

Unrecognized Pollutant Risks to the Great Barrier Reef

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Unrecognised Pollutant Risks to the Great Barrier Reef

A Report for GBRMPA and the Department of Sustainability,
Environment, Water, Population and Communities

Report No. 13/23

May 2013

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EXECUTIVE SUMMARY

This report summarises the occurrence, distribution, risks and toxicity of ten pollutants to the marine environment: marine debris, microplastics, sewage-sourced contaminants, trace metals, anti-foulants, coal dust, petroleum hydrocarbon contaminants, flame retardants, polychlorinated biphenyls (PCBs) and non-photosystem II (PSII) pesticides. These pollutants are under-researched in comparison to other pollutants such as nutrients, sediment and agricultural runoff, which are the pollutants of focus in the Reef Rescue Research and Development Water Quality Program (Reef Rescue R&D).

Marine debris is currently one of the most widespread marine pollution problems, with six million t entering the world's oceans annually (Department of Environment and Conservation 2013). The majority of marine debris is plastic (60-95%) and the major impacts of plastic marine debris are entanglement and ingestion. Additionally, many types of debris can act as a transport platform for invasive species. From 1974-2008 more than 70 species of Australian marine wildlife were impacted by plastic debris by either entanglement or ingestion. A marine debris priority in Australia is ghost nets and major research efforts are being made to reduce the amount of ghost nets in Australian waters. In 2011 3 turtle mortalities and 2 turtle stranding's were attributed to entanglement in ghost nets. Additionally, 11 turtle mortalities were caused by the ingestion of synthetic materials. There is currently a substantial amount of legislation dealing with the management of marine debris in Australian waters; however increased public awareness and monitoring campaigns are required.

Microplastics are plastic pieces < 5mm in size. They can be found in beach sands, the water column and the gut of marine organisms. Ingested plastics have the potential to transfer toxins from the environment to biota, and these leached additives have the potential to interfere with biologically important processes that result in endocrine disruption, and impaired reproduction and development. Waste water discharge into the ocean is a major source of microplastics to the marine environment, suggesting that levels will be higher in urban coastal areas. Currently, very little is known regarding the quantity of microplastics within the Great Barrier Reef or Australia.

Sewage is a source of contamination to marine environments, as many unnatural substances are not completely removed during sewage treatment processes. Pharmaceuticals and personal care products (PPCPs), disinfectants, and antiseptics are entering the water system from households and are being measured within the marine environment. The acute toxicity of PPCPs often occurs at concentrations greater than those normally found in the environment; however, some compounds are of concern due to their propensity to bioaccumulate. Currently, very little research has been conducted on the risk and toxicity these contaminants pose to marine biota. This section outlines the sources and types of contaminants found within treated sewage water and the current state of knowledge about their risk to aquatic organisms.

Trace metal levels within the Great Barrier Reef are generally considered to be relatively low. However, sites adjacent to human activity such as ports and harbours, urban centres and areas adjacent to agricultural activity can contain exceptionally high trace metal concentrations. There are many ports along the Queensland coast (i.e. Gladstone and Townsville) that deal with large quantities of metal products that could be monitored more closely. Some trace metals are essential for biological processes, and only become toxic above threshold levels. Other metals, such as mercury, play no natural role in biological functioning, and are considered hazardous even at low concentrations. Trace metals have been detected in many organisms from the GBR, such as invertebrates, fish, algae, mangroves, and mammals. Exceptionally high concentrations of certain metals have been reported in dugongs from north Queensland in the past.

Anti-foulants are toxic to a wide range of organisms. Anti-foulants have been measured within Australian harbours since the global ban, and ship groundings are a major source of anti-foulants to the Great Barrier Reef. Highly elevated concentrations of anti-foulants in the Great Barrier Reef have been associated with ship groundings (i.e. the 1999 grounding of *New Reach* at Heath Reef, the 2000 grounding of *Bunga Teratai Satu* at Sudbury Reef, and the 2010 grounding of the *Shen Neng* off the Douglas Shoal). Both hard, soft corals and gorgonians around the *Bunga Teratai Satu* grounding site showed symptoms expected from contact with anti-foulants, and were badly damaged or killed within 10 m of the grounding. The concentrations of TBT measured at the Sudbury Reef and Douglas Shoal groundings and butyltin detected at the Heath Reef grounding sites were elevated above ANECC (2000) guidelines. Grounding incidents could be managed by implementing regulations requiring reef pilots to accompany vessels traveling through the Great Barrier Reef.

Coal dust is accidentally lost from stockpiles during coal loading processes for export. Colliery waste can also enter the ocean via runoff to coastal rivers. The processes involved in the transport of coal dust from the land to the reef, and the subsequent behaviour of coal dust in the marine environment are poorly understood, however coal has been found suspended in water as far as the continental shelf break in Australia. Very little research has been conducted on the biological effects of coal dust on tropical marine organisms, however this information would contribute to risk assessments for existing and proposed coal terminals, and inform management of risks to biota in the case of major spills and ship groundings.

Petroleum hydrocarbons enter the marine environment through a variety of point and diffuse sources such as ports, marinas, sewage discharge, as well as the more visible oil spills from ship groundings. After the 2006 oil spill in the Port of Gladstone sediment PAH concentrations exceeded (SQG) ANZECC/AMCANZ guidelines; however concentrations were significantly reduced 6 months after the spill. As was mentioned for anti-foulants, grounding incidents that result in spills could be managed by implementing regulations requiring reef pilots to accompany vessels traveling through the Great Barrier Reef.

Polychlorinated biphenyls (PCBs) pose a serious threat to human and environmental health since these contaminants have been linked with cancer and immunosuppression. Although PCBs have been banned in many countries, they are persistent in the environment and remain a commonly detected contaminant. The management of PCBs in the marine environment poses a challenge since these contaminants are no longer used.

Flame retardants are a global contaminant and are being measured in many marine and terrestrial food chains. It is suggested the components of flame retardants pose similar ecotoxicological effects as PCBs, however information on exposure-effect relationships is lacking. Further research is required in order to establish accurate guideline values. This section outlines the potential effects, occurrence and distribution of flame retardants in organisms and food chains in the northern and southern hemispheres. Flame retardants are likely to be found in high concentrations around urban and industrial areas and have been detected in certain waterways in Queensland.

Non-PSII pesticides have received less research attention in Australia than PSII herbicides. Routine monitoring of PSII herbicides undertaken along the Queensland coast regularly detects the non-PSII pesticides in surface water samples collected during both event and ambient conditions. This section identifies and discusses measured levels of two non-PSII herbicides of concern, metolachlor and imidacloprid in Queensland coastal waterways.

High risk areas in the GBRWHA

The recognisable high risk locations for these pollutants along the coast are largely associated with high urban population centres (cities – Cairns, Townsville, Mackay, Gladstone, Bundaberg, Maryborough)), sites of concentrated heavy industry (Gladstone and Townsville) and major ports (Cairns, Townsville, Abbott Point, Hay Point/Mackay, Gladstone). Toxic metals are associated with metaliferous industries (refineries

and smelters) and ports which tranship metal products (ores, concentrates, metals). Pharmaceuticals and personal care products are discharged from sewage treatment plants in significant quantities from large cities. Hydrocarbons are released accidentally in ports on a regular basis both in continuous small leaks and in occasional major spills. Litter is a greater issue close to urban areas but ship sourced litter is a more widespread issue.

Acronyms used in this report

| | |
|--------------------------------|---|
| AMSA | Australian Maritime Safety Authority |
| ANZECC | Australian and New Zealand Environment and Conservation Council |
| ARMCANZ | Agriculture and Resources Management Council of Australia and New Zealand |
| EDC | Endocrine disrupting chemicals |
| GBR | Great Barrier Reef |
| GBRWHA | Great Barrier Reef World Heritage Area |
| IMO | International Maritime Organization |
| MARPOL | International Convention for the Prevention of Pollution from Ships |
| MEPC | Marine Environment Protection Committee |
| PAH | Polynuclear Aromatic Hydrocarbons |
| PBDE | polybrominated diphenyl ethers |
| PCB | Polychlorinated biphenyls |
| PCDF | Polychlorinated dibenzofurans |
| PPCP | Pharmaceuticals and personal care products |
| PSII | Photosystem II |
| STP | Sewage treatment plant |
| TBT | Tributyltin |
| TPAH | Total Petroleum Aromatic Hydrocarbons |
| USEPA | United States Environmental Protection Agency |
| ppm = mg l⁻¹ | Parts per million |

Table of Contents

| | |
|---|----|
| EXECUTIVE SUMMARY | i |
| 1.0 INTRODUCTION | 5 |
| 2.0 DISCUSSION..... | 6 |
| 2.1 Marine Debris | 6 |
| 2.2 Microplastics | 7 |
| 2.3 Sewage-sourced contaminants | 9 |
| 2.4 Trace Metals | 11 |
| 2.4.1 Invertebrates..... | 13 |
| 2.4.2 Fish..... | 13 |
| 2.4.3 Mangroves..... | 14 |
| 2.4.4 Algae | 14 |
| 2.4.5 Marine Mammals..... | 15 |
| 2.5 Anti-foulants: Tributyltin (TBT) and Alternatives | 15 |
| 2.6 Coal Dust | 17 |
| 2.7 Petroleum Hydrocarbon Contaminants | 18 |
| 2.8 Polychlorinated Biphenyls (PCBs)..... | 19 |
| 2.9 Brominated Flame Retardants | 19 |
| 2.10 Non-PSII Pesticides..... | 21 |
| 3.0 CONCLUSIONS | 21 |
| 4.0 REFERENCES | 23 |

1.0 INTRODUCTION

Marine pollution constitutes any anthropogenic input into the marine environment that results in harm to marine life, threats to human health, and restrictions to marine activities and a decrease in the usefulness and quality of seawater (GESAMP 1969). There are various types of pollutants such as toxins, eutrophication, acidification, waste products, industrial contaminants and noise. The majority of marine pollution sources are land-based; however sea-based sources are also significant. Pollution enters the marine environment by direct discharge of waste into the oceans (point source), runoff into waters (non-point source) and pollutants that are released from the atmosphere (non-point source). Point sources of pollution are classified as a single, identifiable and localised source of pollution, i.e. sewage and industrial discharge, while non-point sources are ill-defined and diffuse, i.e. wind-blown debris and agrochemical runoff. The fate and distribution of pollutants in the marine environment are influenced by many factors such as the degradation time of the pollutant, its solubility, its ability to adhere to suspended particles, as well as hydrodynamic and oceanographic factors. For example, after entering the marine environment chemicals and potential toxins such as trace metals can remain in solution or in suspension and are precipitated to the bottom or taken up by marine organisms (Zhao et al. 2013). Contaminants are taken up by organisms from the surrounding biotic and abiotic environment (bioaccumulation) and can sometimes accumulate (biomagnify) within ocean food chains, resulting in high levels in top predators, including humans (He et al. 2001).

