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Tropical Water Quality Hub

National Environmental Science Programme

Final Report

Identification, impacts, and prioritisation of emerging contaminants present in the GBR and Torres Strait marine environments

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Australian Government

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Identification, impacts, and prioritisation of emerging contaminants present in the GBR and Torres Strait marine environments

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Cover photographs: Beach with marine debris near Yeppoon (Angelika Volz, Tangaroa Blue Foundation); Damselfish (*Pomacentrus amboinensis*) and lizardfish (*Synodus* spp.) inhabiting tyre near Milne Reef, east of Cairns (Frederieke Kroon).

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ACRONYMS

Ag	Silver
AIMS	Australian Institute of Marine Science
AL	Aluminium
AMPTO	Association of Marine Park Tourism Operators
AMDD	Australian Marine Debris Database
AMSA	Australian Maritime Safety Authority
ANZECC	Australian and New Zealand Environment and Conservation Council
APVMA	Australian Pesticides and Veterinary Medicines Authority
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
As	Arsenic
ASS	Acid Sulfate Soils
BPA	Bisphenol A
Cd	Cadmium
CeO_2	Cerium Oxide
Cr	Chromium
Co	Cobalt
Cu	Copper
CuPT	Copper Pyrithione
CQU	Central Queensland University
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DEHP	Diethylhexylphthalate
DGT	Diffusive Gradients in Thin films
DNV	Det Norske Veritas
DOE	Department of the Environment
DSITI	Queensland Department of Science, Information Technology and Innovation
EC10	10% Effect Concentration - the concentration in a toxicity test at which it is expected 10% of the test organisms would show an adverse response
ECOSAR	Eco-toxicological Quantitative Structure Activity Relationship
EDC	Endocrine Disrupting Chemical
EIS	Environmental Impact Statement
FBA	Fitzroy Basin Association Inc.
Ga	Gallium
Fe	Iron
GBR	Great Barrier Reef
GBRMP	Great Barrier Reef Marine Park
GBRMPA	Great Barrier Reef Marine Park Authority
GBRWHA	Great Barrier Reef World Heritage Area
GHHP	Gladstone Healthy Harbour Partnership
GU	Griffith University
Hg	Mercury
HQ	Hazard Quotient
HSP	Heat Shock Protein
JCU	James Cook University
LOR	Limits of Reporting
LTSP	Long Term Sustainability Plan

MAH	Monoaromatic Hydrocarbon
MEC	Measured Effect Concentration
Mn	Manganese
Mo	Molybdenum
MR	Metallothionein
NAGD	National Assessment Guidelines for Dredging
NESP	National Environmental Science Programme
Ni	nickel
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NM	Nanomaterial
NRM	Natural Resource Management
NSAID	Non-Steroidal Anti-Inflammatory Drugs
OUV	Outstanding Universal Value
PAH	Polycyclic Aromatics Hydrocarbon
Pb	Lead
PCIMP	Port Curtis Integrated Monitoring Program consortium
PCP	Personal Care Product
PEC	Predicted Effect Concentration
PNEC	Predicted No-Effect Concentration
PNG	Papua New Guinea
PSII	Photosystem II
RRRC	Reef and Rainforest Research Centre Limited
Sb	Antimony
Se	Selenium
Sn	Tin
SOD	Superoxide Dismutase
SQGV	Sediment Quality Guideline Value
TTBF	Tangaroa Blue Foundation
TBT	Tributyltin
TiO_2	Titanium Oxide
TPH	Total Petroleum Hydrocarbons
TS	Torres Strait
TWQ	Tropical Water Quality
UCL	Upper Confidence Limit
UQ	University of Queensland
US EPA	United States of America Environmental Protection Agency
V	Vanadium
WWTP	Waste Water Treatment Plant
Zn	Zinc
ZnO	Zinc Oxide
ZnPT	Zinc Pyrithione

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EXECUTIVE SUMMARY

Current policy and management for marine water quality in the Great Barrier Reef (GBR) focusses on sediment, nutrients and PSII herbicides. While other so-called emerging contaminants are known to be present in the marine environment, little is known about their sources, role and fate in the GBR and Torres Strait (TS) regions. Changes in agricultural practices and land uses, increasing coastal development including urban and industrial land uses and ports, and associated projected increases in shipping traffic are likely to result in new contaminants being released into marine ecosystems in the near future. This project evaluates the risks of these emerging contaminants to GBR and TS marine ecosystems, and compares these risks to those identified for the current pollutants of concern.

First, we determined the presence and locations of emerging contaminants based on monitoring data and the types of human activities present. During a one-day workshop, the project team and key stakeholders agreed to focus on nine emerging contaminants, namely heavy/trace metals and metalloids, alternate pesticides, petroleum hydrocarbons, coal particles, pharmaceuticals, personal care products (PCPs), nanomaterials (NMs), antifouling paints, and marine debris including microplastics. Several large monitoring datasets were examined for heavy/trace metals and metalloids, and for marine debris; additional datasets were identified but not made available by the respective custodians for our study. For most emerging contaminants, however, little to no monitoring data exists for the study region and our assessments relied primarily on information from other Australian or international studies, as well as on information on potential sources.

Second, we prioritized the identified emerging contaminants based on their potential qualitative risk to the marine ecosystems for each of the seven NRM regions in the study region. Our qualitative risk assessment determined that of the nine emerging contaminants, marine plastic pollution poses the highest risk to the marine ecosystems, particularly in the Cape York and TS NRM regions due to exposure to oceanic and local shipping sources. This is followed by chronic contamination of water and sediments with antifouling paints, and exposure to certain PCPs, in NRM regions south of Cape York. The qualitative risks of all other emerging contaminants are relatively low with some minor differences between NRM regions. We also developed water quality guideline values for four alternate pesticides commonly found in GBR waters

Compared to current pollutants of concern (sediment, nutrients and PSII herbicides), the qualitative risk assessments suggest that marine plastic pollution is likely to pose a higher risk to TS and Cape York marine ecosystems. The relative risk of marine plastic pollution, chronic contamination by antifouling paints, and certain PCPs to marine ecosystems south of Cape York is of concern, and requires further research to improve our understanding of their presence, distribution and ecological impacts. To inform management of and policy for the GBR and TS marine environments, we recommend the following key areas of research:

- ensuring availability of valuable existing environmental data in the public domain for building marine baselines on emerging contaminants in the study region;
- conducting local, targeted monitoring campaigns for priority emerging contaminants with little or no recent monitoring data for the GBR and TS regions; and
- examining the ecological impacts of marine plastic pollution, chronic contamination of antifouling paints, and certain PCPs on GBR and TS marine organisms and ecosystems.

Figure 1: Comparison of qualitative risks of emerging contaminants to the Great Barrier Reef and Torres Strait Environments, presented for each of the seven NRM regions. The scale boundaries are <10, 10-<20, 20-<30, 30-<40, 40-<50, and 50-<60.

1.0 INTRODUCTION

Current policy and management for marine water quality in the Great Barrier Reef (GBR) Marine Park (MP) and World Heritage Area (WHA) focusses primarily on sediment, nutrients and pesticides derived from diffuse source pollution[1] from agricultural land uses (1). Specifically, water quality targets have been set for dissolved inorganic nitrogen (DIN), sediment and particulate nutrients, and pesticides (1). The pesticide target considers five priority photosystem II inhibitor herbicides (ametryn, atrazine, diuron, hexazinone, tebuthiuron). However, at least 49 pesticides have been detected in the GBR catchments and lagoon (3). River load contributions of these so-called alternate pesticides can increase the total pesticide load by up to 28%, depending on the pesticide and the catchment under consideration (3). This is of concern as recent research suggests that neonicotinoids, glyphosate and other prevalent alternate pesticides pose potential ecological risks which are poorly understood in the GBR context.

In addition to alternate pesticides, other contaminants are known to be present in the GBR and the Torres Strait (TS). This includes contaminants such as metals, hydrocarbons, coal particles, pharmaceuticals, personal care products, antifouling paints and marine debris (4). While these so-called emerging contaminants[2] are a topic of intensive research internationally, little is known about their potential risk to the GBR and TS marine ecosystems, especially compared to the risk identified for the current pollutants of concern. Increasing coastal development including urban and industrial land uses and ports, and associated projected increases in shipping traffic are expected to increase the sources and diversity of contaminants being released into marine ecosystems in the near future.

In this study, we evaluate the risks of emerging contaminants to GBR and TS marine ecosystems. The specific objectives of our study are:

1. Determine the presence and locations of emerging contaminants based on monitoring data and the types of human activities present, and
2. Prioritize the identified emerging contaminants based on their potential risk to the marine environment within the context of current contaminants (sediment, nutrients, PSII herbicides).

In addition, we developed quality-assured species sensitivity distributions and water quality guideline values for four alternate pesticides commonly found in GBR waters.

Based on the list of priority emerging contaminants, we developed and recommend key areas of research to inform management and policy decisions that will maintain and improve the condition of the marine environments in the GBR and Torres Strait regions.

---

[1] In this project, we follow the GESAMP definitions of pollution and contamination :

Pollution The introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to maritime activities including fishing, impairment of quality for use of sea water and reduction of amenities.

Contamination An anthropogenic increase in the concentration of a substance in the marine environment, without inference about the existence of any adverse effects.

[2] 'Emerging contaminant' is defined as any contaminant that is not one of the current pollutants of concern to the Reef Water Quality Protection Plan.

2.0 METHODS

2.1 Workshop

At the start of the project, a 1-day workshop with the project team, end users and key stakeholders (**Table 2-1**) was held in Townsville to (i) examine the risk of emerging contaminants to the GBR and Torres Strait marine environments, and (ii) agree on the specific project outputs.

Table 2-1: Organisations and representatives invited to, and attended the 1-day project workshop held in Townsville, 3rd September 2016.

Organisation	Name	Invited	Response	Attended
AIMS	F Kroon (Project Leader)	n/a	n/a	Y
	J Tsang	Y	Y	Y
	A Negri	Y	Y	Y
CSIRO	M Williams	Y	Y	Y
	R Kookana	Y	Y	N (represented by M Williams)
James Cook University	D O'Brien	Y	Y	Y
	S Lewis	Y	Y	Y
	A Davis	Y	Y	Y
University of Qld	J Mueller	Y	Y	Y
Griffith University	J vd Merwe	Y	Y	Y
	F Leusch	Y	Y	N (represented by J vd Merwe)
	P Neal	Y	Y	N (represented by J vd Merwe)
Central Qld University	S Melvin	Y	Y	N (represented by J vd Merwe)
Qld Dept of SITI	R Smith	Y	Y	Y
	M Warne	Y	Y	N (represented by R Smith)
GBRMPA	C Honchin	Y	Y	Y
	K Martin	Y	Y	Y
Burdekin Dry Tropics	S Crawford	Y	Y	Y (representing all 6 GBR NRM groups)
AMPTO	C McKenzie	Y	Y	N (represented by S Moon)
	S Moon	Y	Y	Y
Indigenous representation	M George	Y	N	N
Department of the Environment	K Gale	Y	Y	N
	A McGrath	Y	Y	N

The outcomes of the workshop were:

1. Objective: To examine the risk of emerging contaminants to the GBR and Torres Strait marine environments.
    - Outcome: The project team and stakeholders agreed to assess the risk of nine emerging contaminants (**Table 2-2**), based on expert knowledge from the project team and international studies. Team Leads, and a subset of project team members with relevant expertise, were assigned to each emerging contaminants. Additional potential emerging contaminants were identified and discussed during the workshop, including (i) radio-active material; (ii) unexploded ordnance, explosive ordnance waste, and a wide range of dumped war materials; (iii) thermal pollution; and (iv) perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) contained in firefighting foam. An initial scan revealed available and/or accessible information appeared to be even less than for the other nine emerging contaminants, precluding the project team from

including these four additional categories of emerging contaminants in the risk assessment.

- Outcome: The project team and stakeholders agreed to assess the qualitative risk of these nine emerging contaminants using an established risk assessment framework considering '*Likelihood*' and '*Consequence*' (5), as well as '*Area*' to include the number of water bodies the risk may occur (**Table 14-2**).

- Outcome: The project team and stakeholders agreed to assess the qualitative risk of these nine emerging contaminants for each of the six GBR NRM regions and the TS Regional Authority (hereafter referred to as 'the seven NRM'), given that on-ground natural resource management occurs primarily at this scale.

2. Objective: To determine the specific project outputs.

    - Outcome: The initial mechanism to communicate the project findings is a synthesis report (this report), including recommendations of key areas for future high priority research. The project team and stakeholders agreed that findings will also be published in a journal paper, and presented to the stakeholders and additional target audiences in seminars or group discussions.

