12	0.02	0.01	12.9
Three Mile Beach	38	28	1.97	11.3	<6	25	<8	1.17	444	<10	10	26.9	<12	0.02	<0.01	12.5
Broad Sound	39	26.3	2.59	11.1	<6	41	<8	1.05	331	<10	10	25.2	15	<0.01	<0.01	6
Broad Sound	39	27.7	3.04	11.1	<6	45	<8	1.22	348	10	13	25.4	20	0.01	<0.01	6.8
Broadsound Channel	40	36.7	1.8	13.7	<6	24	<8	0.71	250	<10	9	24.4	<12	0.01	<0.01	9.3
Broadsound Channel	40	40.1	1.74	14.5	<6	20	<8	0.71	251	<10	9	23.4	<12	0.04	<0.01	8.6
Annie Island	41	1.3	0.75	0.4	<6	90	<8	0.76	274	<10	7	41.7	<12	<0.01	<0.01	4.7
Annie Island	41	17.1	1.92	6.23	<6	52	<8	0.82	276	<10	11	33.4	<12	<0.01	<0.01	7.8
Port Clinton	42	18	1.82	6.77	<6	54	<8	0.81	270	<10	11	32.4	<12	<0.01	<0.01	6.7
Port Clinton	42	1.4	0.8	0.39	<6	119	<8	1.03	369	<10	8	41.1	<12	<0.01	<0.01	5.3
Little Corio Bay	43	3.6	1.47	1.3	<6	25	<8	0.42	195	<10	8	40.5	<12	<0.01	<0.01	5.5
Little Corio Bay	43	3.7	1.49	1.35	<6	20	<8	0.41	195	<10	8	40.4	<12	<0.01	<0.01	5.4
Shoal Bay	44	12.9	2.51	5.31	<6	53	<8	1.25	402	<10	8	33.7	21	<0.01	0.01	9
Shoal Bay	44	12.8	2.34	5.29	<6	51	<8	1.2	399	<10	10	33.6	18	0.01	<0.01	8
Keppel Sands	45	7.6	5.82	2.69	<6	62	11	2.6	382	28	13	29.9	47	0.03	0.02	9.2
Keppel Sands	45	8.9	4.4	3.5	<6	39	<8	1.7	381	20	16	32.5	29	0.02	0.01	9.9
Keppel Bay	46	8.5	5.06	3.12	<6	51	10	2.39	276	23	13	30.4	42	0.01	0.02	7.9
Keppel Bay	46	8	5.32	3.12	<6	54	9	2.43	296	25	11	30.6	42	0.01	0.02	9.5
Keppel Bay South	47	2.9	1.84	1.12	<6	47	<8	0.87	475	<10	10	39.7	<12	<0.01	<0.01	8.7
Keppel Bay South	47	2.8	1.81	1.14	<6	78	<8	1.12	626	<10	12	39.4	13	<0.01	<0.01	10
Fitzroy River mouth	48	6.3	3.01	2.75	<6	37	<8	1.11	480	<10	14	35.8	16	<0.01	0.01	7.1
Fitzroy River mouth	48	6.7	4.66	2.6	<6	58	<8	2.1	631	21	11	32.8	37	0.02	0.01	9.7
Curtis Island (north)	49	1.7	0.32	0.65	<6	41	<8	0.45	289	<10	8	42.6	<12	<0.01	<0.01	3.1
Curtis Island (north)	49	4.1	0.49	1.57	<6	26	<8	0.26	233	<10	8	41.8	<12	<0.01	<0.01	4.1
Facing Island	50	7.7	3.65	3.68	<6	31	<8	1.59	564	<10	12	33.6	20	0.01	<0.01	12.8
Facing Island	50	6.3	3.68	3.26	<6	38	<8	1.67	578	<10	9	34.6	19	<0.01	<0.01	14.5
South Channel	51	15.5	3.81	6.01	<6	31	<8	1.41	378	<10	9	29.9	21	<0.01	0.02	7.9
South Channel	51	14.3	4.26	6.49	<6	35	<8	1.58	392	<10	11	28.9	25	0.01	0.01	12.6
Mud Island	52	4.2	7.38	2.04	9	53	19	3.43	435	19	13	26.7	67	0.02	0.04	14.6
Mud Island	52	3.2	6.67	3.09	<6	31	<8	2.33	620	<10	9	32.1	23	0.01	<0.01	5.3

Appendix 3: Subtidal sediment metal concentrations, December 1998. (All concentrations mg kg^{-1} dry weight, Fe, $CaCO_3$ and Si %).