Poor water and sediment quality are considered the most serious known pollutants affecting coastal and marine environments within the Great Barrier Reef Catchment Area (GBRCA) (Australian Government 2013a). The 1995 State of the Marine Environment Report showed that 80% of marine pollution is land-based and poses a major threat to the long-term health of near shore marine ecosystems (Australian Government 2013a). The Reef Rescue Research and Development Water Quality Program (Reef Rescue R&D), funded under the Australian Government's Caring for our Country Program, was implemented in 2010. The aims of the 18 projects were to increase our understanding of the link between management practices and environmental impacts, and to improve water quality across the Great Barrier Reef (GBR) by reducing levels of pesticides (simazine, ametryn, desethyl atrazine, tebuthiuron, atrazine, hexazinone and diuron), nutrients (nitrogen and phosphorus) and sediments released from agricultural lands (Reef Rescue 2013). The Australian Government recently committed \$200 million to continue the Reef Rescue Program for an additional 5 years (Australian Government 2013b).

Although management efforts regarding agriculture related issues are important and have been recognised as a high priority to improve the health of coastal and marine environments with the GBR, current management plans do not address many of the “non-Reef Plan” pollutants of concern for the GBR. Other pollution sources to the GBR include waste and water discharge from urban areas, and activities related to mining, shipping, and ports, which result in the release of a variety of contaminants into coastal and marine environments. Since many pollutants are invisible to the naked eye, they generally go unnoticed unless they are intentionally targeted for analysis. Additionally, hydrodynamic shelf transport processes result in pollutants contaminating much of the GBR. Non-Reef Plan pollutants of concern for the GBR include toxic trace metals, polycyclic aromatic hydrocarbons, marine debris, microplastics, endocrine disrupting chemicals (ECDs), coal dust, pharmaceuticals and more. Many of these substances are currently recognised as a serious threat to coastal and marine ecosystems worldwide, however, there remains a large knowledge gap and hence lack of response to manage the impacts of these pollutants. In a preliminary step to reduce this knowledge gap we review and discuss existing knowledge on the occurrence, status, distribution and impacts of “less monitored” pollutants on global marine ecosystems. Literature was compiled from peer-reviewed scientific journals, university theses, government documents and government and NGO websites. Specifically, this report will discuss: marine debris, microplastics, sewage-sourced contaminants, trace metals, anti-foulants, coal dust, petroleum hydrocarbon contaminants, flame retardants, polychlorinated biphenyls (PCBs) and non-PSII pesticides. When possible, the current knowledge of these pollutants within the GBR lagoon is addressed and areas requiring further research are discussed. This information can be used to inform management of risks to biota and facilitate future research and management efforts.

2.0 DISCUSSION

2.1 Marine Debris

Marine debris is one of the most widespread pollution problems facing the world’s oceans, with six million t entering the world’s oceans annually (Department of Environment and Conservation 2013). Debris is derived from various sources, persists in the environment and can be transported long distances from its source via oceanic currents. The degradation time of debris varies substantially depending on the item (Table 1). Marine debris is generally 60-80% plastic, yet can reach 90-95% in certain areas (Moore et al. 2008). Approximately 10% of the 300 billion lbs of plastic the world produces each year ends up in the ocean, of which > 50% eventually sinks, damaging life on the ocean floor (Moore et al. 2008). In 2006 the United Nations Environment Program (UNEP) estimated that every square mile of ocean hosts 46,000 pieces of floating plastic and researchers have found that within the “Eastern Garbage Patch” the amount of plastic outweighs the amount of plankton by a ratio of six to one (Moore 2001).

Table 1. Degradation time of marine debris.

| Debris Type | Degradation Time |
|-------------------------|-----------------------|
| Paper parking tickets | 2-4 weeks |
| Orange and banana peels | Up to 2 years |
| Cigarette butts | 1-5 years |
| Plastic bags | 10-20 years |
| Foam cups | 50 years |
| Aluminium cans | At least 80 years |
| Fishing net | At least 600 years |
| Glass bottle | Up to 1,000,000 years |

Source: Department of Environment and Conservation 2013.

Each year, one million seabirds, and 100,000 turtles and marine mammals (whales, dolphins, and seals) are killed by marine debris around the world (Department of Environment and Conservation 2013). Marine debris can entangle wildlife or become ingested, which can result in blockage of the airway or starvation (Wilcox et al. 2013, Haynes 1997). Furthermore, debris can act as a transport platform for invasive species (Derraik 2002), injure human health (Dixon and Dixon 1981), and decrease aesthetic values of beach- and ocean-scapes (Haynes 1997) (Fig.1). Economic losses caused by marine debris include losses to fisheries caused by fouling of gear by bottom debris (Dixon & Dixon 1981) and income lost to ‘ghost catch’ (Brown and Macfadyen 2007).

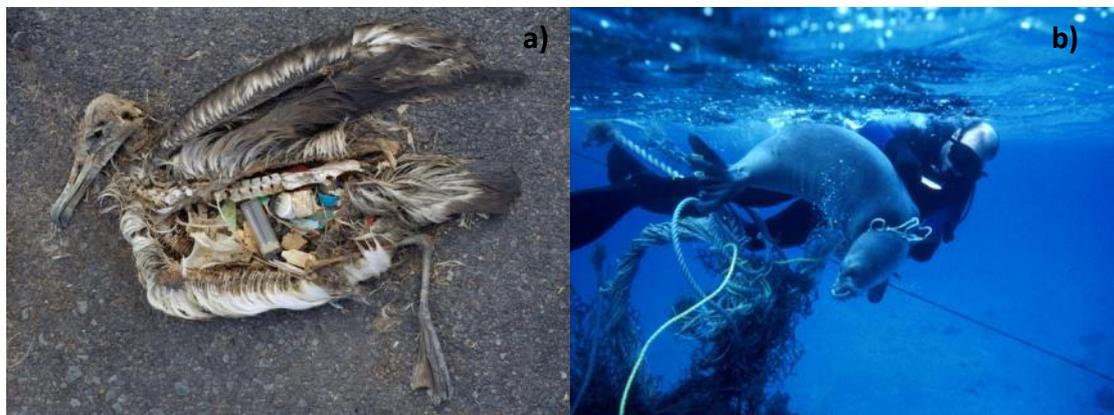


Figure 1. Images of marine debris: a) a juvenile albatross has starved to death as a result of consuming too much plastic, b) a diver tries to free a seal entangled by a derelict net. Sources: a) aquascapeconservation.org, b) coastalcare.org

In 2009, compiled data on interactions between plastic debris and marine wildlife in Australian waters was released (Ceccarelli 2009). The study included all Australian waters, offshore and sub-Antarctic islands and

Australian Antarctic Territories. The study found that from 1974-2008 >70 species of Australian marine wildlife were impacted by entanglement in, or ingestion of, plastic debris. Included in these findings were 6 species of marine turtles, 12 species of cetaceans, >34 species of seabirds, dugongs, 6 species of pinnipeds, >10 species of sharks and rays and more than eight other species groups. The dominant types of debris associated with entanglement were derelict fishing nets and the most common items ingested were synthetic fishing line and hooks (Ceccarelli 2009). It is estimated that 640,000 t of fishing gear is lost at sea each year, and this accounts for only a small percentage of the total volume of marine debris (Wilcox et al. 2013). Patterns of ingestion and entanglement are influenced by factors such as foraging areas, migration patterns, size and distribution of populations, diets, proximity of species to urban areas, changes in fisheries equipment and practices, weather patterns, and ocean currents (Ceccarelli 2009).

Marine Animal Stranding Reports are created annually by the Queensland Government (The Department of Environment and Heritage Protection) and it was reported that in 2011 3 turtle mortalities and 2 turtle strandings were attributed to entanglement in ghost nets (Meager and Limpus 2012). Additionally, 11 turtle mortalities were a result of the ingestion of synthetic materials (Meager and Limpus 2012). Scientists from the CSIRO Wealth from Oceans Flagship program have recently surveyed 100 km intervals along the eastern Australian coastline from north of Cairns and across the south coast to Perth. The survey found that there is a high density of debris near cities as well as in some areas of low population (CSIRO 2013). An earlier national assessment of Australia's marine debris showed that plastics comprised the bulk of the material (Wace 1995). In the GBR, shipping contributed the most debris to ports and coasts in heavily trafficked areas, and fisheries were the most important source of debris on remote coasts (Haynes 1997, Wace 1995). Fishing nets that are accidentally lost or deliberately discarded, but which continue to fish indiscriminately as they travel along currents and tides are "ghost nets" (<http://www.ghostnets.com.au/>). Wilcox et al. (2013) simulated ghost net tracks in the Gulf of Carpentaria and found that the eastern margin and a wide section in the southwest contain ghost nets at levels that present significant risk for turtle entanglement (Wilcox et al. 2013). Past projects on ghost nets have also been funded under Natural Heritage Trust and Caring for our Country as ghost nets are considered as a priority marine debris in Australia.