Table 2-2: Emerging contaminants, and team lead, agreed by the project team and stakeholders to be considered as part of the project.

Emerging contaminants		Team lead	Chapter
1	Heavy and trace metals, metalloids	J Tsang (AIMS)	**Error! Reference source not found.**
2	Alternate pesticides	D O'Brien (JCU)	4.0
3	Petroleum hydrocarbons	A Negri (AIMS)	5.0
4	Coal particles	A Negri (AIMS)	6.0
5	Pharmaceuticals	S Melvin (CQU)	7.0
6	Personal care products	M Williams (CSIRO)	8.0
7	Nanomaterials	M Williams (CSIRO)	9.0
8	Antifouling paints	F Kroon (AIMS)	10.0
9	Marine debris, including microplastics	F Kroon (AIMS)	11.0

2.2 Qualitative risk assessment

To ensure that the qualitative risk assessments for the nine emerging contaminants were conducted in a consistent manner across the project team, a chapter template was developed to guide the Team lead in collating the relevant information from the (international) scientific and grey literature. Following a brief Introduction to the emerging contaminant of concern ('*Introduction*'), the template consisted of four main sections namely:

1. '*Main classes of emerging contaminant*' – A description of the main classes of each of the emerging contaminant category;
2. '*Presence, concentration and location in the GBR and TS marine ecosystems*' – a compilation of available monitoring data to identify the presence, concentration and location of emerging contaminants in the GBR and Torres Strait marine ecosystem;

3. ‘*Likely presence in the GBR and TS marine ecosystems*’ – an assessment of the likely presence of emerging contaminants in the GBR and Torres Strait marine ecosystems based on the types of human activities present (i.e. potential sources); and
4. ‘*Risk to the GBR and TS marine ecosystems*’ – an assessment of the qualitative risk of the emerging contaminant to the GBR and TS marine ecosystems.

The qualitative risk was assessed using an established risk assessment framework considering ‘*Likelihood*’ and ‘*Consequence*’ (5) (**Table 14-2**). ‘*Likelihood*’ gives an indication of the expected frequency of a given threat, ranging on a scale from 1 (‘*not expected to occur within the next 100 years*’) to 5 (‘*expected to occur more or less continuously throughout a year*’). ‘*Consequence*’ gives an indication of the impact to the ecosystem at local and broad scale, as well as to the heritage value, based on current management, ranging on a scale from 1 (‘*insignificant*’) to 5 (‘*catastropic*’).

Preliminary risk assessments conducted during the workshop revealed that only using ‘*Likelihood*’ and ‘*Consequence*’ would not separate out the nine emerging contaminants for prioritisation. Hence, it was agreed to include an additional assessment category, namely “*Area*’ to include the number of water bodies the risk may occur, and allow better separation for prioritisation purposes. ‘*Area*’ ranges from 1 (‘*any one water body*) to 4 (‘*all four water bodies’*).

The qualitative risk assessments were conducted by the Team lead and associated project team members for each emerging contaminant (Table 2-2). The risk assessment scores for ‘*Likelihood*’, ‘*Consequence*’, and ‘*Area*’ for all nine emerging contaminants were subsequently compared by the Project Leader, and adjusted in case of inconsistencies. For example, emerging contaminants discharged from Waste Water Treatment Plants (WWTPs) (e.g. pharmaceuticals, personal care products, nanomaterials) can be expected to have similar categories for ‘*Area*’. Similarly, the ‘*Likelihood*’ of emerging contaminants released during ship collision and/or grounding (e.g. petroleum hydrocarbons, coal particles, antifouling paints) would be similar. The final risk assessment scores for ‘*Likelihood*’, ‘*Consequence*’, and ‘*Area*’ for each emerging contaminant are presented in the Appendix (Table 14.6), while the total risk assessment scores (‘*Likelihood*’ x ‘*Consequence*’ x ‘*Area*’) are presented in their respective chapters.

The final qualitative risk assessment scores for each of the nine emerging contaminants were compared for each of the seven NRM regions separately, and used to develop a list of priority emerging contaminants based on the risk to the GBR and Torres Strait marine ecosystems.

Finally, the relative risks of the nine emerging contaminants were compared with that of current contaminants of concern to the Reef Plan and the Reef 2050 LTSP (sediment, nutrients, pesticides) (1, 2, 5). To this effect, the rankings for ‘*Likelihood*’ and ‘*Consequences*’ for the five central and southern NRM regions were obtained from the GBR 2014 Outlook report (5). Two leading scientists, namely Drs B Schaffelke and K Fabricius from AIMS, provided ranking scores for (i) ‘*Likelihood*’ and ‘*Consequences*’ for the two northern NRM regions (Cape York and TS), and (ii) ‘*Area*’ for all seven NRM regions. Both scientists are professionally qualified to make the assessments, conducted the risk assessments independently of each other, and were not part of the project team. In cases where their rankings did not agree, we used the most conservative score (i.e. the highest ranking).

2.3 Development of water quality guidelines for four alternate pesticides

To support the development of pesticide water quality guidelines for tropical aquatic ecosystems, the project developed quality-assured species sensitivity distributions and water quality guideline values for four alternate pesticides commonly found in GBR waters. The four pesticides (2,4-D, Metribuzin, Imazapic, Isoxaflutole) were determined by DSITI based on discussions between the project team, end users and key stakeholders, using the revised process to derive Australian and New Zealand guidelines for toxicants in fresh and marine waters (6).

3.0 HEAVY AND TRACE METALS, METALLOIDS

Authors: Jeffrey Tsang, Frederieke Kroon

3.1 Summary

Heavy/trace metals and metalloids are major anthropogenic contaminants in estuarine and coastal waters. Their concentrations in the GBR and TS marine environments are typically low, except in areas within ports and harbours and those adjacent to intense urban, industrial or agricultural activity. It is likely that heavy metal contamination in the GBR and TS will increase with increasing coastal and industrial development in these regions. This presents an ecological concern given the persistent nature of heavy metals and metalloids, known toxicity to marine organisms, and their estimated residence in the GBR lagoon ranging from years to decades. Metals and metalloids at some sites in the GBR and TS have concentrations that exceed water and sediment quality guidelines, indicating potential health risks to marine species. While point sources are often highly regulated to ensure that discharges and emissions of contaminants do not exceed levels of environmental concern, less is known about inputs from diffuse sources. For example, runoff from Papua New Guinean (PNG) catchments affects sediment quality in the northern and north-central TS. Similarly, our preliminary estimate of the dissolved aluminium load from the Calliope catchment near Gladstone suggests that diffuse source contribution could be considerable. This suggests that current management arrangements, which do not consider the risks of metals and metalloids from diffuse sources may need to be re-assessed and associated research recommendations are provided.

3.2 Introduction

Heavy/trace metals and metalloids occur naturally in rocks and soils; these can enter the aquatic environment through weathering, erosion and atmospheric deposition. Human activities can augment the burden of heavy metals (7), and in estuarine and coastal waters they are major anthropogenic contaminants (8). In the marine environment, heavy metals have raised concerns due to their potential adverse effects on various life stages of coral development (9-14), including reduction in photosynthesis of algal symbionts (15). To ensure protection of aquatic organisms, it is paramount that water and sediment quality guidelines for heavy metal contaminants not be exceeded.

A review of past monitoring indicated concentrations of heavy metals in the GBR were generally low, except at sites adjacent to human activity such as ports and harbours, urban centres and intensive agricultural activity (16). This information is now more than 15 years old; contamination by heavy metals and metalloids has likely increased since then given the expansion of coastal development and industries in the GBR region (5). This presents an ecological concern given the persistent nature of heavy metals and metalloids, potential toxicity to marine organisms and their estimated residence time in the GBR lagoon ranging from years to decades (17). As for the GBR's Far Northern Region and the TS, sediment in the northern region is influenced by heavy metals and metalloids entrained in discharges from the Fly River, PNG, associated with mining (18-22). Future projects involving mining, oil and gas, port construction, land clearing, proposed logging and oil palm plantation development have been identified for PNG (23, 24); these could contribute to increasing heavy metal and metalloid loads entering the TS and Far Northern GBR regions.

3.3 Main classes of emerging contaminant

Mining, industry, urban runoff, agricultural and port activities can release heavy/trace metals [e.g. aluminium (Al), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), silver (Ag), tin (Sn), vanadium (V) and zinc (Zn)] and metalloids [e.g. antimony (Sb), arsenic (As) and selenium (Se)] of environmental concern to coastal waters (8, 16). Some of these are termed lithophile / A-type metals (e.g. Al, Sn, Mn, Co, Cr, V and Ni) because their mass transport to oceans by streams / rivers exceeds their transport through the atmosphere (7). Whereas atmophile / B-type metal(loid)s (e.g. Hg, As, Se, Sn and Pb) are those with greater atmospheric mass transport than that in streams / rivers (7). Atmophiles can be methylated and released into the atmosphere as vapours; Hg, and probably As and Se, can also be released as inorganic vapour from burning of coal (7).

The presence of heavy metals and metalloids in the water column usually reflects recent inputs (8). Many will readily attach to suspended particles and ultimately accumulate in sediments. Sediment loads in coastal waters are greater than those in the open ocean; especially in estuaries where increasing salinity causes precipitation of iron hydrous oxides which can scavenge / co-precipitate soluble metals and metalloids (8). Depending on their chemical form (i.e. species), heavy metals and metalloids can also accumulate in biota such as oysters and mussels. Although many of these elements are essential micronutrients, all are potentially toxic to organisms above certain threshold concentrations. The bioavailability and toxicity of metals and metalloids depends on their speciation rather than total concentration. Generally, ionic species are more bioavailable and toxic than those bound to particles and organic compounds. Notable exceptions include organic compounds of mercury and tin, which are more toxic than their inorganic forms (25, 26).

3.4 Presence, concentration and location in the GBR and TS marine ecosystems

Heavy metals and metalloids have been detected in water, sediment and bivalve molluscs in the GBR and TS marine ecosystems (**Table 3-1**). Some of these studies are more than ten years old. Recent monitoring programs with information on metals and metalloids in the GBR were identified through collaboration with NESP TWQ project 3.8 (27); of these only the Port Curtis Integrated Monitoring Program (PCIMP) had made their dataset available for this project (Table 2) (28). For the other programs, monitoring data were sourced from environmental reports and EIS documents for the ports of Abbot Point, Cairns, Hay Point and Townsville (29-32). Water quality or sediment monitoring data were not available for the Burnett Mary NRM region. The risk of the Sn contained in the antifouling component tributyltin (TBT) to the GBR and TS marine environments is assessed in the Chapter on Antifouling paints.

Table 3-1: Available monitoring data for concentrations of heavy metals and metalloids in (a) filtered surface water (µg/l), (b) surface sediment (mg/kg dry weight) and (c) bivalve molluscs (mg/kg wet weight; unless stated otherwise) from the GBR and TS marine ecosystems. Bold text/yellow highlight indicates exceedance of ANZECC/ARMCANZ trigger values and/or relevant guidelines. Orange highlight indicates reporting limit greater than trigger. CY = Cape York; MW = Mackay Whitsunday; BM = Burnett Mary; N/A = not available; ND = not detectable.