Location	Site	Depth	$CaCO_3$	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Si	Zn
Horn Island	1	3	70	1.88	2.7	0.06	<6	27	<8	0.58	0.02	79	<10	10	7.07	15
Horn Island	1	3	68	2.42	4	0.05	<6	29	13	0.82	0.02	96	<10	12	8.43	24
Newcastle Bay	2	5	9	0.78	5.5	0.005	<6	16	<8	0.93	0.01	12	<10	6	35.5	<12
Newcastle Bay	2	6	4	0.99	7.2	0.005	<6	19	<8	1.79	0.02	10	<10	7	36.2	<12
Shelburne Bay	3	3.5	37	1.2	2.3	0.01	<6	13	<8	0.28	0.01	68	<10	8	20.1	<12
Shelburne Bay	3	3	37	1.49	2.5	0.01	<6	17	<8	0.44	0.01	76	<10	10	22.1	<12
Temple Bay	4	4	6	2.74	5	0.005	<6	16	8	0.44	0.01	98	<10	18	33.6	<12
Temple Bay	4	4	8	2.67	5.8	0.005	<6	18	<8	0.49	0.01	89	<10	20	32.7	<12
Weymouth Bay	5	3	0.5	1.38	0.7	0.005	<6	<10	<8	0.002	<0.01	5	<10	10	41.8	<12
Weymouth Bay	5	4.5	0.5	1.54	0.7	0.005	<6	<10	<8	0.002	<0.01	25	<10	14	41.4	<12
Lloyd Bay	6	4	17	7.87	9.9	0.02	<6	43	11	2.51	0.03	212	14	25	20.5	49
Lloyd Bay	6	4	15	7.56	9	0.01	<6	40	9	2.47	0.03	183	15	25	21.3	50
Princess C Bay	7	4.7	12	7.97	13	0.005	7	66	14	3.41	0.03	362	22	21	22.7	58
Princess C Bay	7	3.8	13	7.68	12.3	0.005	6	64	12	3.32	0.02	353	22	18	23.2	57
Bathurst Bay	8	4.2	23	6.37	12.1	0.07	<6	52	13	2.68	0.02	256	14	18	20.2	49
Bathurst Bay	8	4.2	28	5.67	10.3	0.02	<6	52	11	2.49	0.02	252	18	16	17.8	46
Cape Flattery	9	3	23	0.72	1.1	0.01	<6	11	<8	0.08	0.01	46	<10	8	28.5	<12
Cape Flattery	9	4	10	0.41	1.4	0.005	<6	13	<8	0.18	<0.01	172	<10	8	35.3	<12
Walker Bay	10	3	12	6.8	11.1	0.01	<6	51	11	2.54	0.03	261	19	19	23.6	51
Walker Bay	10	3	17	5.37	10.1	0.005	<6	44	13	2.1	0.03	263	13	15	25.6	40
Daintree River	11		3.4	3.18	3.3	0.005	<6	13	<8	0.46	<0.01	179	5	19	38.5	19
Daintree River	11		2.8	3.61	4.3	0.005	<6	14	<8	0.75	<0.01	187	11	18	37.4	27
Barron River	12	3.6	8.5	6.39	12.8	0.01	<6	65	11	2.68	0.02	526	26	22	28.6	57
Barron River	12	3.3	6.3	6.8	10.4	0.01	<6	59	14	2.7	0.03	616	30	22	30.1	58
Russell River	13	5.1	7.8	8.53	20	0.01	14	113	16	4.18	0.03	712	42	23	23.7	80
Russell River	13	4.2	6.1	6.69	15.4	0.01	8	90	11	3.21	0.02	570	34	20	29	64
Johnston River	14	3	3.4	8.32	14	0.06	31	190	29	6.12	0.07	780	81	16	21.5	96
Johnston River	14	2.2	1.6	9.37	10.9	0.05	36	207	32	6.73	0.06	1006	90	18	21.3	101
Tully River	15	4.3	5.6	9.42	11.3	0.02	<6	58	12	3.31	0.03	610	29	33	25.6	77

Tully River	15	2.8	4.2	9.16	13.1	0.03	3	48	11	2.93	0.03	753	27	34	26.9	68
Cardwell	16	3.4	6.8	9.53	12.4	0.01	14	62	15	3.92	0.03	521	33	29	23.5	89