National governments and international organisations began to address the importance of marine debris in the 1970's. The International Convention for the Prevention of Pollution from Ships (MARPOL) is the main international convention that deals with the prevention of pollution in the marine environment (IMO 2013). The regulations of this convention are aimed at preventing and minimising pollution from ships, both accidental and from routine operations. Australia currently regulates the deliberate loading, dumping and incineration of waste at sea under the *Environment Protection (Sea Dumping) Act 1981* and the *Environment Protection (Sea Dumping) Amendment Act 1986*, however, under the International Convention for the Prevention of Pollution from Ships, the overboard disposal of paper, glass, metal and crockery (not plastics) and food is permitted from vessels more than 12 nautical miles from land. Marine debris is listed as a key threatening process under the Environment Protection and Biodiversity Conservation Act 1999 and in June 2009, the Australian Government made the *Threat Abatement Plan for the Impacts of Marine Debris on Vertebrate Marine Life* (the Plan) (Australian Government 2013c). The establishment of more monitoring programs will aid in providing better management solutions for Australia's marine debris issue (Haynes 1997; Wace 1995).

2.2 Microplastics

More than 240 million t of plastic are being used each year (Browne et al. 2011) and as a result, beaches, open-ocean and deep-sea environments across the globe are littered with plastic debris (Corcoran et al. 2009). No set definition of microplastics has been established, however, microplastics are generally defined as pieces of plastic either < 5mm (Moore et al. 2008) or < 1mm (Browne et al. 2011) (Fig. 2), and are accumulating in marine habitats around the world. Microplastics are grouped into two main varieties, 1) fragments broken from larger objects, and 2) resin pellets and powders (Moore et al. 2008). Land based sources of microplastics include sewage that contains fibres from laundering clothes (Browne et al. 2011), plastic micro-beads found in exfoliating washes, air blasting technology, and the manufacturing of plastic products that use granules and small resin pellets (Cole et al. 2011). Sediment density loads of microplastics

sampled from sandy beaches in Port Douglas and Busselton, Australia were 1-10 and 21-30 pieces of plastic per 250 m⁻¹, respectively (Browne et al. 2011). Increases in micrometre-sized fragments of acrylic, polyethylene, polypropylene, polyamide, and polyester have been found in surface waters of the northeast Atlantic, the north east Pacific and along sandy, estuarine and sub-tidal habitats of India, Singapore and the United Kingdom (Browne et al. 2011), however, due to the lack of research, the global extent of this form of pollution remains largely unknown.



Figure 2. Microplastics are highly variable in shape, source, colour and composition. These tiny fragments are contaminating oceans and beaches. Sources: a) greenphillyblog.com

Very little research has been conducted on microplastics yet studies are increasing due to the importance of microplastics as a global pollutant. The biological implications of microplastics for organisms are only just emerging, however, zooplankton, invertebrates, echinoderm larvae, seabirds (Bolton and Havenhand 1998; Brilliant and MacDonald 2002; Hart 1991; Wilson 1973), crustaceans and fish (Blight and Burger 1997; Tourinho et al. 2010) have all been found to ingest microplastics (Fig. 3). Ingestion of microplastics by wildlife can cause starvation, reduce fitness etc., however, ingestion is also a potential pathway for the transfer of pollutants, and plastic additives to organisms and the consequences of these substances on health are not yet fully understood (Browne et al. 2011).

Extraneous pollutants, such as endocrine disrupting chemicals (compounds that mimic hormone activity) and persistent organic pollutants (compounds with long environmental half-lives) adhere to and become concentrated upon plastic surfaces, allowing them to be transported long distances (Cole et al. 2011). Extraneous pollutants adhered to microplastics can become dissociated after ingestion, but microplastics can also leach the chemical additives introduced to them during the manufacturing process, so can be toxic even without the presence of extraneous pollutants (Cole et al. 2011). It has been observed that sediment dwelling polychaete worms sequester a proportion of sorbed contaminants from digested plastic (Teuten et al. 2007, 2009). Leached additives have the potential to interfere with biologically important processes that could result in endocrine disruption, and/or have impacts on an organism's mobility, reproduction and development (Cole et al. 2011). Evidence also suggests that plastic-associated contaminants, such as polychlorinated biphenyls (PCBs), can be passed through the food chain (Betts 2008; Teuten et al. 2009).



Figure 3. The 2008 North Pacific Gyre Expedition discovered the widespread ingestion of plastic particles by fish that forage on plankton at night on the ocean surface. Thirty-five per cent of these fish had ingested micro-plastic particles. Source: www.axisoflogic.com

The United Nations, Group of Experts on Scientific Aspects of Marine Environmental Protection, International Oceanographic Commission, European Union, Royal Society and NOAA have all identified the need to improve our understanding about the sources of microplastics, where they are likely to accumulate and how widespread the problem is (Browne et al. 2011).

2.3 Sewage-sourced contaminants

The main aim of sewage treatment is to decrease the pathogen load, biological oxygen demand and organic material within waste water effluents that are discharged into receiving waters. An increasing number of pharmaceuticals and personal care products (PPCPs) are being detected at a greater frequency in sewage treatment effluents and environmental waters. The types of PPCPs detected in sewage treatment plant (STP) effluent are consistent across many major cities of the world (Gros, Petrović et al. 2009; Kasprzyk-Hordern, Dinsdale et al. 2009; Rodil, Quintana et al. 2009; Pal, Yew-Hoong Gin et al. 2010; Bueno, Gomez et al. 2012). It is expected that the major cities along the Queensland coast (including Townsville, Cairns, Rockhampton, Mackay, Bundaberg, Hervey Bay and Gladstone) will be discharging the same range of chemicals.

Table 2 shows that pharmaceuticals such as analgesics and anti-inflammatories, antibiotics, diuretics, lipid regulators, beta-blockers, ulcer healers and caffeine are regularly detected in sewage effluent in the United Kingdom (Kasprzyk-Hordern et al. 2009), Spain (Rodil et al. 2009; Gros et al. 2009; Bueno et al. 2012) and Germany (Pal et al. 2010). The concentration and composition of the chemicals contributing to the load entering and discharged from sewage treatment plants (STPs) varies depending on the type of treatment undertaken (primary/secondary vs tertiary), the rate at which contaminants are used within the sewage treatment catchment area and the types of local regulations being applied to chemical/pharmaceutical use (Kümmerer 2009).

Most pharmaceuticals are incompletely removed during the sewage treatment process (Grover, Zhou et al. 2011). Removal efficiencies, detections in surface waters and references have been outlined in Table 2. Psychostimulants such as caffeine, nicotine, and their metabolites, are regularly detected in most wastewaters (Martínez Bueno, Gomez et al. 2012). While >80% of these compounds are removed during the sewage treatment process psychostimulants are considered persistent/ubiquitous contaminants within aquatic environments because there is a chronic delivery of low concentrations within effluents.

Personal care products differ from pharmaceuticals in that large amounts of these substances can be introduced directly into the environment during recreational use of waters or via volatilisation. Substances included in this category are synthetic fragrances, UV filters (sunscreens), disinfectants and antiseptics.

Synthetic fragrances are of concern environmentally as certain musk's are highly lipophilic (fat soluble) and tend to accumulate within sediments, sludge's and biota. While this lipophilic tendency leads to the high efficiency of removal of musk's when they pass through an STP, it also leads to the bioaccumulation and/or magnification of musk concentrations when they enter environmental waters untreated. UV filters predominantly enter environmental waters during recreational activities however are also detected in STP effluents at variable concentrations (Giokas et al. 2007). Disinfectants and antiseptics are used in a wide variety of commercial products that include clothing, acne creams, toothpaste, soap, and incorporated into children's toys and kitchen utensils. Disinfectants are removed at efficiencies of >70 % when passing through a STP (Gómez et al. 2007) however are detected in concentrations of up to 160 ng l⁻¹ in environmental waters (Gómez et al. 2009; Kasprzyk-Hordern et al. 2009).

The threat PPCPs pose within the environment is specific to their mode of action and has been linked to developmental, reproductive and behavioural changes in exposed organisms. Environmental concentrations of endocrine disrupting chemicals (EDCs) have the potential to disrupt the normal hormonal balance of many species (Mills and Chichester 2005; Liu et al. 2012; Vandenberg et al. 2013). The persistence of antibiotics and antimycotics (antifungals) in the environment is expected to impact on the microbial composition within an ecosystem, and has been linked to the development of antibiotic and antimycotic resistance in enterobacteria and heterotrophs (Rodríguez-Rojas et al.; Kümmerer 2009; Novo et al. 2013). Sex differentiation abnormalities that include testicular development in female salmon (Piferrer et al. 1994) have also been observed in association with these compounds. The toxicology of PPCPs in freshwater ecosystems has been the subject of much research however more research is required on how these compounds affect marine ecosystems (Ellis 2006). The acute toxicity of PPCPs often occurs at concentrations greater than those normally found in the environment (Calisto and Esteves 2009). However, some compounds are of concern due to their propensity to bioaccumulate and their chronic delivery at low concentrations through waste water effluents.