(a)

			NRM regions																							
			Torres Strait		**CY**	**Wet Tropics**						**Burdekin**					**MW**	**Fitzroy**						**BM**	**Trigger Value**		
Main classes of emerging contaminant		**Main sources**	Thursday, Horn, Wednesday, Badu, Warraber, Erub, Saibai and Maizab Kaur Islands*	Northern TS and Gulf of Papua	Lizard I.	Trinity Inlet‡	Trinity Bay‡	False Cape‡	Palm Beach‡	Yorkeys Knob‡	Cape Grafton‡	Orpheus I.	Townsville Outer Harbour^	Inner Cleveland Bay^	Ross Creek estuary	Ross River estuary^	N/A	Heron I.	Port Curtis	Port Curtis, offshore	Port Curtis Harbour	The Narrows	Port Curtis Estuary	N/A	99%	95%	Other
Metals	Aluminium	**Diffuse and Point Sources**	4.82 (0.178–**24.2**)	N/A	N/A	**27.4**	**33.2**	**36.5**	**33**	**31.8**	**37.6**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.0–6.0 (one suspected outlier **334**)	N/A	N/A	N/A	23 (max **46**)	N/A	2.1	24	
	Cadmium		0.006 (0.001–0.017)	<0.0008–0.0292	<0.01–0.03	0.31	0.31	0.31	0.31	0.31	0.33	<0.01–0.06	<1	<1; 0.002–0.010	0.004–0.283	<1	N/A	<0.01–0.02	<0.003–0.009	<0.0015 (<0.0015–0.004)	0.007 (0.002–0.015)	0.008 (0.003–0.0065)	<0.005 (max 0.013)	N/A	0.7	5.5	
	Chromium†		0.262 (0.141–0.491)	N/A	N/A	1.43	1.43	1.43	1.43	1.43	1.43	N/A	3	2	N/A	4	N/A	N/A	<0.4	N/A	N/A	N/A	<2	N/A	0.14 ($\mathrm{Cr^{VI}}$)	4.4 ($\mathrm{Cr^{VI}}$)	
	Cobalt		0.009 (ND–0.096)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	<5	<5	N/A	<5	N/A	N/A	0.012–0.153	N/A	N/A	N/A	N/A	N/A	0.005	1	
	Copper		0.105 (0.004–0.608)	0.032–0.986	0.13 (0.11–0.15)	**3.93**	**3.33**	**2.81**	**2.55**	**3.01**	**3.07**	0.18 (0.16–0.24)	<5	<5	N/A	<5	N/A	0.14 (0.12–0.16)	0.078–1.06	0.040 (<0.019–0.085)	0.510 (0.410–0.620)	0.530 (0.520–0.640)	0.34 (max 1.18)	N/A	0.3	1.3	
	Gallium		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	-	-	
	Iron		N/A	N/A	N/A	11.7	10.0	10.0	54.2	10.0	10.0	N/A	N/A	N/A	N/A	N/A	N/A		<1.5–214	N/A	N/A	N/A	10 (max 15)	N/A	-	-	
	Lead		0.018 (ND–0.084)	N/A	<0.06	0.47	0.43	0.43	0.44	0.43	0.44	<0.06	1	<1	N/A	0.8	N/A	<0.06	<0.016–0.085	N/A	N/A	N/A	<0.1 (max 0.68)	N/A	2.2	4.4	
	Manganese		0.863 (0.182–6.32)	N/A	N/A	55.7	4.97	2.93	2.84	3.65	4.03	N/A	10	16	N/A	36	N/A	N/A	<0.1–6.5	N/A	N/A	N/A	N/A	N/A	-	140$^{\#}$	
	Mercury		N/A	N/A	N/A	<0.1; one sample **0.4**	<0.1	<0.1	<0.1	<0.1	<0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.1	0.4	
	Molybdenum		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	15	15	N/A	19	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	-	-	23
	Nickel		0.143 (0.051–0.396)	0.094–0.460	0.09 (0.07–0.10)	1.4	1.37	1.38	1.39	1.37	1.43	0.12 (0.07–0.16)	5	<5	N/A	5	N/A	0.08 (0.06–0.10)	0.163–0.746	0.150 (0.011–0.190)	0.340 (0.280–0.470)	0.650 (0.470–0.910)	<0.28 (max 0.66)	N/A	7	70	
	Silver		N/A	N/A	N/A	0.46	0.46	0.46	0.46	0.46	0.46	N/A	<5	<5	N/A	<5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.8	1.4	
	Vanadium		2.14 (1.28–3.67)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	50	100	
	Zinc		1.33 (0.016–4.91)	N/A	0.08 (0.03–0.21)	**16.6**	13.6	14.1	12.6	10.3	14.3	0.14 (0.04–0.27)	7	<5	N/A	3	N/A	0.17 (0.09–0.35)	0.018–1.62	0.040 <0.030–0.140	0.170 (0.130–0.230)	0.110 (0.060–0.210)	<0.33 (max 1.03)	N/A	7	15	
Metalloids	Antimony†		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	-	-	270 ($\mathrm{Sb^{III}}$)
	Arsenic†		1.07 (0.272–2.46)	N/A	N/A	2.26	2.32	2.4	2.32	2.32	2.4	N/A	2	0.5	N/A	2	N/A	N/A	0.79–1.27	N/A	N/A	N/A	1.9 (max 10)	N/A	-	-	4.5 ($\mathrm{As^{V}}$)
	Selenium		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.1 (max 0.4)	N/A	-	-	2
	References		(33)	(34)	(35)	(31)	(31)	(31)	(31)	(31)	(31)	(35)	(32)	(32, 36)	(36)	(32)		(35)	(37)	(38)	(38)	(38)	(39)		(40, 41)	(40-42)	(41, 43)

*TS data collected with diffusive gradients in thin films (DGT) passive sampler rather than discrete water sample; † Data for total concentrations for antimony, arsenic and chromium – no elemental speciation data; ‡ 95th percentile of monitoring data collected from July 2013 to July 2014; ^ 95th percentile of monitoring data 2004 to 2010; # Manganese trigger for 95% species protection and corals present cited in (42).

(b)

			NRM regions																				
			Torres Strait	**Cape York**			**Wet Tropics**		**Burdekin**						**Mackay Whitsunday**				**Fitzroy**		**Burnett Mary**		
Main classes of emerging contaminant		**Main sources**	Cape York–Gulf of Papua Transect	Annan River estuary	Walker Bay	Endeavour River Estuary	Port of Cairns – Inner Port‡	Port of Cairns – Outer Channel‡	Townsville Outer Harbour‡	Townsville Port Berth 11‡	Townsville Port Rock Wall‡	Townsville Port Sea Channel‡	Townsville Port Platypus Channel‡	Ross River Estuary	Abbot Point Port dredge area‡	Abbot Point Port dredged material relocation area‡	Hay Point Port Apron Area‡	Hay Point Port Departure Path‡	Port Curtis	Port Curtis	N/A	**Trigger Value (ISQG-Low)**	**ISQG-High**
Metals	Aluminium	**Diffuse and Point Sources**	3,400–96,800	N/A	3,270–9,910	N/A	17,600	18,500	N/A	N/A	N/A	N/A	N/A	N/A	9,040 (3,100–22,900)	13,400 (11,700–15,700)	N/A	N/A	1,720–26,900	N/A	N/A	-	-
	Cadmium		0.02–0.11	<1	<1	<1	NA	NA	0.06	0.17	<0.1	0.15	0.12	<0.2	<0.1	<0.1	0.05	0.05	0.08–0.44	0.10 (<0.10–0.24)	N/A	1.5	10
	Chromium		12–**128**	20–32	9–23	6–26	35.6	35.0	23.9	37.2	11.2	23.1	24.3	9–30	13.5 (4.9–22)	27.6 (24.0–31.9)	16.3	13.1	5–32	50 (13–**85**)	N/A	80	370
	Cobalt		<6–21	N/A	N/A	N/A	11.3	9.5	N/A	N/A	N/A	N/A	N/A	3–11	4.8 (2.1–16.1)	5.74 (5.00–6.60)	N/A	N/A	3–31	N/A	N/A	-	-
	Copper		<8–29	5–23	<5–14	<5–12	14.3	11.3	13.7	20.9	3.41	10.5	15.4	6–18	3.7 (1.3–5.4)	5.53 (4.70–6.30)	6.87	4.66	0.1–22	18 (4–44)	N/A	65	270
	Gallium		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1–10	N/A	N/A	-	-
	Iron		1,200–57,500	N/A	<50	N/A	30,300	29,300	N/A	N/A	N/A	N/A	N/A	N/A	10,700 (3,770–16,500)	14,800 (12,600–17,200)	16,400	11,900	4,970–62,600	N/A	N/A	-	-
	Lead		<4–34	7–11	<5–9	<5–**56**	20.2	18.1	16.7	**78.4**	7.91	17.5	18.4	7–28	4.4 (2.2–9.6)	6.34 (5.60–7.30)	5.81	4.63	2–13	30 (5–18)	N/A	50	220
	Manganese		109–1,363	N/A	97–228	N/A	705	672	N/A	N/A	N/A	N/A	N/A	N/A	250 (66–684)	275 (241–312)	333	181	74–1,330	N/A	N/A	-	-
	Mercury		N/A	<0.1	<0.1	<0.1–**1.1**	**0.196**	0.033	N/A	N/A	N/A	N/A	N/A	N/A	0.005 (<0.01–0.01)	0.01 (<0.01–0.02)	0.01	0.01	<0.02–0.05	0.01 (0.001–0.055)	N/A	0.15	1
	Molybdenum		N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.1–2	N/A	N/A	-	-
	Nickel		<10–**42**	7–11	3–10	3–10	16.2	16.3	15.5	**44.9**	7.43	14.9	17.5	4–17	5.2 (1.1–10)	10.1 (9.0–11.7)	9.60	6.64	2–16	14 (4–**33**)	N/A	21	52
	Silver		N/A	N/A	N/A	N/A	0.1	-	0.28	0.65	0.45	0.42	0.41	<0.1	0.06 (<0.1–0.2)	<0.1	N/A	N/A	0.01–0.07	N/A	N/A	1	3.7
	Vanadium		N/A	N/A	N/A	N/A	46.0	44.4	NA	NA	NA	NA	NA	NA	18.3 (8.8–26.6)	24.6 (21.0–28.4)	N/A	N/A	11–114	N/A	N/A	-	-
	Zinc		<12–113	16–34	9–31	8–56	48.1	44.8	63.9	79.9	27.8	39.2	49	23–76	13.1 (4.4–38.4)	25.6 (22.0–29.2)	21.3	10.8	6–57	32 (11–113)	N/A	200	410
Metalloids	Antimony		N/A	N/A	N/A	N/A	N/A	N/A	<0.5	<0.5	<0.5	<0.5	<0.5	<0.05	<0.5	<0.5	0.63	0.47	0.05–0.35	N/A	N/A	2	25
	Arsenic		3–**32.3**	10	<5–10	7–16*	**20.4**	19.0	10.9	14.2	6.89	9.68	10.2	<5–7	5.8 (2.5–**29.6**)	3.23 (2.82–3.80)	5.13	5.44	6–**54**	18 (6–**36**)	N/A	20	70
	Selenium		N/A	N/A	<5	N/A	**3.2**	**2.8**	N/A	N/A	N/A	N/A	N/A	<1	0.4 (<0.1–0.7)	0.56 (<0.1–0.60)	N/A	N/A	0.02–0.51	N/A	N/A	2^	-
	References		(22)	(44)	(44)	(44)	(31)	(31)	(32)	(32)	(32)	(32)	(32)	(45)	(30)	(30)	(29)	(29)	(37)	(39)		(41, 43)	(41)

SQG = interim sediment quality guideline; * Max value may be higher – low As recovery in spike sample; ‡ Monitoring data = 95% upper confidence limit; ^ Alert concentration (43)

(c)

			NRM regions													
			Torres Strait	**CY**		**Wet Tropics**		**Burdekin**				**MW**	**Fitzroy**		**BM**	
Main classes of emerging contaminant		**Main sources**	Torres Strait Islands†	Olive River	Endeavour River	Johnstone River	Herbert River	Townsville Harbour Breakwater	Ross Estuary	Magnetic I	Orpheus I	NA	Port Curtis	Port Curtis Reference	N/A	**Food Codes**
Metals	Aluminium	**Diffuse and Point Sources**	2.83–19.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	26–248	10–37	NA	-
	Cadmium		0.05–0.46	**2.88 ± 1.20***	0.63 ± 0.19*	0.77 ± 0.41*	1.20 ± 0.44*	NA	NA	NA	**2.41 ± 0.73***	NA	0.14–0.42	0.14–0.26	NA	2$^{\#}$
	Chromium		0.47–1.00	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.2–9.4	<0.1–1.5	NA	-
	Cobalt		0.12–0.59	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Copper		1.93–5.37	NA	NA	NA	NA	NA	NA	NA	NA	NA	**114–363**	**93–186**	NA	30^
	Gallium		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Iron		50.5–463	NA	NA	NA	NA	NA	NA	NA	NA	NA	35–252	26–56	NA	-
	Lead		0.21–**4.16**	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.04–0.09	<0.04–0.18	NA	2$^{\#}$
	Manganese		0.74–9.04	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Mercury		0.01–0.56	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.03–0.09	0.03–0.07	NA	1.0–1.5$^{\#\ddagger}$
	Molybdenum		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Nickel		0.67–3.79	NA	NA	NA	NA	NA	NA	NA	NA	NA	<0.2–9.3	<0.2–0.9	NA	-
	Silver		0.02–0.04	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Vanadium		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Zinc		65.6–112	**1093 ± 589***	**3030 ± 1200***	**1303 ±430***	N/A	**2080 ± 453; 3000–4200**	**1273 ± 389**	**876 ± 404**	**2547 ± 799; 2560 ± 800***	NA	**463–1400**	187–**388**	NA	290^
Metalloids	Antimony		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	-
	Arsenic		**3.03–9.07**	NA	NA	NA	NA	NA	NA	NA	NA	NA	**3.3–6.9**	11.2–15.7	NA	1$^{\#}$
	Selenium		**1.65–7.75**	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.3–**1.5**	0.4–0.7	NA	1^
	References		(18)	(46)	(46)	(46)	(46)	(47, 48)	(47)	(47)	(46, 47)		(39)	(39)		(49)

† dry weight; * dry weight; divide by 5.5 to convert to wet weight (46); ^ Generally expected level = 90th percentile; # Maximum level; ‡ 1.0 mg/kg if insufficient samples; Green highlight = dry weight concentration exceeds benchmark; may not be the case for wet weight concentration.