Cardwell	16	3.5	8	9.25	12.2	0.01	11	58	15	3.85	0.03	491	31	32	23.4	89
Hinchinbrook	17	4.8	3.8	3.21	8.1	0.005	3	18	<8	1.38	0.01	199	<10	16	36.4	25
Hinchinbrook	17	3.6	14.1	6.11	11.9	0.01	3	35	11	2.62	0.03	303	18	24	26.2	64
Herbert	18	1.5	3.4	7.43	8.3	0.03	3	33	12	2.04	0.03	231	20	28	30.6	58
Herbert	18	1.5	3.8	9.86	14.1	0.04	18	60	27	4.28	0.05	773	35	39	23.2	117
Lucinda	19	4.6	4.9	7.24	10.6	0.02	3	27	11	2.15	0.03	427	21	30	29.8	56
Halifax Bay	20	2.9	10.9	7.24	10.7	0.02	10	54	15	3.36	0.03	775	21	25	25.1	73
Halifax Bay	20	2.6	4.4	9.62	10.1	0.03	12	50	20	4.17	0.03	565	25	31	24.5	92
Cleveland Bay	21	3	6.5	4.74	14.8	0.005	3	25	<8	1.61	0.01	514	11	17	30.5	28
Cleveland Bay	21	3	11.3	4.45	17.5	0.005	3	24	<8	1.55	0.01	564	11	16	30.7	21

Appendix 2: Intertidal sediment metal concentrations, 1997. (All concentrations mg kg^{-1} dry weight, Fe, $CaCO_3$ and Si %).

Site	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Si	Zn	Cd	Hg	$CaCO_3$
Lochart River	1.31	4.0	<6	<9	<8	0.54	62	<10	7	40.20	<12	<0.01	0.02	2.2
Lochart River	0.88	6.0	<6	<9	<8	0.43	101	<10	<4	29.80	<12	<0.01	0.02	19.4
Lochart River	1.90	5.5	<6	11	<8	0.77	90	<10	8	36.70	<12	<0.01	0.02	5.9
Flinders Island	2.08	4.3	<6	18	<8	0.77	111	<10	9	14.80	27	0.03	0.02	47.2
Flinders Island	1.45	4.9	<6	13	<8	0.52	93	<10	<4	13.40	<12	<0.01	0.02	50.6
Flinders Island	1.07	4.5	<6	12	<8	0.37	88	<10	<4	11.90	<12	<0.01	0.02	53.8
Princess Bay	3.40	7.0	<6	30	<8	1.26	355	10	12	24.10	20	<0.01	0.02	21.1
Princess Bay	2.88	6.4	<6	29	<8	1.07	354	11	9	24.30	15	<0.01	0.02	25.8
Princess Bay	3.32	7.0	<6	30	<8	1.23	397	11	13	23.00	16	<0.01	0.02	26.8
Bathurst Bay	5.24	8.0	<6	43	<8	2.03	224	15	15	18.14	49	0.02	0.04	28.9
Bathurst Bay	4.89	7.4	<6	34	<8	1.73	200	13	11	18.84	38	0.02	0.03	29.7
Bathurst Bay	3.69	7.4	<6	24	<8	1.21	189	<10	13	16.97	28	0.02	0.03	35.5
Bathurst Bay	4.03	6.9	<6	28	<8	1.35	185	<10	15	17.42	30	0.02	0.03	35.3
Low Isles	0.20	1.0	<6	<9	<8	<0.005	72	<10	<4	0.83	<12	0.01	0.02	93.2
Low Isles	0.21	1.1	<6	<9	<8	<0.005	72	<10	<4	0.92	<12	<0.01	0.02	90.9
Low Isles	0.17	1.0	<6	<9	<8	<0.005	64	<10	<4	1.12	<12	0.02	0.01	94.9
Cairns	2.37	3.7	<6	12	<8	0.53	257	<10	11	37.00	14	<0.01	0.02	7.3
Cairns	3.16	7.1	<6	22	<8	1.03	312	11	11	36.70	24	0.02	0.02	2.3
Cairns	3.24	7.1	<6	24	<8	1.12	293	13	15	36.80	27	0.05	0.02	1.4
Cardwell	4.99	7.0	<6	14	<8	1.23	632	13	26	36.10	27	<0.01	0.01	1.8