Table 2: Global STP removal efficiencies (after primary/secondary and or tertiary treatment) and surface water detection of PCPPs

| Chemical | STP removal efficiency | Reference | Surface water detection | Reference |
|---|---------------------------------|--|---|---|
| Pharmaceuticals | | | | |
| Antibiotics | | | | |
| Analgesics & anti-inflammatories | 40 - 65% In most cases >50 % | Spain (Bueno et al. 2012) Bueno et al. 2012; Gomez et al. 2008; Gómez et al. 2007; UK (Kasprzyk-Hordern et al. 2009), Spain (Rodil et al. 2009; Gros et al. 2009), Germany (Pal et al. 2010). | Spain UK and Italy | Martínez Bueno et al. 2010; Kasprzyk-Hordern et al. 2009; Zuccato et al. 2005 |
| Beta-blockers & diuretics anti-hypertensive | 50 – 60 % | Zuccato et al. 2005; Martínez Bueno et al. 2010, UK (Kasprzyk-Hordern et al. 2009), Taiwan (Yu-Chen Lin et al. 2009) | Spain | Martínez Bueno et al. 2010; Hernando et al. 2007 |
| Lipid regulators | 50 - 60% | Germany (Ternes, 1998), Spain (Gros et al., 2009, Bueno et al. 2012) | Spain | Martínez Bueno et al. 2010 |
| Anziolytics antidepressant/ psychiatric drugs | In most cases <50%) | | Up to 200 ug l ⁻¹ in rivers from Wales, Spain, Italy and up to 1 mg l ⁻¹ in Germany | Kasprzyk-Hordern et al. 2009; Martínez Bueno et al. 2010; Zuccato et al. 2005; Ternes, 1998 |
| Ulcer healing e.g. anitidine and omeprazole | 39 – 84 % | Bueno et al. 2012; Gros et al. 2009; Castiglioni et al. 2006 | | |
| Bronchodilators | 58 – 74 % | Bueno et al. 2012 | 2.5 ng l ⁻¹ in Italy and 4 ng l ⁻¹ in Spain | Zuccato et al. 2005; Martínez Bueno et al. 2010 |
| Psychostimulants caffeine, nicotine and their metabolites | >80% | | Spain waters range from 0.3 – 22 ng l ⁻¹ | Martínez Bueno et al. 2011 |
| Personal care products | | | | |

| | | | | |
|---|-----------|---|--|--|
| Synthetic fragrances e.g. polycyclic musk's | 70 – 90 % | Yamagishi et al. 1981; Carballa et al. 2004; Bueno et al. 2012 | Germany and Switzerland | Quednow and Puttmann 2008; Rodil et al. 2010 |
| Disinfectants & antiseptics | ~70 % | Daughton and Ternes 1999; Gómez et al. 2009; Gómez et al. 2007 | River water between 24-157 ng l ⁻¹ | Gómez et al. 2009; and 1-5 ng l ⁻¹ ; Kasprzyk-Hordern et al. 2009 |
| UV filters | >80 % | Rodil et al. 2009; Giokas et al. 2007 | UK (<160 ng l ⁻¹) Spain (<59 ng l ⁻¹) | Kasprzyk-Hordern et al. 2009; Benito Quintana et al. 2007 |

2.4 Trace Metals

Trace metals are of ecological importance because they are not removed naturally from water, and therefore accumulate in reservoirs and within food chains (Ghrefat 2006). Trace metals are classified as either essential elements (i.e. copper, zinc) or non-essential elements (i.e. arsenic, cadmium, mercury). Essential elements are required by all living organisms in trace amounts to complete certain biological processes, while non-essential elements are not required within organisms and are potentially hazardous at low concentrations (Lata and Rohindra 2002). Metals enter the environment in two possible ways: 1) through natural processes such as rock weathering, forest fires, and volcanic activity or 2) through anthropogenic sources including contaminated river water, effluent discharges, shipping accidents, and agricultural activities (Anu et al. 2007).

Metals are of particular concern in the aquatic environment because they are persistent and can be transported long distances. Metals are often found in sediment and water column samples collected from the marine system (Anderson 2004; Jones et al. 2005; Apte et al. 2006; Angel et al. 2010). Bioavailable metals in water are examined using either grab samples, passive samplers, or by examining the metal content within indicator species (i.e. oysters). Metals are well known to have serious effects on marine biota when present in elevated concentrations (Furness and Rainbow 1990). Many metals act on specific physiological and biochemical sites, and certain metals such as Cu are more toxic to invertebrates than vertebrates (Dallinger and Rainbow 1993). Metal toxicity profiles can vary within a genus or even within a taxonomic family, so it is important that toxicity risk assessments are performed and applied consistently across groups with similar sensitivities (Nieboer and Richardson 1980).

The following eight metals pose potential or immediate threats to aquatic organisms and ecosystems:

- i. **Mercury (Hg)** is not an essential element for biological functions and any accumulation of Hg is considered as potentially hazardous contamination (NRC 2000). Fungicides, mining, refineries, ports and ship traffic are important sources of Hg to aquatic environments (Guzmán and Garcia 2002). Mercury can be found in elemental, inorganic, and organic forms, each of which has different toxicological properties (WHO 1989a). When inorganic Hg undergoes methylation by microbial activity it becomes methyl mercury, which is the most toxic form and can be bio-magnified by organisms in the food chain (United States Environmental Protection Agency 1997). Uptake of Hg by biota is a fast process and even with the removal of Hg sources depuration is slow (WHO 1989b; NRC 2000). Depuration of Hg is dependent on the magnitude of contamination, the chemical form of Hg and the physical and chemical conditions of the environment such as hydraulic turnover (NRC 2000). The Minamata Convention on Mercury aims to control and reduce Hg products, processes and industrial uses and governments recently agreed to a global, legally-binding treaty to prevent Hg emissions and releases (UNEP 2013). The treaty will be open for signature in October 2013.
- ii. **Copper (Cu)** is an essential element required in low concentrations by all living organisms and is a catalyst for many enzyme systems (Depledge and Rainbow 1990). Additionally, it plays an active role as an electron carrier in intracellular structures (Reichert-Brushett and Harrison 1999). Copper is a main component in organotin-free antifouling products, which serve to eliminate the settlement of algae and marine invertebrates (Negri and Heyward 2001). As a result, Cu is found in high levels around ports and harbours due to uncontrollable releases into the aquatic environment, resulting in Cu toxicity towards many non-target marine invertebrates such as corals (Negri and

Heyward 2001). Copper is more toxic to invertebrates such as crabs, lobsters, prawns and algae than vertebrates. Copper is also a main component of some fungicides and fertilizers (Pietrzak and McPhail 2004). Agricultural chemicals are being addressed through Reef Plan, thus Reef Rescue initiatives are managing to a small extent the copper that is found in these products. Unpolluted ocean water contains approximately $0.0008 \mu\text{g l}^{-1}$ - $92.2 \mu\text{g l}^{-1}$ Cu (ANZECC 1992).

- iii. **Zinc** (Zn) is an essential element required for the regulation of metabolic functions such as protein synthesis and repair, however can become toxic once certain threshold levels are exceeded (Anu et al. 2007). Main sources of Zn into the marine environment are herbicides, anti-foulants, sewage discharge and mining wastes (Riley and Chester 1989). Unpolluted seawater contains approximately $5 \mu\text{g l}^{-1}$ Zn (ANZECC 1992).
- iv. **Cadmium** (Cd) is targeted by all international conventions seeking to protect aquatic environments due to its high toxicity and persistence (Taylor 1983). Anthropogenic sources of Cd are smelting, fossil fuel combustion, waste disposal and the addition of sewage sludge to agricultural soils (Wright and Welbourn 2001). Unpolluted surface waters in the open ocean contain on average 40 mg l^{-1} of Cd (Ray 1984).
- v. **Arsenic** (As) is widely used in agricultural and industrial practices and increasing concerns have been raised about its carcinogenic, mutagenic and teratogenic properties (NRC 2000). Bioaccumulation of organic As compounds is possible, however there is no evidence of biomagnification (WHO 2001). The effects of As on aquatic organisms include inhibition of growth, photosynthesis, and reproduction (WHO 2001). On average, open ocean water concentrations of As range between $1\text{-}2 \mu\text{g l}^{-1}$ (WHO 2001).
- vi. **Aluminium** (Al) is released into the environment along the Queensland coast from mining sources and through its use as an antifouling agent. The toxicity of Al to fish is related to water pH as the solubility of Al increases with acidity. The majority of effects to aluminium exposure is observed in the gills and physiological processes relating to this organ (Waring and Brown 1995; Teien, Kroglund et al. 2006).
- vii. **Cobalt** (Co) is essential for the normal development of many organisms. Co occurs naturally and is also released during the smelting of ores and the combustion of fossil fuels. Minimal effects have been observed on hatching zebra fish following exposure up to 15 mg l^{-1} however survival after 9 days was affected when fish were exposed to concentrations of $60\text{-}15360 \mu\text{g l}^{-1}$ (Dave and Xiu 1991). No specific studies have been undertaken to assess the toxicity of Co on marine fish (Blust 2011). LC50 for 10 different fish species have been reported in the USEPA ECOTOX database which show that freshwater species are more sensitive (LC50 of between $0.5\text{-}332 \text{ mg l}^{-1}$) than the marine organisms tested (LC50 of between $52\text{-}1000 \text{ mg l}^{-1}$) (Blust 2011).
- viii. **Manganese** (Mn) is essential for the normal development of many organisms. Mn occurs naturally and is also released during the smelting of ores (Mn is a common constituent of steel) and the combustion of fossil fuels. Mn toxicity has been linked to immunosuppression, affecting lymphocyte proliferation, humeral immune response and phagocytic activity (Dunier 1994; Anderson 1996). Toxicity to freshwater and marine organisms has been observed (e.g. fresh water fish: Davies and Brinkman (1994, 1995), Reimer (1999); and marine crab: Eisler (1977), mussels: Morgan et al. (1986), and brine shrimp: Gajbhiye and Hirota (1990)).

Past monitoring of heavy metals within the GBR Marine Park and World Heritage Area has indicated relatively low pollution levels, with the exception of sites adjacent to human activity such as ports and harbours, urban centres and areas adjacent to agricultural activity (Haynes and Johnson 2000). Ports and harbours where local industrial influences include mining and/or the refining and manufacturing of mining products represent an additional significant source of metals to the environment. As such the monitoring of metals (Al, Sb, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, V, Zn) is undertaken as part of the required

environmental impact statement (EIS) prior to any proposed development within the marine and near shore areas (PCIMP 2013). Major ports for trace metals and minerals along the Queensland coast include the ports of Gladstone and Townsville. The Port of Townsville is the principal port in North Queensland and serves a large area that includes the Greenvale nickel refinery and the mining community at Mount Isa (Queensland Government 2013). Metal pollution in the environment surrounding these ports can be attributed to many metal-related industries. At the Port of Townsville, the main imports include refined fuel products and nickel ore, while exports include zinc and copper concentrates, refined lead, zinc, copper and nickel (Queensland Government 2013). In Gladstone, local industry includes the production of industrial chemicals, the export of coal and liquid nitrogen gas, and the world's largest aluminium smelter and refinery (Queensland Government 2013). Port Curtis is known to have higher than normal concentrations of contaminants, especially metals, in the harbour sediment and water (Anderson 2004; Jones et al. 2005; Apte et al. 2006; Angel et al. 2010).