Table 3-2: PCIMP monitoring data (November 2012 – August 2015) for concentrations (mean (SE) [range]) of metals and metalloids in (a) filtered surface water (µg/L) and (b) surface sediment (mg/kg dry weight) **(28)**. Exceedances of ANZECC/ARMCANZ trigger values and/or relevant guidelines highlighted yellow / bold text.

(a)	**PCIMP Monitoring Zones**																
Element	Auckland Inlet	Boat Creek	Lower Boyne Estuary	Mid Boyne Estuary	Lower Calliope Estuary	Mid Calliope Estuary	Inner Harbour	Mid Harbour	The Narrows	Graham Creek (Lower)	Outer Harbour (Open Coastal Reference)	Rodds Bay (Estuarine Reference)	Colosseum Inlet (Estuarine Reference)	South Trees Inlet (Lower)	Western Basin	Port Curtis (all sites)	**Trigger Value***
Aluminium	17 (4) [2.5–**210**]	17 (5) [2.5–**130**]	**31** (16) [2.5–**180**]	**40** (23) [2.5–**560**]	**28** (12) [2.5–**390**]	**64** (44) [2.5–**510**]	6.9 (0.8) [2.5–16]	11 (2) [2.5–**100**]	16 (3) [2.5–**190**]	6.9 (1.2) [2.5–23]	15 (6) [2.5–**260**]	6.6 (1.2) [2.5–**31**]	5.6 (0.6) [2.5–16]	10 (2) [2.5–**150**]	12 (1) [2.5–**47**]	15 (2) [2.5–**560**]	24
Arsenic†	1.1 (0.1) [0.1–2.9]	0.86 (0.08) [0.1–1.6]	1.2 (0.2) [0.1–2.1]	1.5 (0.1) [0.1–2.7]	0.88 (0.08) [0.1–1.7]	1 (0.1) [0.1–1.5]	1.1 (0.1) [0.1–1.7]	1.1 (0.1) [0.1–2.2]	0.87 (0.06) [0.1–1.9]	0.67 (0.08) [0.1–1.4]	1.2 (0.1) [0.1–2]	1.2 (0.1) [0.1–2.2]	1.1 (0.1) [0.1–2.3]	1.1 (0.1) [0.1–**4.7**]	1 (0.1) [0.1–1.9]	1.1 (0) [0.1–**4.7**]	4.5 (As^{V})
Cadmium	0.09 (0.02) [0.1–0.5]	0.1 (0.02) [0.1–0.5]	0.13 (0.05) [0.1–0.5]	0.1 (0.03) [0.1–0.5]	0.09 (0.02) [0.1–0.5]	0.09 (0.04) [0.1–0.5]	0.08 (0.02) [0.1–0.5]	0.09 (0.01) [0.1–0.5]	0.1 (0.02) [0.1–0.5]	0.1 (0.03) [0.1–0.5]	0.1 (0.02) [0.1–0.5]	0.09 (0.02) [0.1–0.5]	0.09 (0.02) [0.1–0.5]	0.09 (0.01) [0.1–0.5]	0.1 (0.02) [0.1–0.6]	0.09 (0.01) [0.1–0.6]	0.7
Chromium†	0.57 (0.05) [0.5–3.1]	0.63 (0.08) [0.5–2.9]	0.5 (0) [0.5–0.5]	0.78 (0.13) [0.5–2.5]	0.52 (0.02) [0.5–1.3]	0.58 (0.08) [0.5–1.4]	0.55 (0.03) [0.5–1.3]	0.57 (0.03) [0.5–2.4]	0.55 (0.03) [0.5–2.6]	0.5 (0) [0.5–0.5]	0.52 (0.02) [0.5–1.4]	0.54 (0.03) [0.5–1.3]	0.53 (0.03) [0.5–1.7]	0.53 (0.02) [0.5–1.4]	0.53 (0.01) [0.5–1.2]	0.55 (0.01) [0.5–3.1]	4.4 (Cr^{VI})
Cobalt	0.5 (0) [0.5–0.5]	0.52 (0.02) [0.5–**1.1**]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.52 (0.02) [0.5–**1.1**]	0.5 (0) [0.5–0.5]	0.51 (0.01) [0.5–**1.1**]	0.5 (0) [0.5–0.5]	0.51 (0.01) [0.5–**1**]	0.52 (0.02) [0.5–**1.3**]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–**1.3**]	1
Copper	0.68 (0.06) [0.1–**2.1**]	0.76 (0.12) [0.1–**3.6**]	0.65 (0.14) [0.1–**1.8**]	0.93 (0.28) [0.1–**6.9**]	0.74 (0.1) [0.1–**2.3**]	1.1 (0.2) [0.1–**2.6**]	0.52 (0.04) [0.1–1.2]	0.49 (0.02) [0.1–**1.5**]	0.57 (0.04) [0.1–**1.6**]	0.59 (0.07) [0.1–**1.3**]	0.46 (0.02) [0.1–0.5]	0.46 (0.02) [0.1–0.5]	0.46 (0.02) [0.1–0.5]	0.49 (0.02) [0.1–**1.5**]	0.67 (0.06) [0.1–**3**]	0.59 (0.02) [0.1–**6.9**]	1.3
Gallium	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	1 (0.2) [0.5–4.3]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.55 (0.03) [0.5–1.9]	0.5 (0) [0.5–0.5]	0.52 (0.01) [0.5–4.3]	-
Iron	21 (9) [0.5–380]	16 (8) [0.5–250]	8.7 (5.9) [0.5–73]	21 (13) [0.5–320]	29 (13) [0.5–380]	62 (40) [0.5–370]	3.5 (0.5) [0.5–12]	4.2 (1.2) [0.5–83]	4.6 (0.7) [0.5–43]	3.2 (0.6) [0.5–13]	11 (7) [0.5–310]	2.8 (0.3) [0.5–9.5]	3.3 (0.4) [0.5–12]	4.9 (1.5) [0.5–110]	6.4 (1.1) [0.5–48]	10 (2) [0.5–380]	-
Lead	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.56 (0.06) [0.5–1.1]	0.58 (0.08) [0.5–2.3]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.52 (0.02) [0.5–1.8]	0.52 (0.02) [0.5–1.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.51 (0.01) [0.5–1.3]	0.51 (0.01) [0.5–1.4]	0.51 (0) [0.5–2.3]	4.4
Manganese	23 (4) [1.3–**200**]	61 (17) [2.4–**400**]	18 (12) [1.4–**150**]	24 (7) [0.5–**160**]	16 (7) [1.9–**250**]	10 (2) [1.8–22]	8.6 (3.4) [0.5–82]	6.2 (2) [0.3–87]	10 (3) [0.5–**200**]	21 (6) [1.7–**140**]	2.4 (0.6) [0.3–17]	7.1 (0.8) [0.3–21]	6.9 (1.1) [0.5–44]	17 (3) [0.5–**160**]	10 (2) [0.5–110]	15 (1) [0.3–**400**]	140
Mercury	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–**0.11**]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–0.05]	0.05 (0) [0.03–**0.11**]	0.1
Molybdenum	9.3 (0.5) [0.5–14]	9.1 (0.7) [0.5–15]	12 (2) [0.5–**24**]	17 (2) [0.5–**41**]	8.8 (0.7) [0.5–13]	6.8 (1.2) [0.5–11]	10 (1) [0.5–14]	10.3 (0.4) [0.5–14]	10.1 (0.4) [0.5–14]	9.9 (0.7) [1.1–14]	10.2 (0.5) [0.5–13]	9.8 (0.5) [0.5–12]	9.9 (0.5) [0.5–13]	12 (1) [0.5–**23**]	9.9 (0.4) [0.5–15]	10.3 (0.2) [0.5–**41**]	23
Nickel	0.62 (0.06) [0.5–2.8]	0.65 (0.09) [0.5–3.5]	0.5 (0) [0.5–0.5]	0.53 (0.03) [0.5–1.3]	0.57 (0.04) [0.5–1.6]	0.7 (0.1) [0.5–1.2]	0.5 (0) [0.5–0.5]	0.51 (0.01) [0.5–1]	0.62 (0.05) [0.5–3.6]	0.63 (0.13) [0.5–3.4]	0.5 (0) [0.5–0.5]	0.62 (0.07) [0.5–2.8]	0.5 (0) [0.5–0.5]	0.53 (0.02) [0.5–2.1]	0.55 (0.03) [0.5–2.4]	0.56 (0.01) [0.5–3.6]	7
Selenium	0.72 (0.06) [0.5–**2**]	0.79 (0.15) [0.5–**5**]	0.61 (0.07) [0.5–1.2]	0.53 (0.03) [0.5–1.1]	0.68 (0.08) [0.5–**2.1**]	0.55 (0.05) [0.5–1]	0.55 (0.04) [0.5–1.2]	0.56 (0.03) [0.5–**2**]	0.71 (0.09) [0.5–**6**]	0.7 (0.1) [0.5–**2**]	0.61 (0.05) [0.5–1.9]	0.58 (0.04) [0.5–1.3]	0.59 (0.05) [0.5–**2**]	0.86 (0.08) [0.5–**3**]	0.68 (0.05) [0.5–**3**]	0.67 (0.02) [0.5–**6**]	2
Silver	0.56 (0.08) [0.3–**5**]	0.5 (0) [0.5–0.5]	0.48 (0.02) [0.3–0.5]	0.48 (0.02) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.02) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.5 (0) [0.3–0.5]	0.5 (0) [0.5–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.48 (0.01) [0.3–0.5]	0.49 (0.01) [0.3–**5**]	1.4
Tin	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.5 (0) [0.5–0.5]	0.54 (0.04) [0.5–3.5]	0.51 (0.01) [0.5–3.5]	10
Uranium	2.7 (0.1) [0.5–3.9]	2.9 (0.2) [0.5–4]	2.7 (0.4) [0.5–5.1]	2.2 (0.2) [0.5–3.8]	2.5 (0.2) [0.5–4]	2 (0.3) [0.5–3.2]	2.9 (0.2) [0.5–3.7]	3 (0.1) [0.5–4]	3.5 (0.1) [1.1–5.6]	3.3 (0.2) [1.9–5.4]	3 (0.1) [0.5–4]	3 (0.1) [0.5–4.6]	2.9 (0.1) [0.5–3.6]	2.9 (0.1) [0.5–3.7]	2.9 (0.1) [0.5–4]	2.9 (0) [0.5–5.6]	-
Vanadium	2 (0.1) [0.5–4]	2.2 (0.2) [0.5–4.1]	2 (0.4) [0.5–5]	2.6 (0.4) [0.5–9.8]	2.4 (0.2) [0.5–4.2]	3 (0.3) [0.5–4.8]	2 (0.1) [0.5–3.2]	1.8 (0.1) [0.5–3.9]	2 (0.1) [0.5–3.8]	1.9 (0.2) [0.5–3.7]	1.7 (0.1) [0.5–3.4]	1.7 (0.1) [0.5–4]	1.7 (0.1) [0.5–3.6]	2.4 (0.2) [0.5–11]	2.3 (0.1) [0.5–4.2]	2.1 (0) [0.5–11]	100
Zinc	1.7 (0.2) [0.5–7.7]	2.1 (0.3) [0.5–6.1]	2.2 (1.3) [0.5–15]	2.2 (0.7) [0.5–10]	1.5 (0.2) [0.5–4.1]	2.3 (0.6) [0.5–5.6]	1.1 (0.3) [0.5–5]	1 (0.2) [0.5–9.2]	2.2 (0.4) [0.5–**24**]	2.1 (0.6) [0.5–12]	1.5 (0.3) [0.5–11]	1.2 (0.3) [0.5–6.1]	1.1 (0.2) [0.5–10]	1.3 (0.2) [0.5–10]	1.7 (0.2) [0.5–8.1]	1.6 (0.1) [0.5–**24**]	15

^ To calculate means, half the detection limit was substituted for non-detectable values in the dataset; † Data for total concentrations for arsenic and chromium – no elemental speciation data; * Sourced from (40-43)