Cardwell	8.22	13	<6	42	13	3.06	914	23	32	28.40	69	0.02	0.04	<0.1
Cardwell	8.24	10	<6	45	11	2.96	848	24	36	28.40	65	0.02	0.04	2.3
Pallarenda	4.77	9.1	<6	22	<8	1.34	783	<10	15	35.00	27	0.01	0.01	3.2
Pallarenda	6.21	9.2	<6	26	9	1.93	757	18	18	32.10	44	0.02	0.02	2.3
Pallarenda	5.39	9.8	<6	27	<8	1.90	990	16	13	34.60	38	0.02	0.02	0.9
Cleveland Bay	4.90	13	<6	28	<8	1.93	689	16	10	33.60	30	<0.01	0.02	5.0
Cleveland Bay	4.77	13	<6	29	<8	1.86	685	10	12	34.30	30	<0.01	0.02	3.6
Cleveland Bay	5.14	12	<6	33	<8	2.08	651	13	11	33.20	36	0.01	0.02	4.1
Upstart Bay	6.71	3.1	<6	16	<8	1.78	418	<10	13	35.00	19	0.01	0.01	0.5

Upstart Bay	6.66	3.8	<6	14	<8	1.53	459	<10	12	34.90	16	0.01	0.01	0.5
Upstart Bay	6.52	4.8	<6	39	<8	3.69	836	<10	11	33.40	31	0.01	0.01	<0.1
Newry Bay	4.49	13	<6	44	9	2.36	283	10	9	33.80	31	<0.01	0.02	3.6
Newry Bay	4.86	13	<6	55	11	2.33	261	12	6	34.90	31	0.01	0.02	1.4
Newry Bay	4.31	13	<6	56	10	2.25	289	11	6	34.20	29	0.01	0.02	3.6
Shoalwater Bay	3.31	5.9	<6	35	<8	1.13	167	<10	7	29.80	17	0.01	0.01	12.3
Shoalwater Bay	0.95	1.9	<6	23	<8	0.19	68	<10	<4	40.70	<12	<0.01	0.01	0.5
Shoalwater Bay	3.29	5.7	<6	38	<8	1.25	147	<10	9	31.30	17	0.01	0.02	9.5
Gladstone Harbour	4.62	10	<6	27	<8	1.95	510	<10	5	34.20	30	<0.01	0.01	3.6
Gladstone Harbour	4.62	11	<6	40	8	2.04	519	<10	<4	30.10	32	<0.01	0.02	9.1
Gladstone Harbour	4.76	10	<6	42	<8	2.27	603	<10	6	31.30	36	<0.01	0.02	5.1
Hervey Bay	0.59	9.3	<6	11	<8	0.22	71	<10	<4	41.30	<12	<0.01	0.01	3.0
Hervey Bay	1.03	10	<6	20	<8	0.45	105	<10	<4	38.80	<12	<0.01	0.01	5.1
Hervey Bay	0.68	9.9	<6	12	<8	0.27	75	<10	<4	41.20	<12	<0.01	0.01	2.3
Moreton East	1.27	5.5	<6	179	<8	0.61	169	<10	<4	41.40	<12	0.02	0.01	<0.1
Moreton East	0.99	3.6	<6	85	<8	0.29	90	<10	<4	42.50	<12	<0.01	0.01	<0.1
Moreton East	1.03	4.2	<6	119	<8	0.37	109	<10	4	42.30	<12	<0.01	0.01	<0.1
Moreton West	5.89	5.7	<6	47	10	2.24	254	16	14	33.70	50	0.04	0.04	<0.1
Moreton West	6.13	7.1	<6	60	11	2.44	269	16	10	33.70	57	0.04	0.04	<0.1
Moreton West	6.47	5.8	6	65	10	2.68	299	17	14	32.90	60	0.04	0.05	<0.1
Moreton East	0.51	2.2	<6	23	<8	<0.005	19	<10	<4	43.60	<12	<0.01	<0.006	<0.1
Moreton East	0.45	2.9	<6	20	<8	<0.005	19	<10	<4	44.40	<12	<0.01	<0.006	<0.1
Moreton East	0.53	3.6	<6	21	<8	0.01	20	<10	<4	44.10	<12	<0.01	<0.006	<0.1

Appendix 1: Intertidal seagrass metal concentrations, 1997. (All concentrations mg kg^{-1} dry weight).