Trace metal concentrations in a variety of biota are relatively well documented along the Queensland coast; however the majority of trace metal data within the GBR is now dated and further research would be required to ascertain current levels and impacts of trace metals. The majority of the information provided below is from the Great Barrier Reef World Heritage Area (GBRWHA).

2.4.1 Invertebrates

Between 1980 and 1983 metal concentrations (Cd, Cu, Pb, Ni, Zn) in various soft (octocorallian) and hard (scleractinian) corals from Heron, Lizard and Orpheus Islands were examined (Denton and Burdon-Jones 1986a). Octocorals accumulated significantly higher concentrations of all detectable metals (e.g. Zn max = $29.0 \pm 6.7 \text{ ug g}^{-1}$) compared to the scleractinian corals (e.g. Zn max = $1.3 \pm 0.65 \text{ ug g}^{-1}$). Esslemont (1998) determined the utility of *Goniastrea aspera* and *Pocillopora damicornis*, which are resident in the Townsville harbour and Heron Island as biomonitors of ambient metal concentrations. Esslemont (2000) later measured extremely high concentrations of Zn, Cr, and Cu in tissues of *Goniastrea aspera* sampled in proximity to the Townsville harbour.

Ecotoxicological studies examining the impact of metals on coral ecology have increased in recent years. Trace metals can result in acute or chronic toxicity in corals, causing lethal effects or long term impacts to key biological processes of corals such as fertilisation and metamorphosis (Reichelt-Brushett and Michalek-Wagner 2005; Reichelt-Brushett and Harrison 1999; Negri and Heyward 2001; Heyward 1988) and larval settlement (Reichelt-Brushett and Harrison 2000; Goh 1991). Other effects of metals on corals include physiological stress (Howard and Brown 1984), reduced growth (Howard and Brown 1987), loss of zooxanthellae (Esquivel 1986; Harland and Brown 1989), enhanced mortality (Mitchellmore et al. 2007) and reduced scleractinian coral abundance (Berry et al. in press) and biodiversity (Ramos et al. 2004). Cu significantly decreased successful fertilisation of soft coral gametes exposed to minimum concentrations of $69 \text{ } \mu\text{g l}^{-1}$ (Reichelt-Brushett and Harrison 1999). Inhibition of fertilisation and metamorphosis was found in a hard coral after exposure to anti-foulants containing Cu (Negri and Heyward 2001), and exposure of a sea anemone to Cu resulted in increased zooxanthellae loss with increased length of exposure (Harland and Nganro 1990). Cu has also been shown to alter symbiotic algal response to coral host signalling compounds that regulate zooxanthellae (Grant et al. 2003).

High concentrations of arsenic have been measured within the tissues of various bivalves collected from GBR waters (Benson and Summons 1981). Nine species of tropical bivalves were collected from the Greater Townsville region in 1979 and were analysed for Ag, Cd, Cu, Co, Pb, Ni and Zn (Klumpp and Burdon-Jones 1982). Although concentrations were variable between locations, most bivalves were found to be strong accumulators of metals.

2.4.2 Fish

Fish are generally able to regulate the accumulation of most metals, with the exception of Hg (Phillips and Rainbow 1993). However, exposure of fishes to excessive metal concentrations can compromise their immune system, and lead to secondary infections of pathogenic microorganisms like fungi, bacteria and

viruses (Austin 1999, 2007; see Iwama 2006 for a review of stress responses and Maule et al. 1989 for a specific case).

Zinc, Cu, Cd, Ni, Pb and Hg were measured in the muscle and liver from 50 species of fish from the GBR (Denton and Burdon-Jones 1986b). Levels of Zn, Cu, Cd and Hg in liver samples were generally greater than the levels measured in the muscle samples, while Ni and Pb were rarely detected. Overall, the metals measured within the tissues of these fishes were ranked low among the lowest reported in the literature (Denton and Burdon-Jones 1986b). With the exception of 5% of the samples, Hg levels were below the Australian National Health and Medical Research Council's standards for human consumption (Denton and Burdon-Jones 1986b). Studies conducted on fish show that Zn interferes with the uptake of calcium in fish gills and at high concentrations can cause irreversible destruction of the gill epithelium (Kennedy 2011), leading to reduced oxygen uptake, tissue hypoxia, osmoregulation, and acidosis (Wood 2011). Long term exposure to Zn toxicity affects growth, egg fragility, mortality and reproduction in fish (Clearwater, Farag et al. 2002; Jezierska, Ługowska et al. 2009; Kennedy 2011). Zinc has been detected at concentrations below the National Food Authority's Maximum Residue Limits in muscle tissue collected from fish, sharks and rays, squid and cuttlefish and crustacean collected from Cleveland Bay (Jones, Mercurio et al. 2000). The effects of Cu on fish in saline waters include suppression of the immune systems and secondary infections. Copper increases the susceptibility of fish to disease following external damage to the gills, opercula, fins or skin (Austin 1999). Exposure to Cu results in coagulation of the mucus layer of gills and leads to inhibition of oxygen transport and respiratory distress (Austin 2007).

Exposure to high aluminium concentrations has been shown to compromise the immunity of fish by affecting the integrity of both the skin of the fish and protective mucus layer that protects from infection (Tierney, Baldwin et al. 2010). A change in the integrity of the skin and protective mucus layer provides an opportunity for naturally occurring infectious organisms (bacteria, viruses, and fungi) to more easily infect the fish (Camargo, Fernandes et al. 2009).

Chromium VI (Cr) has been measured in tissues of marine fish (Jones, Mercurio et al. 2000) but its toxicity to these organisms is unknown. There is evidence for lethal and sub-lethal Cr toxicity to freshwater fish at alkaline pH (Van der Putte et al. 1981a). Freshwater fish exposed to 2.6 ppm Cr for 30 days had altered enzyme activities, while exposures of 120 days were life threatening (Van der Putte et al. 1981a). Sub-lethal exposures to Cr in freshwater have caused declines in disease resistance and serum agglutinin production (Sugatt 1980a) as well as impairment of salinity tolerance and serum osmolarity (Sugatt 1980b).

2.4.3 Mangroves

Mangrove forests are extremely valuable as they capture effluents from land based runoff. They provide a buffer for metals entering coastal waters as their root systems physically trap fine sediments, which contain high loads of heavy metals and other toxicants (Harbison 1986; Robertson and Phillips 1995). Mangroves tend to have a high tolerance for certain trace metals, however both field and laboratory studies have resulted in increases in peroxidase activity and decreases in photo-pigments with increasing levels of Cu and Zn (MacFarlane 2001). High levels of heavy metals also resulted in the inhibition of photosynthesis and respiration in mangroves, which resulted in a die back (Melville and Burchett 2002).

From a management point of view, any changes to mangrove forests would alter the physical and chemical conditions of the forest, impeding this ecosystem from acting as a potential pollutant trap. As a consequence, a high proportion of the metals that are normally trapped in the forest would be released into the marine environment rather than being stored in the sediments (Saenger and McConchie 2004).

2.4.4 Algae

Denton and Burdon-Jones (1986c) measured Zn, Cu, Cd, Ni, Pb and Hg content in 48 species of brown, red and green algae from the GBR. Metal levels in GBR algae showed considerable inter- and intra-specific variations, and overall, levels were substantially lower than values reported from areas highly contaminated by metals.

2.4.5 Marine Mammals

Exceptionally high concentrations of Fe and Zn, and high levels of Cu, Cd, Ag and Co in livers and high levels of Cd in kidneys were reported in dugongs from north Queensland (Denton et al. 1980; Denton 1981). Positive correlations between Fe, Zn, Cd, Co (in the liver) and Cd (in the kidney) concentrations and dugong age suggest bioaccumulation may be occurring (Denton et al. 1980). Similar concentrations were reported in the muscle, liver and kidney of three dugongs that were stranded following a cyclone in northern Australia in 1984 (Marsh 1989).

2.5 Anti-foulants: Tributyltin (TBT) and Alternatives

Organotin compounds directly enter the marine environment from their use as antifouling paints on ships and shipping facilities (Tang and Wang 2008). Tributyltin (TBT) is the main active biocide in antifouling paint (Tang and Wang 2008). The chemicals industry developed cost-effective and efficient anti-fouling paints in the 1960's and within a decade the majority of seagoing vessels had TBT painted on their hulls (IMO 2002). Environmental studies reveal that organotin compounds leach from the paint, persist in water and sediments, and kill non-target sea life. TBT has been considered the "most toxic substance ever deliberately introduced to the marine environment by mankind" (Goldberg 1986) and has been found in remote areas of the GBR and the Antarctic (Negri et al. 2004; Negri and Marshall 2009). Organotins such as TBT are highly toxic to many marine organisms including octocorals (Sebens 1983), scleractinian corals (Morse et al. 1988, Allemand et al. 1998, Negri and Heyward 2001, Smith et al. 2003), other cnidarians (Mercier et al. 1996; Leitz 1997), bryozoans (Kitamura and Hirayama 1987), molluscs (Labare et al. 1997) and echinoderms (Jonson and Sutton 1994). TBT causes shell deformations in oysters (Scammell et al. 1991), sex changes (imposex) in dog whelks (Gibbs and Bryan 1986; Gibbs et al. 1988), neurotoxic (Féral and Le Gall 1983) and genetic effects (Bettin et al. 1996), and immune response in other marine organisms (Lilley et al. 2012). TBT accumulates in organisms and food chains and eventually reaches humans through fish consumption (Laughlin 1986; Murai et al. 2008; Airaksinen et al. 2010). From 1970-1980, elevated concentrations of TBT in shellfish from France caused the collapse of commercial shell-fisheries in at least one area, which prompted many States to enforce restrictions on the use of TBT in anti-fouling paints (IMO 2002).