(b)	**PCIMP Monitoring Zones**																		**Trigger value**	
Element	Auckland Inlet	Boat Creek	Boyne Estuary	Lower Boyne Estuary	Mid Boyne Estuary	Calliope Estuary	Lower Calliope Estuary	Mid Calliope Estuary	Inner Harbour	Mid Harbour	The Narrows	Graham Creek (Lower)	Outer Harbour (Open Coastal Reference)	Rodds Bay (Estuarine Reference)	Colosseum Inlet (Estuarine Reference)	South Trees Inlet (Lower)	Western Basin	All Sites	ISQG-Low	ISQG-High
Aluminium	27500 (1500) [17700–35900]	23500 (4400) [4300–38600]	9100 (1200) [4300–14700]	8600 (1200) [6400–10700]	9400 (1800) [4300–14700]	8700 (2600) [2700–34100]	9300 (3400) [2700–34100]	7200 (2600) [3900–12200]	20800 (2500) [11000–28200]	9300 (1400) [2100–25800]	20200 (1900) [2300–30800]	17100 (4700) [1600–28500]	3800 (400) [2600–7100]	7000 (500) [4500–9600]	7000 (1200) [1100–13200]	18700 (2000) [2700–35100]	12600 (1600) [1900–24000]	14500 (800) [1100–38600]	-	-
Arsenic	11.7 (0.4) [9.3–15]	12 (1.3) [6–18]	8.5 (0.7) [6.2–13]	8.9 (1.1) [7.5–11]	8.3 (1) [6.2–13]	4.6 (0.8) [2.5–13]	4.9 (1.1) [2.5–13]	3.8 (0.6) [2.6–4.8]	15.6 (2.3) [10–**27**]	13.5 (1.2) [8.2–**24**]	13.5 (1.1) [7.7–**25**]	10.9 (1.6) [6.7–17]	13.7 (2.4) [8.2–**34**]	15.7 (2.3) [4.3–**27**]	7.6 (0.9) [4.1–14]	14.1 (1.7) [6.4–**33**]	10.7 (0.8) [4.5–17]	11.8 (0.4) [2.5–**34**]	20	70
Cadmium	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.44 (0.19) [0.3–**3.7**]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.25 (0) [0.3–0.3]	0.27 (0.02) [0.3–**3.7**]	1.5	10
Chromium	32 (1) [24–43]	27 (4) [9–40]	15 (2) [7–23]	13 (3) [8–18]	15 (3) [7–23]	12 (2) [5–36]	13 (3) [5–36]	10 (1) [8–12]	26 (2) [19–35]	15 (2) [6–32]	31 (2) [9–45]	22 (5) [4–35]	10 (1) [5–15]	11 (1) [8–18]	13 (2) [4–24]	25 (2) [6–40]	17 (2) [4–28]	20 (1) [4–45]	80	370
Cobalt	12 (0) [8–15]	13 (1) [6–17]	6 (1) [4–10]	5 (1) [4–6]	6 (1) [4–10]	7 (1) [4–14]	7 (1) [4–14]	6 (1) [5–9]	12 (1) [10–15]	10 (1) [3–18]	12 (1) [5–20]	9 (2) [3–13]	4 (0) [3–5]	5 (0) [4–6]	4 (0) [2–6]	10 (1) [3–16]	12 (1) [6–25]	9 (0) [2–25]	-	-
Copper	35 (3) [19–52]	25 (4) [6–38]	9 (1) [5–16]	7 (1) [6–8]	10 (2) [5–16]	11 (3) [4–40]	12 (4) [4–40]	8 (2) [6–11]	19 (2) [12–26]	8 (2) [1–26]	17 (2) [4–31]	17 (4) [3–27]	2 (0) [1–4]	3 (0) [1–4]	3 (1) [1–7]	17 (2) [2–31]	14 (2) [4–23]	14 (1) [1–52]	65	270
Gallium	8.2 (0.7) [3.8–13]	7.1 (1.5) [0.5–13]	6.1 (1) [1.8–11]	3.9 (1.2) [1.8–5.9]	7.2 (1.3) [4.4–11]	2.8 (0.9) [0.3–12]	2.9 (1.2) [0.3–12]	2.3 (0.6) [1.6–3.4]	6.4 (0.9) [2.9–9.1]	2.9 (0.5) [0.3–7.8]	5.5 (0.7) [0.3–9.9]	4.7 (1.3) [0.3–9.4]	1 (0.2) [0.3–2]	1.8 (0.4) [0.3–3.8]	1.8 (0.4) [0.3–3.8]	7.7 (1.1) [0.5–17]	3.8 (0.5) [0.3–8.1]	4.7 (0.3) [0.3–17]	-	-
Iron	32800 (1400) [23800–42700]	32500 (2800) [15000–40500]	18400 (1300) [13600–23800]	16600 (1000) [15200–18500]	19300 (1800) [13600–23800]	16300 (2300) [7900–36200]	16500 (2900) [7900–36200]	15800 (3200) [11100–22000]	29200 (1500) [23500–36500]	17200 (1500) [5700–28800]	27100 (1400) [15600–34900]	20700 (4300) [6400–33400]	10800 (1200) [6800–21300]	14100 (1500) [7300–22800]	10300 (1400) [3800–18900]	26300 (2000) [9400–42200]	21100 (1600) [8200–30900]	21600 (800) [3800–42700]	-	-
Lead	12.2 (1) [8.6–26]	9.6 (1) [4.4–13]	5.4 (0.7) [3.3–9.1]	4.7 (0.9) [3.3–6.3]	5.8 (1.1) [3.3–9.1]	3.1 (0.9) [1.2–12]	3.4 (1.1) [1.2–12]	2.1 (0.4) [1.5–2.9]	8.4 (0.6) [6.4–10]	4.6 (0.5) [1.9–9.2]	8.9 (0.6) [3.9–12]	7.8 (1.8) [2–13]	3.1 (0.4) [2.1–6.3]	4.9 (0.3) [3.8–6]	4 (0.5) [1.1–6]	8.7 (0.7) [2.9–14]	5.4 (0.6) [1.4–9.4]	6.7 (0.3) [1.1–26]	50	220
Manganese	371 (35) [170–670]	517 (96) [200–1030]	317 (34) [180–460]	313 (58) [250–430]	318 (46) [180–460]	240 (23) [120–410]	236 (19) [180–310]	253 (85) [120–410]	357 (52) [210–590]	510 (53) [230–930]	251 (24) [120–470]	130 (12) [93–160]	279 (16) [180–350]	210 (29) [82–330]	98 (15) [21–200]	283 (19) [160–420]	459 (80) [150–1330]	324 (16) [21–1330]	-	-
Mercury	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.1 (0) [0.1–0.1]	0.15	1
Molybdenum	0.73 (0.06) [0.5–1.5]	1.23 (0.15) [0.7–2.1]	0.52 (0.17) [0.25–1.8]	0.77 (0.52) [0.25–1.8]	0.4 (0.1) [0.25–0.78]	0.3 (0.05) [0.25–0.86]	0.32 (0.07) [0.25–0.86]	0.25 (0) [0.25–0.25]	0.39 (0.09) [0.25–0.81]	0.25 (0) [0.25–0.25]	0.72 (0.08) [0.25–1.3]	1.28 (0.31) [0.25–2]	0.32 (0.07) [0.25–0.97]	0.32 (0.05) [0.25–0.58]	0.6 (0.16) [0.25–1.8]	1.21 (0.28) [0.25–5.4]	0.43 (0.06) [0.25–1]	0.62 (0.05) [0.25–5.4]	-	-
Nickel	17 (1) [12–21]	14 (2) [4–21]	9 (1) [5–14]	8 (0) [7–8]	10 (1) [5–14]	7 (1) [3–19]	7 (2) [3–19]	6 (1) [5–7]	14 (1) [12–17]	8 (1) [2–16]	18 (2) [4–**31**]	12 (3) [2–19]	5 (0) [4–7]	5 (0) [3–8]	5 (1) [1–10]	12 (1) [4–20]	10 (1) [3–17]	11 (0) [1–**31**]	21	52
Selenium	0.88 (0.09) [0.52–1.5]	0.63 (0.16) [0.25–1.6]	0.42 (0.07) [0.25–0.78]	0.43 (0.18) [0.25–0.78]	0.42 (0.08) [0.25–0.74]	0.37 (0.05) [0.25–0.7]	0.38 (0.06) [0.25–0.7]	0.33 (0.08) [0.25–0.5]	0.52 (0.13) [0.25–1]	0.36 (0.04) [0.25–0.78]	0.57 (0.05) [0.25–0.95]	0.67 (0.16) [0.25–1.1]	0.36 (0.04) [0.25–0.61]	0.38 (0.07) [0.25–0.88]	0.4 (0.06) [0.25–0.75]	0.67 (0.08) [0.25–1.5]	0.45 (0.05) [0.25–0.91]	0.52 (0.02) [0.25–1.6]	2^	-
Silver	0.33 (0.03) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.08) [0.25–0.5]	0.33 (0.05) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.08) [0.25–0.5]	0.32 (0.05) [0.25–0.5]	0.33 (0.03) [0.25–0.5]	0.33 (0.03) [0.25–0.5]	0.33 (0.05) [0.25–0.5]	0.34 (0.04) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.33 (0.03) [0.25–0.5]	0.33 (0.03) [0.25–0.5]	0.33 (0.01) [0.25–0.5]	1	4
Tin	1.01 (0.08) [0.63–2]	0.7 (0.12) [0.25–1.1]	0.43 (0.06) [0.25–0.76]	0.42 (0.09) [0.25–0.51]	0.44 (0.09) [0.25–0.76]	0.43 (0.07) [0.25–1]	0.47 (0.09) [0.25–1]	0.33 (0.08) [0.25–0.5]	0.65 (0.08) [0.25–0.83]	0.35 (0.04) [0.25–0.82]	0.69 (0.05) [0.25–0.97]	0.59 (0.12) [0.25–0.9]	0.34 (0.04) [0.25–0.5]	0.33 (0.04) [0.25–0.5]	0.34 (0.04) [0.25–0.54]	0.68 (0.05) [0.25–1.1]	0.43 (0.04) [0.25–0.75]	0.54 (0.02) [0.25–2]	-	-
Uranium	1.1 (0) [0.9–1.4]	1.1 (0.2) [0.3–1.8]	0.5 (0.1) [0.3–0.9]	0.6 (0.2) [0.3–0.8]	0.5 (0.1) [0.3–0.9]	0.5 (0.1) [0.3–1.2]	0.5 (0.1) [0.3–1.2]	0.4 (0.1) [0.3–0.5]	1.3 (0.1) [0.9–2.1]	0.6 (0.1) [0.3–1]	1.3 (0.1) [0.5–2]	1.5 (0.4) [0.3–2.5]	0.5 (0.1) [0.3–0.8]	0.6 (0.1) [0.3–0.8]	1 (0.2) [0.3–2.8]	1.2 (0.2) [0.3–3.3]	0.7 (0.1) [0.3–1.5]	0.9 (0) [0.3–3.3]	-	-
Vanadium	61 (3) [40–82]	69 (6) [38–94]	33 (5) [21–64]	26 (3) [21–29]	36 (7) [23–64]	36 (4) [18–74]	36 (6) [18–74]	34 (3) [29–39]	56 (3) [47–66]	34 (3) [12–63]	52 (3) [30–85]	44 (8) [14–65]	21 (3) [12–44]	25 (3) [14–40]	19 (2) [11–31]	50 (4) [18–76]	42 (3) [17–56]	42 (1) [11–94]	-	-
Zinc	70 (4) [47–100]	49 (8) [12–75]	27 (3) [20–41]	23 (2) [20–25]	30 (4) [20–41]	23 (5) [10–75]	24 (7) [10–75]	22 (7) [12–36]	46 (3) [33–55]	24 (3) [7–52]	45 (4) [10–84]	35 (8) [7–56]	11 (1) [8–17]	13 (1) [10–21]	13 (2) [3–22]	40 (4) [10–70]	33 (3) [8–54]	34 (2) [3–100]	200	410

Table 3-3: Mean concentrations (µg/L; range in parenthesis) of metals and metalloid in the TS marine environment determined using DGT passive samplers (33). Exceedances of ANZECC/ARMCANZ trigger values and/or relevant guidelines highlighted yellow / bold text.