Site	*Species*	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Zn
Lochart River	*Halodule uninervis*	2.05E+03	32.3	0.1	1.8	45.3	4.2	1.18E+04	0.028	175	4.4	6.9	0.41	17.4
Lochart River	*Halodule uninervis*	3.69E+03	9.9	0.13	2.4	21.6	4.3	5.72E+03	0.036	218	3.7	6	0.25	17.5
Lochart River	*Halodule uninervis*	1.58E+03	26.8	0.082	1	10.5	2.8	9.22E+03	0.029	147	2.2	6	0.33	20.2
Flinders Island	*Cymodocea serrulata*	3.32E+03	12.1	0.4	1.6	8.4	3.6	4.84E+03	0.013	141	4.6	4.1	0.41	17
Flinders Island	*Cymodocea serrulata*	2.24E+03	5.3	0.23	1.3	6.1	3.2	3.19E+03	0.012	172	4.1	2.7	0.38	10.8
Flinders Island	*Cymodocea serrulata*	4.50E+03	6.7	0.23	2.3	10	3.7	5.05E+03	0.013	143	6.8	3.9	0.39	15.9
Princess C Bay	*Halodule uninervis*	1.81E+03	34.5	0.074	1.6	6.9	3	7.91E+03	0.011	120	3.1	3.8	0.51	14.3
Princess C Bay	*Halodule uninervis*	3.54E+03	10.9	0.051	2	12.5	2.6	6.68E+03	<0.01	207	4.4	3.5	0.45	14.7
Bathurst Bay	*Cymodocea serrulata*	1.19E+03	36.2	0.084	0.87	3.7	2.2	7.01E+03	<0.01	88.8	2.2	3.2	0.37	9.6
Bathurst Bay	*Cymodocea serrulata*	5.91E+03	34.9	0.31	1.5	7.9	2.7	1.29E+04	0.016	168	4.5	8.3	0.4	11.7
Bathurst Bay	*Cymodocea serrulata*	1.24E+03	62.6	0.063	0.91	3.5	1.7	1.01E+04	<0.01	136	2	3	0.37	7.5
Bathurst Bay	*Cymodocea serrulata*	7.78E+03	86	0.12	2	10.6	3.6	2.01E+04	0.015	242	6.2	7.1	0.45	18
Low Isles	*Cymodocea serrulata*	881	6.2	0.034	0.81	16.9	1.3	2.86E+03	0.01	58.8	2.5	2.4	0.81	5.7
Low Isles	*Cymodocea serrulata*	891	5.6	0.035	0.89	14.7	1.3	2.41E+03	<0.01	59	2.4	2.4	0.83	6
Low Isles	*Cymodocea serrulata*	894	4.2	0.016	0.63	13.2	1	2.19E+03	<0.01	67.9	1.3	2.1	0.16	4.3
Cairns Harbour	*Zostera capricorni*	2.20E+03	4.3	0.1	4	5.4	9.2	3.81E+03	0.012	339	2.3	2.7	0.1	28.7
Cairns Harbour	*Zostera capricorni*	4.48E+03	5.3	0.082	6.4	12.3	11.3	7.43E+03	0.012	437	3.9	4.9	0.12	27.2
Cairns Harbour	*Zostera capricorni*	4.62E+03	7.6	0.085	7.9	11.6	12.5	8.50E+03	0.016	656	4.1	5.3	0.15	33.4
Cardwell	*Halodule uninervis*	7.80E+03	3.8	0.31	5.9	8.4	15.2	7.11E+03	0.022	843	4.7	8.6	0.14	39.3
Cardwell	*Halodule uninervis*	5.88E+03	3.2	0.22	4.6	5.9	10.9	5.06E+03	0.015	700	3.5	4.4	0.13	29.6
Cardwell	*Halodule uninervis*	2.94E+03	21.1	0.2	11.2	11.9	26.8	6.06E+04	0.03	955	30.6	5.1	0.46	41.2
Pallarenda	*Halodule uninervis*	3.88E+03	3.8	0.38	3	9.4	9.2	3.74E+03	0.016	364	3.9	4	0.47	109
Pallarenda	*Halodule uninervis*	4.30E+03	16	0.28	3.1	13.7	6.9	1.61E+04	0.014	363	4.5	5.9	0.46	234
Pallarenda	*Halodule uninervis*	2.84E+03	3.8	0.49	1.8	4.6	9.4	2.87E+03	0.013	204	3	3.2	0.38	90.7
Cleveland Bay	*Cymodocea serrulata*	2.23E+03	1.4	0.61	1.6	3.7	4.2	1.87E+03	0.018	580	3	2	0.22	15