The International Maritime Organization (IMO) adopted an Assembly resolution that called on the Marine Environment Protection Committee (MEPC) to develop a global resolution to address the harmful effects of ships (IMO 2002). This resolution called for a global prohibition on the application of organotin compounds that act as biocides and anti-fouling systems on ships by 2003, and a complete prohibition by 2008. Since the ban, ambient levels of TBT have decreased in the water column, sediments, and mollusc tissues, and dog whelks and oysters have recovered from imposex and shell deformation, respectively (Evans et al. 1995).

TBT generally enters the environment via two main mechanisms, 1) through leaching of paint from ship hulls (Negri and Heyward 2001) and 2) via the loss of paint chips from ship hulls, which are then deposited on the seabed (Negri et al. 2002; Marshall et al. 2002; Turner 2010). Marine sediments act as a temporary and long-term sink for TBT that is not rapidly degraded, releasing TBT and its degradation products into the water column over time (Seligman et al. 1996). TBT based paints are designed to last up to 7 years, making lost paint particles a chronic source of pollution (Marshall et al. 2002). Approximately 6,000 large vessels (> 50 m in length) pass along two main shipping routes within the GBRWHA each year (AMSA 2001) and more than 40% of these vessels are coated with TBT-containing anti-foulant paints (Negri and Marshall 2009). Although TBT is no longer registered for use in Australia, concentrations were measured in 1999 in marine sediments from commercial harbours, marinas and mooring locations on mid-shelf continental islands, and outer reef sites in four regions within the GBR (Haynes and Loong 1999). Background concentrations were found for copper at boat mooring sites and mid-shelf continental islands, while highest concentrations were found at commercial harbour sampling sites (Haynes and Loong 1999). Butyltin (a metabolite of TBT) was only detectable in 4 of the 42 samples taken from commercial harbours and marinas, suggesting that it could potentially still be in use illegally on small recreational vessels (Haynes and Loong 1999). A survey of anti-fouling biocides (tributyltin (TBT), copper, zinc, diuron, Irgarol 1051, dithiocarbamates (including thiram and zineb), chlorothalonil and dichlofluanid) was conducted in Perth in 2006. Significant contamination by

unregistered biocides including Irgarol and TBT was detected at a number of sites; however gross contamination was largely attributed to historic contamination (Reitsema 2008).

Ship groundings are a major source of TBT to the marine environment as the hull of the ship is dragged along the reef at the time of impact, and also when attempts to re-float the vessel are made. Paint chips settle onto the surrounding sediments and benthic environment, where they can be re-suspended and dispersed from the source. A total of 27 ship groundings and 14 collisions were recorded within the GBRWHA from 1985-2000 (AMSA 2001). Evidence from three recent groundings clearly demonstrates the link between groundings and anti-foulant contamination in the GBR.

Grossly elevated concentrations of butyltin were associated with the prior grounding of a 22,000 t cargo ship at Heath Reef in the far northern GBR (Haynes and Loong 2002). In November 2000 the cargo ship *Bunga Teratai Satu* ran aground on Sudbury Reef (Fig. 4a) in the GBRWHA for 14 days (Haynes et al. 2002). Both hard, soft corals (Fig. 4b) and gorgonians around the grounding site showed symptoms expected from contact with anti-foulants, and were badly damaged or killed within 10 m of the grounding (Marshall et al. 2002). Partial mortality was observed in some corals as far as 250 m away (Marshall et al. 2002). Both the concentrations of TBT measured at the Sudbury Reef grounding and butyltin detected at the Heath Reef grounding sites were elevated above ANZECC (2000) guidelines (72 ng Sn g^{-1}) (Haynes et al. 2002).

Recently, in 2010, the *Shen Neng 1* coal carrier ran aground off the Douglas Shoal in the Southern GBR. An estimated $115,000 \text{ m}^2$ of the shoal was damaged or completely destroyed and TBT toxicity was severe, although highly patchy (GBRMPA 2011). Sediments sampled on the third site visit contained concentrations of TBT as high $545,000 \mu\text{g Sn kg}^{-1}$ dry weight (or 0.5 g Sn kg^{-1}). This value is approximately 100,000 times the low trigger level for the ANZECC 2000 guidelines, and 7,700 times the high guideline (GBRMPA 2011). A detailed impact assessment report was completed by GBRMPA (GBRMPA 2011).



Figure 4. a) Aerial image of the grounded *Bunga Teratai Satu* on Sudbury Reef and, b) soft coral showing signs of damage consistent with anti-foulant exposure. Source: Marshall et al. (2002).

Since the ban of TBT most paint manufacturers have switched to alternative biocides such as Irgarol, atrazine and copper-based paints, which are rendered more potent by the use of so-called 'booster biocides' (Reitsema 2008). Irgarol 1051 was measured in sediment samples taken during the Perth surveys (range = $0.006\text{-}1.34 \text{ mg kg}^{-1}$), which is concerning since it is not currently registered for use in antifouling paints in Australia, and has been banned in several other countries. Levels of Irgarol measured in the Florida Keys, Bermuda and St. Croix have been shown to range between $3\text{-}294 \text{ ng l}^{-1}$ (Owen et al. 2002). Reductions in net photosynthesis of the coral *Madracis mirabilis* was found at Irgarol concentrations of 100 ng l^{-1} with little or no photosynthesis at concentrations exceeding 1000 ng l^{-1} after 2-8 h exposure at all irradiances (Owen et al. 2002). Irgarol has also been detected in the North-eastern Caribbean (Puerto Rico, and the US Virgin Islands). Concentrations were generally below 100 ng l^{-1} , however higher concentrations were found at 3 sites within Benner Bay in U.S. Virgin Islands of $223\text{-}1300 \text{ ng l}^{-1}$ (Carbery et al. 2006). Irgarol has been shown to be acutely toxic to sea greases and mangroves and corals (Carbery et al. 2006). Diuron was also sampled for the first time in waters, biota and sediments of Perth coastal waters

(Reitsema 2008). Since diuron is currently used in almost half of the 49 antifouling products registered in Australia, it is not surprising to find significant concentrations of this herbicide (Reitsema 2008).

Considering that TBT and its replacement chemicals such as Irgarol continue to contaminate areas highly influenced by marine vessels, it is essential that port and harbour areas are monitored regularly to ensure that guideline levels are not surpassed. As port expansion projects proceed and vessel traffic is expected to increase throughout the GBR, it is important that strict guidelines regarding these toxic chemicals are set and enforced to ensure the safety of non-target organisms.

2.6 Coal Dust

Coal enters the environment via a variety of mechanisms such as the natural erosion of coal seams, and anthropogenic inputs during various stages of coal processing such as disposal of colliery waste, wind and water erosion of coal stockpiles, and accidental spillage (Ahrens and Morrissey 2005). Once coal particles enter the marine environment, larger particles tend to sink close to the input source, while smaller particles that are positively and neutrally buoyant are dispersed via currents throughout coastal ecosystems (Fig. 5) (Johnson and Bustin 2006). The dispersal of coal particles is dependent on a variety of factors such as the settling behaviour of the coal particle (related to the size and density of the coal particle) and hydrodynamic drivers such as currents. The SLIM oceanographic model was used to determine whether fine neutrally buoyant coal particles released from coastal waters off Abbot Point are able to reach the coral reefs offshore Mackay (Andutta and Wolanski 2012). The model showed that under the influence of real wind conditions, tides and the East Australian current, a coal plume emanating from Abbot Point would reach the reefs offshore Mackay within three months (Andutta and Wolanski 2012).

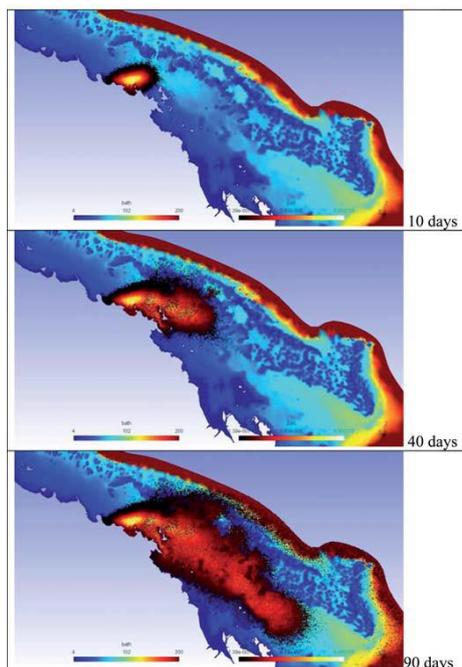


Figure 5. Predicted plumes of suspended fine coal particles emanating from Abbot Point at 10, 40 and 90 days after release in the tradewind season. Source: Andutta and Wolanski 2012.

The GBR and adjacent lagoon waters are high energy tidally driven mixing zones. Eight meter tides at Mackay in the central zone and a normal trade wind of 15 to 25 knots continually resuspends sediments and redistributes land-derived organics that make their way to the GBR lagoon from industrial loading facilities, coastal rivers and wetlands. The process of out-flushing land-derived materials to the reefs has been a primary management concern for the entire GBR ecosystem. This process of sediment re-suspension and transport offshore was described in estuarine eco-hydrology models (Wolanski 2007).

Burns and Brinkman (2011) used a series of organic biomarkers which detailed the cyclical processes of sediment re-suspension, recolonising with marine algae and bacteria, packaging into zooplankton faecal

pellets and resettlement to sediments where the organics undergo further diagenesis. With each cycle the inshore sediments are diluted with CaCO₃ reef sediments and moved further offshore with the strong ebb tide currents. This results in transport of land derived materials offshore and little storage of organic materials in the lagoon or reef sediments. These processes were detailed with measurements such as %CaCO₃ and Al/Ca ratios, and by the compositions of hydrocarbon, sterol, alcohol, and fatty acid lipid fractions. Persistent contaminants such as Polynuclear Aromatic Hydrocarbons (PAH) sourced from coal dust from a coastal loading facility were detected in high concentration inshore and decreased out to the shelf break at 180 m depth approximately 120 km offshore. The normal processes would likely be amplified during cyclonic and other storms.