	TS Monitoring Locations									**Trigger Values***		
Element	Thursday I	Horn I	Wednesday I	Badu I	Warraber I	Erub I	Saibai I	Maizab Kaur I	All sites	99%	95%	Indicative interim working level¶
Aluminium	4.5 (4.01–4.99)	8.93 (5.43–14.4)	9.79 (2.37–17.2)	10.8 (4.19–17.4)	ND	0.79 (0.178–2.18)	6.31 (0.437–**24.2**)	1.28 (0.273–2.87)	4.8 (0.178–**24.2**)	2.1	24	
Arsenic	1.95 (1.81–2.13)	0.99 (0.869–1.13)	1.87 (1.33–2.46)	1 (0.935–1.06)	0.636 (0.384–0.823)	0.837 (0.272–1.12)	1.25 (0.875–1.57)	0.962 (0.692–1.2)	1.07 (0.272–2.46)	-	-	4.5 (As^{V})
Cadmium	0.005 (0.003–0.006)	0.008 (0.007–0.01)	0.002 (0.001–0.003)	0.007 (0.004–0.011)	0.002 (0.001–0.003)	0.005 (0.002–0.008)	0.011 (0.007–0.017)	0.006 (0.004–0.009)	0.006 (0.001–0.017)	0.7	5.5	
Chromium	0.411 (0.26–0.491)	0.26 (0.173–0.339)	0.184 (0.141–0.242)	0.194 (0.15–0.261)	ND	ND	ND	ND	0.262 (ND–0.491)	0.14 (Cr^{VI})	4.4 (Cr^{VI})	
Cobalt	0.017 (0.003–0.041)	0.011 (0–0.025)	0.009 (0.002–0.019)	0.009 (0.003–0.017)	0.003 (0.002–0.005)	0.003 (ND–0.013)	0.019 (0.004–0.096)	0.004 (0.002–0.007)	0.009 (ND–0.096)	0.005	1	
Copper	0.054 (0.008–0.086)	0.068 (0.039–0.093)	0.076 (0.032–0.238)	0.074 (0.053–0.1)	0.012 (0.004–0.018)	0.055 (0.027–0.089)	0.251 (0.129–0.608)	0.133 (0.063–0.249)	0.105 (0.004–0.608)	0.3	1.3	
Lead	0.035 (0.005–0.084)	0.029 (0.012–0.051)	0.022 (0.005–0.046)	0.027 (0.013–0.059)	0.003 (0.001–0.006)	0.008 (ND–0.015)	0.021 (0.007–0.082)	0.008 (0.003–0.016)	0.018 (ND–0.084)	2.2	4.4	
Manganese	1.64 (0.642–3.81)	0.983 (0.201–2.01)	0.9 (0.371–1.69)	0.733 (0.441–1.1)	0.246 (0.182–0.336)	0.359 (0.196–0.546)	1.57 (0.749–6.32)	0.518 (0.352–0.767)	0.86 (0.182–6.315)	-	140	
Nickel	0.178 (0.099–0.291)	0.179 (0.118–0.262)	0.154 (0.098–0.242)	0.178 (0.115–0.241)	0.065 (0.051–0.085)	0.092 (0.071–0.117)	0.211 (0.153–0.396)	0.103 (0.089–0.124)	0.143 (0.051–0.396)	7	70	
Vanadium	2.23 (1.99–2.48)	1.63 (1.54–1.76)	2.41 (1.81–3.36)	1.71 (1.65–1.77)	1.72 (1.28–2.22)	2.33 (1.51–3.09)	2.58 (1.69–3.67)	2.07 (1.76–3.1)	2.14 (1.28–3.67)	50	100	
Zinc	ND	2.79 (1.16–4.91)	3.31 (3.2–3.41)	1.18 (0.556–1.5)	0.016 (0.016–0.016)	0.935 (0.1–2.4)	0.938 (0.215–3.55)	0.591 (0.189–1.25)	1.33 (ND–4.91)	7	15	

* Sourced from (40-42); ND: Not detectable; ¶ indication of trigger value reliability following (41).

The compiled metal/metalloid monitoring data indicate that dissolved metal/metalloid concentrations in GBR surface water were typically low (**Table 3-1**a). However, the 95th percentile concentrations of Al, Cu and Zn during 2013–14 monitoring around the Port of Cairns exceeded respective water quality guidelines[3] (31); there was also one Hg exceedance. Past monitoring reported Al exceedances for individual water samples collected from Port Curtis (37, 39).

For sediment samples, recent EISs for Cairns and Townsville Ports reported 95% upper confidence limits for As, Hg, Ni, Pb and Se concentrations that exceeded trigger values (**Table 3-1**b) (31, 32). Past studies also indicate that individual sediment samples from the Endeavour River estuary, Port of Abbot Point and Port Curtis exceeded trigger values for As, Cr, Ni, Hg and Pb (30, 37, 39, 44). Elevated concentrations of As (>20 mg/kg), Cr (>80 mg/kg) and Ni (>21 mg/kg) measured in sediments collected in the Gulf of Papua and northern TS also exceeded ANZECC/ARMCANZ sediment quality guidelines (22).

For Ag, Co, Cu and Se the reporting limits were greater than trigger values for some water and sediment samples (**Table 3-1**). Hence the potential risk of these metals for these particular samples to the environment cannot be assessed.

For the 2012–15 PCIMP dataset, mean concentrations of heavy/trace metals and metalloids were typically below water and sediment quality guidelines (**Table 3-2**). Exceptions were mean concentrations for dissolved Al in the lower and mid sections of the Boyne and Calliope estuaries, which exceeded the 24 μg/L trigger value for 95% species protection. Moreover, dissolved concentrations of Ag, Al, As, Co, Cu, Mn, Hg, Mo, Se and Zn in some individual samples exceeded respective water quality guidelines. Some individual sediment samples also contained As, Cd and Ni that exceeded their trigger values. The elevated As, Cr and Ni in Port Curtis sediments were attributed to natural mineralogy rather than an anthropogenic source (38, 39).

Bioavailable heavy/trace metals and metalloid in TS seawater were recently monitored using diffusive gradients in thin films (DGT) passive samplers (**Table 3-1**a, **Table 3-3**) (33). Their concentrations were typically low, however one sample from Saibai Island had elevated Al that marginally exceeded the trigger value (24 μg/L) for 95% species protection. The mean Al concentration for all monitoring sites exceeded the 99% trigger value (2.1 μg/L). The highest Cu concentration (~0.6 μg/L) was also measured near Saibai Island; it was double the 99% trigger value (0.3 μg/L) but below the 95% trigger value (1.3 μg/L). Most sites had mean Co concentration greater than the 99% trigger value (0.005 μg/L) but all were below the 95% trigger value (1 μg/L).

Heavy/trace metals and metalloids have been detected in a variety of marine biota from the GBR and TS marine ecosystems (16, 18, 36, 39, 50-57). High concentrations of Cd, Cu, Hg, Se and Zn were detected in fish, crayfish, dugong and turtle commonly eaten by TS Islanders; weekly consumption of these seafood would exceed established health standards

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[3] Geographic zones within the GBR and TS marine ecosystem can vary from areas of high ecological value (HEV) to those that are moderately disturbed. As such, water quality guidelines for heavy metals and metalloids can range from values for protection of 99% species to 95% species (Table 1a). When comparing similar concentrations of a contaminant in different geographic zones, application of different trigger values for the same element can potentially create a misleading impression of poorer water quality in HEV zones compared to moderately disturbed sites. This was recognised in the Gladstone Harbour Report Card 2015 Technical Report. Water quality data compiled for this study were compared to ANZECC/ARMCANZ (2000) trigger values for slightly–moderately disturbed marine systems (grey cells in Table 1a). Where this was not available, indicative interim working levels and international guidelines were adopted. When only reviewing water quality for HEV sites, trigger values for 99% species protection should be applied.

for Cd (18). Crabs located near urban and industrial locations in the GBR contained elevated Cd, Cu, Hg, Pb, Se and Sn than those from sites away from such activities (50); some concentrations of Cu, Se and Zn exceeded Generally Expected Levels (GEL) for crustacea defined by Food Standards Australia New Zealand (49). Bioaccumulation of contaminants also occurs in remote locations; crabs from Normanby River contained elevated As (100 mg/kg dry weight; as well as Cd, Cu, Hg, Se and Zn) attributed to its association with gold ore and historical mining in the adjacent catchment (53). Seagrass, oysters and whelks in Port Curtis had high concentrations of heavy metals and metalloids (39); with Cu and Zn concentrations exceeding GEL for molluscs (49). Bioaccumulation of Cu and Zn in oysters was also evident in PCIMP monitoring data (28). Oysters collected from other regions of the GBR also exceeded the GEL for Zn (**Table 3-1**c).

3.5 Likely presence in the GBR and TS marine ecosystems

Various anthropogenic sources can introduce heavy/trace metals and metalloids into the GBR and TS marine ecosystems. These include diffuse and point sources such as agriculture and mining runoff, ports and harbours, drainage from acid sulfate soils (ASS), industrial effluents/emissions, atmospheric deposition, urban centres and WWTPs. An emerging contaminant is metal nanomaterial released in WWTP effluent; its risk to the GBR and TS is assessed in the Chapter on Nanomaterials. The contribution of contaminants from point sources is usually relatively small compared to diffuse sources, but their discharges can be locally and over short time periods highly significant (58).

The GBR catchment is rich in mineral and energy (i.e. coal) resources and has long supported diverse mining activities (5). Small scale mining has previously released toxicants into streams and creeks, for example arsenic associated with tin mining near Herberton, resulting into severe local effects (5). This can also occur at discontinued mine sites, e.g. tailings dam at Collingwood Bluestone tin mine near Cooktown continues to release water into Annan River (44). Queensland[4] has >15,000 abandoned mines with many occurring in the GBR catchment (e.g. Mount Morgan gold mine) and a few in the TS (e.g. Horn Island gold mine) that are potential sources of contaminants to adjacent marine environment. An emerging issue is the large volume of water requiring emergency releases from mines and refineries after high rainfall events (5).

Contaminants are expected in coastal environments adjacent to ports of Townsville, Abbot Point, Hay Point and Gladstone, where metalliferous commodities and coal are handled and shipped (59). Deposition of coal dust and other metal-bearing particles into seawater can leach contaminants (60). Metal-related industries such as refineries located in Townsville and Gladstone are additional sources of contaminants. Sediment with elevated Cu (460 mg/kg), Ni (139–11,800 mg/kg), Pb (53 mg/kg) and Zn (460–3,680 mg/kg) were associated with Townsville Port shipping ores and refined materials containing these metals (61). These exceed respective sediment quality guidelines, in some cases by 1–2 orders of magnitude. Numerous point and diffuse sources of metals and metalloids exist in the highly industrialised areas such as Port Curtis, where it is difficult to single out the major source (39, 62).

Land practices and catchment runoff can be sources of metals and metalloids to adjacent inshore areas. High concentrations of dissolved Al (that exceed the 24 µg/L trigger value)

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[4] https://www.qld.gov.au/environment/land/abandoned-mines/about/, accessed November 2015

were measured in Boyne and Calliope estuaries (**Table 3-2**a) (28). The highest dissolved Al concentration (64 µg/L) was in the mid Calliope estuary. With a mean monthly discharge of 13,874 ML[5], an estimate of 10,655 kg of dissolved Al per year could potentially enter the estuary from the Calliope catchment; this load does not include particulate Al. Higher loads of Al (and other elements) are expected in runoff from larger GBR catchments and may influence GBR and TS marine ecosystems. The Fitzroy River contains elevated dissolved heavy metals and therefore a source of these contaminants to the local coastal region (62). Elevated As, Cd and Hg in sediments near GBR catchments influenced by agriculture were attributed to applications of phosphatic fertilisers and fungicides containing these elements (63, 64). Elevated Hg in a sediment core from Bowling Green Bay was determined to be a legacy of mining in the adjacent catchment where it was used to process gold (63). Areas with elevated Hg in sediment also contained crabs enriched in this contaminant (53). Discharges from the Fly River (impacted by mining) and other, smaller coastal rivers flowing from PNG contribute heavy metals and metalloids to sediments in northern and north-central regions of the TS (18-22, 65).

An estimated 666,000 ha of ASS occur along the coastal plains within the GBR catchment in close proximity to reef waters (66), which makes them if disturbed a potential threat to water quality. Drainage from ASS occurs widely along the Queensland coast and is usually related to land disturbances for agriculture, aquaculture and coastal developments (67, 68). Oxidation of iron sulfide in ASS causes acidification, metal contamination, deoxygenation and iron precipitation in reef receiving water (69). Elevated Al (510 µg/L), Fe (800 µg/L) and Zn (190 µg/L) were measured in marine water receiving drainage from the highly disturbed East Trinity site at Cairns (67); Al and Zn concentrations were one order of magnitude greater than relevant water quality guidelines (24 µg Al/L; 15 µg Zn/L) for 95% species protection. Disturbed soils were also depleted in Cd, Mn and Ni (70), and likely transported downstream with Al and Zn. Estuarine sediments impacted by drainage can be enriched with Al, Cd, Co, Cu, Mn, Ni and Zn; concentrations 5–100 times greater than background have been reported (71). Most TS islands also have ASS[6], which is a potential risk that needs to be managed for urban development (24).