Cleveland Bay	*Cymodocea serrulata*	1.78E+03	4.3	0.29	1.5	5.3	3.4	2.57E+03	0.015	441	2.6	2.1	0.26	17.7
Cleveland Bay	*Cymodocea serrulata*	2.86E+03	8.2	0.21	2.3	7.7	3.1	4.40E+03	0.014	446	3.2	2.6	0.3	20.2
Upstart Bay	*Zostera capricorni*	4.17E+03	2.8	0.18	2.6	8.4	5.2	5.51E+03	<0.01	316	3.4	2.7	0.31	35.9
Upstart Bay	*Zostera capricorni*	3.38E+03	3.6	0.15	3.5	58.9	5.5	5.59E+03	<0.01	495	5.1	2.7	0.2	18.4
Upstart Bay	*Zostera capricorni*	1.40E+03	2.9	0.2	2.5	21.1	4.6	3.48E+03	<0.01	238	2.6	2.3	0.15	14.2
Newry Bay	*Zostera capricorni*	1.91E+03	9.2	0.13	1.9	5.2	3.3	4.82E+03	<0.01	391	2.1	1.8	0.18	18
Newry Bay	*Zostera capricorni*	5.28E+03	14.5	0.12	3.1	20.5	4.1	9.56E+03	0.012	308	4.3	3.4	0.24	21.8

Newry Bay	*Zostera capricorni*	2.81E+03	13.6	0.13	2.1	9.5	2.8	6.60E+03	<0.01	284	2.7	1.9	0.19	23.5
Shoalwater Bay	*Zostera capricorni*	2.52E+03	5.1	0.093	1	11.4	1.8	4.22E+03	0.011	70.1	2.7	2	0.17	13.2
Shoalwater Bay	*Zostera capricorni*	3.26E+03	6.2	0.1	1.3	16	2.1	5.11E+03	0.013	73.9	3.6	2.4	0.13	24.9
Shoalwater Bay	*Zostera capricorni*	6.39E+03	13.8	0.061	2	18.2	3.2	1.04E+04	0.012	112	7.1	4.2	0.14	20
Gladstone Harbour	*Zostera capricorni*	4.51E+03	4.6	0.13	3.3	7.9	5.3	5.44E+03	0.022	267	4.4	1.8	0.13	16.2
Gladstone Harbour	*Zostera capricorni*	3.22E+03	12.6	0.15	2.8	7.1	5.1	6.25E+03	0.013	226	3.1	1.8	0.16	18.4
Gladstone Harbour	*Zostera capricorni*	2.96E+03	11	0.092	2.6	15.3	4.2	5.83E+03	<0.01	186	3.9	1.7	0.24	16.5
Hervey Bay	*Zostera capricorni*	1.35E+03	12.5	0.074	1.1	11.2	5.4	3.41E+03	0.014	156	2.4	2.2	0.14	24.9
Hervey Bay	*Zostera capricorni*	3.70E+03	12.6	0.079	1.9	15.2	5.4	5.62E+03	0.02	254	5.2	3.5	0.19	25
Hervey Bay	*Zostera capricorni*	2.87E+03	21.2	0.069	1.8	22.4	5.9	5.36E+03	0.013	192	4.6	3.2	0.15	24.4
Moreton East	*Zostera capricorni*	600	1.4	0.35	0.47	2.9	2.2	791	<0.01	76.3	1.5	0.72	0.27	11.4
Moreton East	*Zostera capricorni*	1.17E+03	1.6	0.2	0.52	4.8	1.7	1.26E+03	0.033	38.1	1.7	0.74	0.34	9.8
Moreton East	*Zostera capricorni*	686	1.8	0.26	0.41	2.5	2	902	<0.01	49.5	1.3	0.58	0.34	10.8
Moreton West	*Cymodocea serrulata*	2.48E+03	4.5	0.33	2.7	6.5	5.1	5.11E+03	0.016	185	3.8	2.9	0.29	18.9
Moreton West	*Cymodocea serrulata*	1.12E+03	5.4	0.39	2	4.7	4.9	4.18E+03	<0.01	151	2.3	1.6	0.18	15.7
Moreton West	*Cymodocea serrulata*	1.75E+03	8.1	0.33	2.3	3.7	6.1	6.08E+03	0.018	162	2.4	3	0.1	27.8
Moreton East	*Zostera capricorni*	957	1.5	0.35	1.2	2.1	3.4	1.03E+03	<0.01	113	1.9	7.3	0.081	31
Moreton East	*Zostera capricorni*	403	1.2	0.41	0.96	0.94	2.6	507	<0.01	111	0.94	1.5	0.075	13.2
Moreton East	*Zostera capricorni*	553	1.4	0.34	0.94	1	1.8	619	<0.01	100	1.1	0.86	0.076	9.8