Physical modelling of the movement of suspended particulates offshore from the Queensland coal ports showed transport of coal dust from the Abbot and Hay Point terminals would reach the outer reefs of the southern GBR (Andutta and Wolanski 2011). This was confirmed by the lipid biomarker study which detected the PAH sourced from the coal all the way to the shelf break (Burns and Brinkman 2011). Coal has been shown to be highly absorbent to aromatic hydrocarbons (Cornelissen et al. 2004, 2005). Thus this relatively new geopolymer in the GBR ecosystem provides a mechanism for absorption of lipid soluble organic contaminants during re-suspension in the coastal zone followed by transport to offshore reefs and sediments. Coal dust has been shed into the coastal waters in increasing amounts over recent years with the construction of the coal export terminals. Due to plans to dramatically increase the volume of coal exports over the next few years, it is reasonable to assume that the volume of coal dust and its organic loading that reaches the outer reef will also increase without additional management measures. To keep this from happening, the coal ports must put in place measures to reduce the coal dust input to the GBR.

2.7 Petroleum Hydrocarbon Contaminants

Petroleum hydrocarbons enter the GBR ecosystem from many locations, including both point source and diffuse source inputs. These include ports, marinas, dredge spoil dumps, sewage discharge, street runoff to rivers and creeks, motors on boats, as well as the more visible oil spills from ship groundings. Petroleum hydrocarbons released into the water column are rapidly bio-accumulated (Burns and Smith, 1981). The impact of diffuse sources from municipal waste and street runoff is also significant (Eganhouse and Kaplan 1982; Prahl et al. 1984). The impact of petroleum oil on the marine environment is well researched.

Teal and Howarth (1984) reviewed the ecological effects of oil spills and concluded that: oil regularly reaches sediments after a spill; oil in anoxic sediments is persistent; zooplankton is often contaminated by oil; fish are also contaminated but to a lesser extent; and oil contamination reduces the abundance and diversity of benthic communities. Surface and sediment-dwelling animals can also be impacted by physical smothering or by the ambient toxicity (Forde, 2002, MacFarlane and Burchett, 2003 and Reid and MacFarlane, 2003). Boehm et al (2007) summarized a series of lab and field studies after the Exxon Valdez spill. Concentrations of PAHs (Polynuclear Aromatic Hydrocarbons) in the upper water column at scattered locations in the spill zone were elevated in the first few weeks after the spill to levels that were potentially high enough to cause harm to some individual marine organisms; however, only nine of the 1288 water samples taken along the spill path in Prince William Sound in 1989 contained more than 10 ppb TPAH (Total Petroleum Aromatic Hydrocarbons), which is the State of Alaska's water-quality standard for total aromatic hydrocarbons. TPAH concentrations in shallow water adjacent to oiled shorelines were elevated after the spill, however, average concentrations in the water column decreased to 0.5 ppb by the time herring spawned along the shore (several weeks after the spill), and when herring larvae and juvenile pink salmon were abundant in coastal waters (2 to 3 months after the spill). A concentration of 0.5 ppb is lower than concentrations known to cause harm to sensitive early life stages of these species. Water column concentrations of TPAH resulting from the spill returned to background levels by 1990, ranging from 0.001 to 0.1 ppb TPAH. Schmidt (2012) compared the environmental impact studies of the Exxon Valdez and the Deep Horizon oil spill in the Gulf of Mexico. Thus, there is now a baseline for estimating ecological effects on the GBR ecosystem as a starting point for water quality management.

The disastrous impacts of oil spills on Queensland's coastal mangrove ecosystems have been well documented (Burns et al. 2000; Duke et al. 2000), however if mangroves are not killed, ecosystem recovery can take a few years to a decade (Burns and Codi 1999). Toxicity of sediments can be estimated based on their content of polynuclear aromatic hydrocarbons (PAH). PAHs are widely accepted as toxic components of hydrocarbons (Neff and Anderson 1981). Interim Sediment Quality Guidelines (I-SQGs) are available for PAHs in Australia and New Zealand (ANZECC/ARMCANZ 2000 and Simpson et al. 2005), based on guidelines developed in the US (Long et al. 1995, Mc Donald et al. 1996, Buchman 2008). In June 2006 25 tonnes of heavy fuel oil spilled into the Port of Gladstone, of which, 18 tonnes of oil was recovered (Melville et al. 2009). One month after the spill the highest sediment PAH concentrations were measured at the impacted site, some of which exceeded (SQG) ANZECC/AMCANZ guidelines; however concentrations significantly decreased within 6 months of the spill. Burns and Brinkman (2011) showed that contaminants such as petroleum are degraded as the particles move offshore in the GBR ecosystem. This is in sharp contrast to the persistent organic contaminants that have much slower degradation rates and will accumulate. The toxic impact of petroleum is real time when oil is spilled. Impacts can persist if the petroleum is incorporated into anoxic sediments and tidal flushing is minimal, or if the input is a continuous diffuse source (Burns and Codi 1999; Burns et al. 1994). The International convention on Oil Pollution Preparedness Response and Cooperation (OPRC 90), which has been ratified by Australia, bestows responsibility for ensuring the highest possible level of protection is afforded.

2.8 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) do not naturally occur in the environment. PCBs were produced commercially in large quantities until the late 1970s and are known thermodynamically stable by-products generated during combustion processes. The range and utility of the physic-chemical properties of PCBs, such as inflammability and electric conductivity, led to their wide spread industrial application as conducting fluids within electrical and heat transfer processes; as flame retardants, pesticide extenders and plasticizers; and within lubricants, sealants and paints. PCBs however are extremely lipophilic, persistent and of concern to human and environmental health as they bioaccumulate and biomagnify within the food chain. Some PCB congeners have been found to cause hormone imbalance (Abdelouahab, Mergler et al. 2008) and/or have been linked to cancer risk and immunosuppression (Kuusisto, Lindroos et al. 2007) in humans. Studies into the toxicity of PCB congeners have demonstrated that they cause weight loss, reproductive impairment, thymus atrophy, immune disorders, teratogenesis and neurotoxic and developmental effects during cases of poisoning (Umeda 1972; Wyman and O'Connors Jr 1980; Lundy, Wurster et al. 1984; Safe 1990; Borrell, Aguilar et al. 1996; Foekema, Deerenberg et al. 2008).

The persistence and toxicity of PCBs led to their being classified among the 12 initial harmful persistent organic pollutants (POPs) classified under the Stockholm convention (Bilcke 2002). While the importation of PCBs into Australia has been banned since 1975, they remain a common contaminant in the environment due to their stable nature and limited mobility. Further, it is anticipated that PCBs will continue to be produced as combustion by-products and exposure will continue via secondary sources, such as sediments and top soils already contaminated with PCBs, land fill and the breakdown of waste products containing PCBs (e.g. transformers, capacitors, fluorescent light ballasts and miscellaneous electrical components), or released during the recycling of materials and building demolitions. Further, the dredging of industrial harbours/ports may also lead to the re-mobilization of PCBs within the environment. Within the marine environment PCBs have been detected in tissue and/or blood samples taken from bivalves, crustaceans, fish, fish eating seabirds and turtles from around the world (for example: Borlakoglu, Wilkins et al. 1990; Porte and Albaiges 1994; Nhan, Carvalho et al. 2001). Within the GBR, PCBs have been detected in tissue samples collected from marine organisms including dugong (Haynes, Müller et al. 1999), mud crabs (Negri, Mortimer et al. 2009) and green turtles (Gaus, Grant et al. 2012).

2.9 Brominated Flame Retardants

Brominated flame retardants are used to reduce the flammability of common daily-use items such as clothes, electronics and furniture. There are approximately 80 different types of brominated flame

retardants used commercially, and polybrominated diphenyl ethers (PBDEs) are the most widely used (Australian Government 2013d). PBDEs are among the most abundant brominated flame retardants detected in the environment due to their high production value, persistence in the environment and environmental stability (Sørmo et al. 2009). It is believed that flame retardants are released into the air during the manufacturing of an article, during an article's life span, in small amounts leached from landfills, and emissions (from incineration of waste) (Australian Government 2013d). The dominant transport routes for these chemicals are thought to be long-range transport by the atmosphere, ocean currents, sea-ice drift and river inputs (Herzke et al. 2003). The structural, chemical, physical and toxicological characteristics of flame retardants, in particular PBDEs, are similar to the better-known persistent organic pollutants (POPs), such as polychlorinated dibenzofurans (PCDFs) and PCBs (discussed in Section 3.8) (Sørmo et al. 2006; Hermanussen et al. 2008). These similarities suggest that PBDEs may have a similar ecotoxicological impact to PCBs (Sørmo et al. 2006). In 2001 global estimates of the annual production of PBDEs exceeded 65,000 t (BSEF 2004).

Flame retardants are a global contaminant and are being detected in many terrestrial and marine organisms. In the northern hemisphere most flame retardants are biomagnified as a function of trophic level in the marine food chain, with the exception of the polar bear, suggesting that polar bears may be able to metabolize and biodegrade most flame retardants (Sørmo et al. 2006).

A significant body of evidence is developing which suggests that flame retardants bioaccumulate in exposed seabirds. An almost 40-year monitoring program showed steadily increasing concentrations of PBDE in endangered Canadian ivory gull eggs (Braune et al. 2007). These increases in concentration were consistent with patterns of significant increase that have been observed over the last two decades in North America (Hale et al. 2003; Law et al. 2003; Braune et al. 2007). For example, dramatic increases in PBDE concentrations have also been documented in northern fulmars and thick-billed murrelets (Braune et al. 2005), ringed seals (Ikonomou et al. 2002) and beluga whales from the Canadian arctic (Stern and Ikonomou 2000) and from the St. Lawrence Estuary (Lebeuf et al., 2004), killer whales from western Canada (Ross, 2005), double crested cormorants and great blue herons from the Canadian Pacific coast (Elliott et al., 2005), herring gulls from the Great Lakes (Norstrom et al. 2002), as well as peregrine falcons from South Greenland (Vorkamp et al. 2005). These studies mainly focused on temporal and spatial trends rather than toxicological endpoints.