3.6 Risk to the GBR and TS marine ecosystems

The occurrence and effects of heavy/trace metals and metalloids in marine species and ecosystem has been widely studied and reviewed (8, 18, 52, 72). Marine organisms accumulate metals and metalloids from the environment. Although many are essential micronutrients, all are potentially toxic above certain threshold concentrations (8). It is noted that chemical form rather total concentrations influence the bioavailability and toxicity of metals and metalloids. The toxic effect of metals and metalloids on organisms can vary depending on their capacity to store, remove, or detoxify these contaminants; for example some organisms can regulate body concentrations of particular metals / metalloids over a wide range of ambient concentrations (72). Based on the information summarised below, a priority ranking based on the qualitative risk of metal and metalloid contaminants to the GBR and TS marine ecosystems is presented (**Table 3-4**), with higher scores applying to larger catchments influenced by anthropogenic sources.

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[5] Flow volume for Castlehope Gauge Station (132001A) sourced from https://water-monitoring.information.qld.gov.au/host.htm, accessed March 2016

[6] http://www.tsirc.qld.gov.au/about-council/dept-engineering-services/planning, accessed September 2015

Heavy/trace metals can exert toxic effects at environmentally relevant concentrations. For instance, a large number of estuarine and marine organisms are significantly impacted at 1–10 µg/L dissolved Cu; concentrations commonly detected in surface waters of the Cairns Port and Gladstone Harbour areas. At these concentrations, increased mortality has been reported for scallops (*Argopecten irradians*), clams (*Spisula solidissima*), and isopods (*Idotea balthica*) (72). Cadmium can be deleterious to a wide variety of marine organisms at 1–5 µg Cd/L, which can inhibit growth of phytoplankton (P*rorocentrum micans*), lower rates of reproduction in a copepod (*Psuedodiaptomus coronatus*), decreased population abundance of an isopod (*Idotea balthica*) and depress growth of juvenile plaice (*Pleuronectes platessa*) (72). The marine diatom *Ceratoneis closterium* (formerly *Nitzschia closterium*) is particularly sensitive to dissolved Al; 14 µg Al/L inhibited growth of tropical *C. closterium* by 10% (EC10) (73), whereas EC10 of 18–80 µg Al/L were reported for the temperate strain (40, 74). The EC10 values for effects on embryo development in oysters and mussels ranged from 250–410 µg Al/L (40). Dissolved concentrations up to 560 µg Al/L have been measured in mid Boyne estuary (**Table 3-2**a) (28).

Heavy metals in tropical marine ecosystems have potential adverse effects on various life stages of coral development that include fertilisation success, larval motility, larval settlement success, and metamorphosis (9-14, 75-77). Lead, Zn, Cd and Ni were generally less toxic than Cu to the early life stages of coral (9, 10, 13, 14, 77). Fertilisation rates of various coral species were reduced by 50% (i.e. EC50) in the presence of 15–40 µg Cu/L (10, 77). Higher EC50 values were reported for Pb (>1,450 µg/L) and Ni (1,420 µg/L) (10, 77). Fertilisation responses to Zn were variable; a significant reduction in coral fertilisation for *Acropora tenuis* occurred at 10 µg/L, whereas 500 µg Zn/L did not affect fertilisation success of *Goniastrea aspera* (10, 14). Significant reduction in fertilisation of *A. tenuis* only occurred at >2,000 µg Cd/L (10). Other effects of heavy metals on corals includes photosynthesis reduction in algal symbionts, zooxanthellae loss and changes in oxygen consumption (10, 15).

Iron sulfide oxidation in disturbed ASS can adversely affect many species due to generation of high acidity and mobilisation of large quantities of Fe, Al, heavy metals and metalloids. Their concentrations in marine receiving waters can greatly exceed water quality guidelines and poses health risks to aquatic organisms. Additional impacts occur when Al and Fe in acidic drainage mix with receiving water. Iron oxidation removes oxygen from water, while acidification results from hydrolysis of Al and Fe (67). Formation of Fe and Al flocs can smother benthic communities (67). These Fe precipitates can contain high concentrations of heavy metals and metals (e.g. 300–700 mg As/kg, 100–500 mg Zn/kg were reported in Trinity Inlet (78)). Sediment diagenetic processes will dissolve Fe precipitates and release toxicants to pore water and could affect benthic and bottom-feeding organisms. Hydrolysed Al can cause detrimental effects on fish by accumulating on gill tissue (79). Toxicity of ASS leachate and aluminium to the embryos and larvae of Australian bass (*Macquaria novemaculeata*) in estuarine water has been demonstrated (80). Extensive fish kills have been reported in both naturally (81) and artificially (82, 83) drained ASS catchments in north-eastern Australia. Fish kills have also been reported for many GBR rivers, however, a causal link with ASS discharge has not been determined (84, 85). The seasonal occurrence of epizootic ulcerative syndrome, a cutaneous ulcerative disease affecting freshwater fish, has also been related to discharge from ASS (66, 83-85). Chronic effects such as habitat degradation, mortality of marine worms, bivalves, invasion of acid-tolerant species (both plant and animal) and avoidance of habitat have been documented (67). The latter can potentially affect the migration of fish and invertebrate species (86). Release of soluble Fe from drained ASS is known to stimulate harmful/nuisance marine algal blooms, in particular *Lyngbya majuscula* (66).

Trichodesmium blooms are common in the GBR, possibly stimulated by nutrient inputs from terrestrial runoff, in particular phosphorus, iron and organic material (5). Significant changes in water quality occur during these blooms that include increased concentrations of several heavy metals (48, 87), with particulate fractions of Fe and Mn being the most significant. Of particular concern is the increase in bioavailable concentrations of Cd, Cu and Pb during extended *Trichodesmium* blooms (48, 87). Increased bioaccumulation of Ag, Cd, Cu, Fe, Mn and Zn in oysters coincided with increased bioavailability of heavy metals during the blooms (48); concentrations of Cd, Cu and Zn exceeded food standards by one to two orders of magnitude which poses a human health risk. Increased bioavailable concentrations of heavy/trace metals was demonstrated for inshore *Trichodesmium* blooms but may also occur in other GBR regions that experience extended bloom events, with the potential of having adverse effects on marine biota (48).

A major concern of contaminant bioaccumulation in marine biota is their potential biomagnification with increasing trophic levels along the food chain. This is a particular issue associated with methylmercury in seafood, which is the most toxic form of mercury to humans. Biomagnification of mercury in barramundi was reported for (but not unique to) Port Curtis and identified as a potential risk to human health (39).

Elevated heavy metals and metalloids (e.g. As, Cd, Cu, Fe, Mn, Ni, Hg, Pb, Se and Zn) have been detected in dugong and turtles in the GBR and TS (18, 54). Consumption of these culturally significant seafoods pose health risks to TS Islanders and other Indigenous Australians. Concerns with heavy metal/metalloid contamination and poor health of animals have resulted in Indigenous people omitting them from their cultural practices (5).

The endocrine disrupting effects of TBT on marine organisms are well known, its risk to GBR and TS marine ecosystem is assessed in the Chapter on Antifouling paints. Exposures to Cd, Se, Zn, Hg and Pb have also been implicated in the endocrine disruption of marine invertebrates (88). Cadmium, Mn, Hg (in particular as methylmercury) and As are well-established endocrine disrupting chemicals (89, 90). The aforementioned heavy metals and metalloids have been detected in marine organisms in the GBR and TS regions (16, 18, 50, 52-57), and could potentially disrupt hormonal systems in these species.

Australian coastal waters are generally characterised by currents that follow the coastline and are less likely to transport contaminants to deeper water (8). Hence, there would be a greater risk of metals and metalloids to marine biota and the quality of water and sediment in the inshore GBR. However, some offshore sediment repositories of these contaminants may exist, for example as reported for the Whitsundays due to soil erosion in the Proserpine catchment (91). For the TS, contaminants derived from PNG river discharges are known to be confined to the northern and north-central regions (18-22).

Table 3-4: Priority ranking of metal and metalloid contaminants, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Metals & Metalloids (water and sediment quality)	24	24	20	20	20	20	16

3.7 Discussion, recommendations and conclusion

Heavy/trace metals and metalloids have been detected throughout the GBR and TS regions (**Table 3-1**, **Table 3-2**, **Table 3-3**). A 2000 review of contaminants concluded low concentrations of heavy/trace metals and metalloids in the GBR lagoon, except in areas within ports and harbours and those adjacent to intense urban, industrial or agricultural activity (16). The estimated residence time of these contaminants in the GBR lagoon range from years to decades (17). Contamination by heavy metals and metalloids has likely increased since then given the expansion of coastal development and industries in the GBR region. The data compiled for this study typically indicate low concentrations of heavy/trace metals and metalloids in the GBR and TS marine ecosystems. However, at some locations water and sediment trigger values for certain contaminants were exceeded. Additional measurement of their bioavailable concentrations would be required to determine if there is a health risk to marine organisms (41).

Monitoring of metals and metalloids typically involves collection of discrete samples and measurement of total dissolved concentrations of these contaminants. This only provides a snapshot of water quality conditions at the time of sampling. However, concentrations of metals in coastal water can vary with tidal (and other) conditions (92), and only a fraction of the total metal / metalloid inventory is bioavailable. Monitoring of potentially toxic metals and metalloids would benefit from applications of DGT passive samplers; these provide time-integrated average concentrations of bioavailable heavy/trace metals and metalloids in surface and sediment pore waters (92-99). These samplers were previously used to monitor water quality in Port Curtis (100). The variety of commercially available DGT has increased recently to allow monitoring of a broader range of heavy/trace metals and metalloids in seawater (92, 95, 96, 98) and sediment (97, 99). These have been used for water monitoring in TS (33), and deployed in Upstart Bay, Cleveland Bay and in the Howicks Island group to monitor heavy/trace metals and As for a project on turtle health (D. O'Brien, JCU, pers. comm.).

Based on results of DGT monitoring, bioavailable concentrations of heavy/trace metals and As were typically low in seawater of the TS. The exception was high concentrations of Al (24.2 µg/L = 897 nM) and Cu (0.608 µg/L = 9.57 nM) measured near Saibai Island which exceeded their respective 95% and 99% water quality trigger values (**Table 3-3**). Copper is a reliable tracer of terrigenous sediments, particular those derived from PNG catchments influenced by mining (65, 101-103). Coastal PNG sediments have a Cu/Al ratio = 0.01 (101, 103), this is also the case for sediments around Saibai Island; indicating seabed sediments in northern TS are part of a sediment pathway generated from dispersal of terrigenous sediments from PNG to as far as Saibai Island (65). Coincidentally, the DGT Cu/Al (molar) ratio is also 0.01, suggesting dispersion of bioavailable Cu and Al from PNG river discharges. This highlights the benefit of passive samplers to detect episodic events, which may be missed by discrete sampling particularly in remote locations like the TS.

In a 2000 study, sediments in the northern TS had high concentrations of As, Cr and Ni that exceeded sediment quality guidelines (**Table 3-1**b). However, no recent data are available and increased loads can be expected from discharges by the Fly River and other smaller rivers flowing from PNG into the TS.

Reef water quality is known to be affected by elevated concentrations of suspended sediment, excess nutrients and pesticides in catchment runoff (5). River discharges can also transport substantial loads of metals and metalloids from catchments to inshore areas where they are likely to deposit in estuarine and coastal sediments. This study estimates that 10,655 kg per annum of dissolved Al could be entering inshore areas of southern GBR from Calliope catchment runoff. This estimate needs confirmation from monitoring, but highlights the potential of substantial metal and metalloid loads entering the GBR from neighbouring catchments.

Sediments are considered sinks for heavy metals and metalloids which are less bioavailable than dissolved metals. However, the health of benthic and bottom-feeding organisms may be adversely affected if exposed to dissolved metals in pore water and ingestion of metal-bearing particles that dissolve in the acidic juices of their gut. Although sediments are repositories of contaminants, they can also be sources if disturbed (e.g. dredging, ship movement, cyclonic events). An emerging issue is the effect of ocean acidification (OA) on the bioavailability of sediment-bound metals and metalloids; the physiological effects of OA may also increase the susceptibility of marine organisms to contaminants (104). To provide appropriate environmental protection under future conditions of OA, sediment quality guidelines may need to be re-evaluated (104). Increase in sea surface temperature (SST) is another global stressor that interacts with water quality; Cu contamination was shown to reduce the tolerance of coral larvae to thermal stress (105). Hence, reducing the concentration of this contaminant can protect coral from the negative effects of rising SST.