Fewer studies have been conducted on environmental levels of flame retardants in the southern hemisphere. Levels of PBDEs were detected in all marine turtles, dugongs and commercial seafood species sampled from Queensland (Hermanussen et al. 2008; EPA Vic 2007) (Table 3). These levels are relatively low in comparison to marine biota from the northern hemisphere, likely due to a lower level of PBDE input into the marine system (Hermanussen et al. 2008). Elevated levels of PBDEs have been detected in sediments adjacent to highly urbanised and industrialised areas, and sewage treatment plants in Australia (Toms et al. 2006, 2008). Nine samples were collected from Queensland that included four sites from the Brisbane River, one from Moreton Bay, and four from the vicinity of sewage treatment plant outfalls (Toms et al. 2006). The Brisbane River (City and Indooroopilly) samples contained the highest PBDE concentrations from the Queensland sites, with only low concentrations detected in the Upper Brisbane River and Lower Brisbane River samples. When comparing all states, the highest levels were detected at industrial and urban sources in Victoria and New South Wales (Toms et al. 2008).

Table 3. PBDE levels (expressed in lipid weight) measured in marine biota from Queensland, Australia (Hermanussen et al. 2008¹ and EPA Victoria 2007²).

| Biota Type | Sample size (n) | Mean (ng g ⁻¹) | Range (ng g ⁻¹) |
|---|-----------------|----------------------------|-----------------------------|
| Megafauna ¹ | 8 | 19 | 0.33-130 |
| Crustaceans ¹ | 3 | 39 | 10-64 |
| Fish ¹ | 7 | 22 | 6-43 |
| Seafood (estuarine fish species) ² | 10 | NA | 56-250 |

Flame retardants are being found in many organisms around the world, yet information on exposure-effect relationships is still lacking. Due to their potential to impact environmental and human health, PBDEs have attracted increased international attention (Australian Government 2013e). As such, certain PBDE compounds have been nominated for potential inclusion under the Stockholm Convention on Persistent Organic Pollutants, to which Australia is a party (Australian Government 2013e). Further research is required to underpin the development of appropriate and effective management strategies for this class of contaminants.

2.10 Non-PSII Pesticides

The assessment of pesticides within the GBRCA has in recent years focused on the photosystem II (PSII) herbicides that have a demonstrated ecological risk (e.g. individual herbicides: Lewis et al. 2009a; additive PSII herbicides: Davis et al. in press; Lewis et al. 2012; Kennedy et al. 2012a, 2012b; Smith et al. 2012). Amongst these studies there have also been reports of the detection of non-PSII herbicides, insecticides and anti-microbial agents. Non-PSII pesticides that have been identified as a concern include metolachlor and imidacloprid.

Metolachlor is a plant growth inhibitor and has been detected at concentrations exceeding the low reliability guideline for fresh and marine waters ($0.02 \mu\text{g l}^{-1}$) in freshwater samples collected within the Burdekin ($0.01\text{-}0.06 \mu\text{g l}^{-1}$), Fitzroy ($1.4 \mu\text{g l}^{-1}$), Burnett-Mary Regions ($0.04 \mu\text{g l}^{-1}$) and Mackay Whitsunday Region ($0.8\text{-}0.44 \mu\text{g l}^{-1}$), along the eastern Queensland coast. Metolachlor has been detected at concentrations of up to $0.02 \mu\text{g l}^{-1}$ in flood plumes discharging from the Fitzroy River.

Imidacloprid is a neonicotinoid insecticide that is currently causing much controversy in Europe and the USA as there is ever increasing evidence demonstrating the detrimental effects of this chemical on the health of bees and the efficiency of pollinators in areas where imidacloprid has been applied. Imidacloprid has been detected at concentrations of up to $0.17 \mu\text{g l}^{-1}$ in samples collected from Tropical Queensland rivers including North Johnstone and Tully Rivers within the Wet Tropics, the Pioneer River and Sandy Creek within the Mackay Whitsunday Region; and has been detected in flood plumes discharging from the Tully River ($0.05 \mu\text{g l}^{-1}$), and the Fitzroy River (up to $0.14 \mu\text{g l}^{-1}$). While Australia does not currently have a guideline value for Imidacloprid, the values measured at the end of river systems approach Canadian guideline values ($0.23 \mu\text{g l}^{-1}$) for freshwater ecological protection. This freshwater value and a Canadian marine value ($0.65 \mu\text{g l}^{-1}$) are currently the only known ecological values and can be used as an indication of risk before relevant local guidelines are set.

The assessment of the risk of non-PSII pesticides such as Imidacloprid and metolachlor is hampered by a lack of relevant toxicity data where either low reliability guidelines or guidelines from other countries are relied upon to provide limited insights on the possible impacts of these pesticides. The changing management practices of the agricultural sector is also resulting in the use of new/alternative products (e.g. imazapic, trifloxysulfuron sodium, isoxaflutole, metribuzin, glufosinate-ammonium, pendimethalin), which are only beginning to be monitored for in rivers and flood plumes of the GBR. Assessing the risk of these new/alternative products will also pose a challenge as there is limited environmentally relevant toxicity data available

3.0 CONCLUSIONS

This report outlines and reviews non-Reef Plan pollutants that currently pose risks to the marine environment and the organisms that live and feed within it. The ten pollutants discussed are of particular concern due to knowledge gaps that disallow the competent evaluation of the true threat they currently pose to marine biota. For example, sewage-sourced contaminants and flame retardants are emerging contaminants. Levels of these pollutants are increasing in the marine environment worldwide, yet increased information on exposure-effect relationships is required in order to establish accurate guideline values. Information regarding the biological effects of coal dust to marine organisms is also lacking in

tropical environments. Since coal exports from Queensland are expected to increase, it is likely that the amount of coal entering the marine environment will also increase. In order to facilitate the sustainable export of coal, increased research into the distribution and effects of coal dust in the marine environment is required. Additionally, increased management efforts can be made to reduce the accidental loss of coal dust and spillage of larger coal particles during ship-loading processes.

We are aware of the potential toxicity or threats that some of these ten pollutants pose to marine biota; however we are missing information on the occurrence and extent of contamination. Marine debris is a widespread global pollutant that impacts a range of species each year. Since it is difficult to accurately quantify marine wildlife that is impacted by marine debris, it is not well understood how significant the threat really is. However, it is certain that many injuries and mortalities are not being observed and that the impact of marine debris is underestimated. Monitoring programs in Queensland and other parts of Australia are working towards reducing the amount of marine debris, especially ghost nets. Since this is mainly a land-based pollutant, increased public awareness could also be an essential tool to involve the public in taking measures to reduce marine debris. The potential of microplastics to transfer pollutants and leached additives upon ingestion are relatively well understood, however the global extent of this pollutant is unknown. The amount of microplastics entering the marine environment could be substantially reduced if filters for washing machines and sewage treatment plants are re-designed to entrap these potentially microscopic pollutants. Additionally, restrictions can be placed on the use of microbeads in body-wash products, and natural products can be used instead. Further information is required for both marine debris and microplastics on sources, hot spots for accumulation and the extent so that appropriate management mitigation efforts can be developed.

There has been a substantial amount of research conducted on the effects of trace metals to the marine environment and it is well understood that metals have the potential to pose serious toxic threats to many biological processes in organisms. However, data from the GBR is dated and current levels of trace metals are lacking. This is of particular concern since industrial expansion is projected to increase along the Queensland coast and because many metals are known to persist in the environment and biomagnify. Industrial waste discharge, and port and harbour activities are major sources of trace metals to the GBR. In the marine environment metal accumulation is variable amongst species and accumulation rates are dependent on factors such as metal speciation (the form that the metal occurs in), availability of the pollutant, biological, chemical and environmental factors such as temperature, salinity, dissolved oxygen, light and pH. Thus, more frequent monitoring of trace metal levels during more than one season is required.

Anti-foulants and PCBs are known to be highly toxic, and although PCBs and TBT have been fully or partially banned, respectively, they are still being detected in the marine environment. Considering that TBT and its replacement chemicals such as Irgarol continue to contaminate areas highly influenced by marine vessels, it is essential that port and harbour areas are monitored regularly to ensure that guideline levels are not surpassed. As port expansion projects proceed and vessel traffic is expected to increase throughout the GBR, it is important that strict guidelines regarding these toxic chemicals are set and enforced to ensure the safety of non-target organisms. As shipping vessel traffic increases petroleum hydrocarbons are also likely to become a greater risk to the marine environment. Due to the magnitude of the Queensland coastline, it can be difficult to have emergency oil spill response teams arrive at the scene of an accident quickly. The threat of oil spills could be managed by creating and enforcing regulations that require all ships to have a reef pilot on board while navigating through the Great Barrier Reef.

The level of pollutants entering the ocean can be managed and Australia has made enormous progress over recent years at addressing the issue of agricultural waste runoff into the GBRCA; however increased research, monitoring, and management efforts are required to decrease the large knowledge gaps on the occurrence, extent and toxic effects of many non-Reef Plan pollutants. Obtainment of this information will help to assess the risks of non-Reef Plan pollutants to marine biota and facilitate future management efforts.

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Abstract Nonessential metals (e.g., aluminium, calcium, mercury, and lead) have no demonstrated biological function, and toxicity rises with increasing concentration. Essential metals (e.g., copper, zinc, and iron) have a biological role, and toxicity occurs with both deficiencies and high concentrations. The dissolved ionic form of metals is believed to be most bioavailable form, resulting in toxicity. Considerable toxicity to fish can also occur with the organic forms of several metals including tin and mercury. Multiple physiological systems are affected by metals (commonly the gills) and depend on metal form and speciation, bioavailability, toxicokinetics (absorption, distribution, biotransformation, and excretion), and toxicodynamics (interactions with ligands).

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