To improve the assessment of risks posed by heavy/trace metals and metalloids to the GBR and TS marine environments, we recommend:

(i) develop a comprehensive, integrated approach that brings together existing datasets of metals/metalloids held by governments and government agencies, universities and industry (a good example is PCIMP involving various stakeholders working cooperatively to monitor the environmental health of Port Curtis);
(ii) determine metal/metalloid loads entering the coastal environment via catchment runoff;
(iii) measure bioavailability of metals/metalloids contaminants at sites where total concentrations have exceeded, or are approaching, water and sediment quality trigger values; and
(iv) application of integrating samplers such as DGT which provide better representation of water quality conditions than discrete sampling. Determination of bioavailable concentrations of metals/metalloids would also be more ecologically relevant than analysis of total concentrations in discrete samples.

4.0 ALTERNATE PESTICIDES

Authors: Dominique O’Brien, Stephen Lewis, Aaron Davis

4.1 Summary

Water quality monitoring undertaken to date in the GBR catchment and marine areas have detected 55 pesticides (including associated metabolites and additives). Currently five priority photosystem II-inhibiting herbicides are included in management efforts aimed to reduce losses via paddock runoff and thus loads discharging into the GBR. In recent years, improvements in analytical methods and equipment have resulted, at least in part, in an increase in the number of so-called alternate pesticides (i.e. non-priority pesticides) being detected in marine and freshwaters. Based on the analysis in this chapter we have identified two pesticides, namely metolachlor (herbicide) and imidacloprid (insecticide) as the alternate pesticides of highest concern. On occasion concentrations of these three pesticides, used in various cropping commodities, exceed ecologically relevant values (41, 106) within the estuary and inshore GBR lagoon, and have the capacity to cause negative effects in marine organisms including inshore/sub-tidal seagrass meadows and microphytobenthos. With the dynamic nature of agricultural pesticide application, ongoing revision of monitoring programs will be needed to ensure analytical suites are appropriate to on-ground pesticide application behaviours in the GBR catchment area.

4.2 Introduction

Pesticides have been included as part of Australian environmental monitoring and management efforts for some time and are, along with nutrients and sediments, current pollutants of concern targeted by the Reef Water Quality Protection Plan (Reef Plan) (1). The Reef Plan aims to ensure that the quality of water discharging from “broad scale land use has no detrimental impact on the health and resilience of the GBR” through the reduction of pollutant loads. Five photosystem II (PSII) inhibiting herbicides (ametryn, atrazine, diuron, hexazinone and tebuthiuron) are identified to be of considerable risk to the GBR, based on the level and extent of use and detections within the GBR. These have been identified as priority pesticides for target reduction. Further, concerns with regard to the potential environmental harm caused by diuron in the environment have led to tighter restrictions on the use of this PSII herbicide in Australia.

Extensive industry engagement has been undertaken to stress the importance of effectively managing pesticide use and to educate users about the risks associated with offsite transport of applied pesticides. Key industry groups have developed best management practices (BMP) as part of the Reef Plan in an effort to reduce the loss of fertilisers, sediment and pesticides. As part of the Reef Plan efforts to reduce the loads of priority PSII herbicides from application sites, a shift has occurred in both application methods and the choice of herbicides employed. First, changing application methods, such as banded spraying, used by the sugar industry (107), has the potential to significantly reduce the amount of pesticides applied and thus minimising herbicide migration into the off-farm environment. Second, there have been additional efforts to encourage industry to replace the priority PSII herbicides with alternate pesticides (i.e. non-priority pesticides) in their weed management efforts. This could be of concern given that many alternate pesticides have a higher or equivalent toxicity to sensitive organisms than the priority PSII herbicides (108). In fact, results from recent water quality monitoring programs have highlighted that some alternate pesticides have been detected at higher concentrations and frequency than several of the priority PSII herbicides (109-112). In addition to Reef Plan efforts, potential changes in cropping commodities (e.g. rice, cotton) could also change the pesticide product selection used by primary producers and hence alter the pesticide risk profile.

This chapter documents the alternate pesticides that have been detected in monitoring programs, identifies alternate pesticides of concern that may warrant further management attention, and potential pesticides that may be increasingly used in the future with changed land use scenarios.

4.3 Main classes of alternate pesticides

Contaminant classes included in this chapter include herbicides, insecticides and fungicides registered for use in the GBR catchments, and additives such as surfactants and production by-products (113-116). Herbicides include (i) PSII herbicides (excluding current priority PSII herbicides) such as triazine, triazinone, uracil and urea herbicides, and (ii) non–PSII herbicides such as those that disrupt normal cellular function (i.e. root/shoot growth inhibitors, growth regulators); inhibit the synthesis of pigments, aromatic amino acids and glutamine; or disrupt cell membrane function (e.g., inhibit protoporphyrinogen oxidase or disrupt photosynthesis at photosystem I). Herbicides that fall within the non-PSII herbicide group include chemical classes such as: nitrophenyl ethers, phenoxyacetic acids, phenoxypropionic acids, pyridines, imidazolinones and sulfonylureas.

Insecticides include neurotoxins such as the prethroids, pyrethins, phenylpyrazoles, organophosphates and neonicotinoids. Fungicides include inhibitors of ergosterol biosynthesis (i.e. triazoles, imidazoles, pyrimidines, morpholines, piperazines, pyridyls); strobilurins/respiratory chain inhibitors (i.e. methoxyacrylates); and other fungicides that interfere with enzyme function such as dithiocarbamates (organic sulphur compounds that are multisite inhibitors), acylalanines (interfere with ribosomal RNA synthesis). Metals such as copper and sulphur are also employed in the management of fungicides and biofoulants (particularly in marine environments) but are considered in detail in Chapter 2.0 **Error! Reference source not found.** and 10.0 Antifoul.

Pesticide formulation adjuvants and by-products are also potential contaminants that may impact on ecosystem health (117). Adjuvants are used to enhance or modify the performance of pesticides and include surfactants, oils, acidifiers and buffers (117). By-products include any impurities that may be produced during the manufacture of pesticides and include polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs); metals (i.e. arsenic, lead and cadmium); *S*-methyl isomers; hexachlorobenzene (HCB); sulfotep, a highly toxic impurity that has been detected in organophosphorus pesticides such as diazinon and chlorpyrifos (118, 119).

4.4 Presence, concentration and location in the GBR and TS marine ecosystems

The assessment of pesticides in the GBR catchment and coastal surface waters began in the 1990s (120). Since then, the number of pesticides detected in the monitoring programs has continued to rise over time, at least partly as a result of improvements in sampling and analytical methods but potentially also due to changes in pesticide usage (3). This chapter considers data collected from 2009 onwards.

4.4.1 Pesticides in the catchments

By 2009, a total of 55 pesticides (and metabolites and additives) have been detected across the GBR catchment area (3). Hence, outside of the 5 priority PSII herbicides, a further 50 pesticides, metabolites and additives have been detected in the GBR catchment area (**Table 4-1**). These include 47 different residues in the Burdekin region (predominantly from Barratta Creek), 40 in the Wet Tropics, 32 in the Mackay-Whitsunday, 16 in the Fitzroy, and 15 in the Burnett-Mary region (**Table 4-1**). No recent monitoring has occurred in the Torres Strait and monitoring undertaken in the 1990s did not detect any pesticides (121).

Of these 50 alternate pesticides, ecologically relevant concentrations[7] for metolachlor, imidacloprid and simazine have been exceeded at some locations, while chlorpyrifos and diazinon concentrations were just below their respective guidelines (e.g. (109, 122-124). Many of the 50 alternate pesticides detected in monitoring programs do not have ecologically relevant Australian or international values to determine their risk to aquatic ecosystems. For example, metribuzin is a herbicide that has been receiving wider use and has been detected in higher concentrations (109); recent ecotoxicological work suggests this PSII herbicide is less toxic than diuron but more toxic than atrazine (125).

4.4.2 Pesticides in the coastal and marine waters

In coastal and marine waters, a total of 13 pesticides including 2 metabolites (outside of the 5 priority PSII herbicides) have been detected in flood plume samples and/or passive sampler devices in the GBR lagoon (Table 4-1). The majority of detections occur in samples collected from within riverine flood plumes discharging from catchments that contain sugar cane, broad-acre cropping and horticulture land uses (126-129). These flood plumes and associated pesticide residues reach mangroves, seagrass beds and inshore coral reefs.

Alternate pesticides detected in coastal waters above water quality guideline/trigger values include metolachlor (detected in flood plumes in the Fitzroy and Wet Tropics regions and in passive samplers deployed off the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy Regions), and imidacloprid (detected in flood plumes in the Wet Tropics region and in passive samplers deployed off the Wet Tropics, Burdekin, Mackay Whitsunday and Fitzroy Regions). Furthermore, chlorpyrifos, diazinon metribuzin, and simazine have been detected in the GBR lagoon but at concentrations well below the trigger values[8] outlined in the ANZECC and ARMCANZ water quality guidelines (41). Pesticides such as bromacil, imazapic, terbutyn, prometryn and fluometuron have also been detected in the GBR lagoon but either concentrations are well below available guideline values or no ecological threshold values exist.

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[7] We define ecologically relevant concentrations as available ecological protection guidelines/trigger values (with preference to ANZECC/ARMCANZ values, otherwise international values), proposed threshold values, and studies which have documented 'effect concentrations' on relevant marine or freshwater biota.

[8] *Simazine*: In the absence of marine data, 3.2 µg/L was adopted as a marine low reliability trigger value. This should only be used as an indicative interim working level. *Diazinon*: With very limited marine data, 0.01 µg/L was adopted as a marine low reliability trigger value. This figure should only be used as an indicative interim working level. *Chlorpyrifos*: A marine high reliability trigger value of 0.009 µg/L was derived for chlorpyrifos using the statistical distribution method with 95% protection. The 99% protection level is 0.0005 mg/L, which is currently unachievable analytically.

Table 4-1: Main sources and the maximum concentrations (µg/L) of alternate pesticides in the GBR (from all available monitoring data collected after 2009 (3, 111, 124, 130-133)) measured in water samples collected in the GBR marine waters and key fresh and estuarine systems in the GBR catchment area. Bold values indicate concentrations exceeding ANZECC and ARMCANZ water quality guidelines (41).

			Registered associated land use (source)										Marine waters (including plume sampling)^A						Barratta^B		Herbert: freshwater^C
		Mode of Action	Sugar	Horticulture	Legume	Cotton	Rice	Sunflower	Mango/Lychee	Urban/industrial	Grazing	Forestry	Burdekin	Fitzroy	Mackay Whitsunday	Russell Mulgrave	Tully	Wet Tropics	Freshwater	Estuarine	
Fungicide	Flusilazole	Inhibition of ergosterol biosynthesis	🕵										ND	ND	ND	ND	ND	ND	<0.001	<0.001	ND
Herbicides	2,4-D	Action like indole acetic acid (plant hormone) promoting uncontrolled growth	🕵		🕵	🕵	🕵	🕵		🕵			0.500	ND	ND	ND	ND	ND	2.233	0.016	21.
	Fluroxypyr		🕵										ND	ND	ND	ND	ND	ND	0.035	0.001	20.
	MCPA		🕵				🕵			🕵			ND	ND	ND	ND	ND	ND	0.089	0.03	0.01
	Mecoprop									🕵			ND	ND	ND	ND	ND	ND	<0.001	ND	ND
	Triclopyr								🕵	🕵			ND	ND	ND	ND	ND	ND	0.302	0.003	0.67
	Isoxaflutole	Bleaching: Inhibition of 4-hydroxyphenyl-pyruvatedioxygenase (4-HPPD)	🕵										ND	ND	ND	ND	ND	ND	0.402	0.274	ND
	Clomazone	Disrupts synthesis of chlorophyll		🕵	🕵		🕵						ND	ND	ND	ND	ND	ND	<0.001	<0.001	ND
	Imazapic	Inhibition of acetolactate synthase ALS	🕵										<0.001	<0.001	<0.001	<0.001	0.009	0.078	0.009	<0.001	0.02
	Imazethapyr		🕵										ND	ND	ND	ND	ND	ND	0.003	<0.001	ND
	Metsulfuron methyl			🕵	🕵						🕵		ND	ND	ND	ND	ND	ND	0.015	0.002	0.48
	Haloxyfop	Inhibition of acetyl				🕵		🕵	🕵	🕵			ND	ND	ND	ND	ND	ND	0.015	0.003	0.02

			Registered associated land use (source)										Marine waters (including plume sampling)^{A}						Barratta^{B}		Herbert: freshwater^{C}
		Mode of Action	Sugar	Horticulture	Legume	Cotton	Rice	Sunflower	Mango/Lychee	Urban/industrial	Grazing	Forestry	Burdekin	Fitzroy	Mackay Whitsunday	Russell Mulgrave	Tully	Wet Tropics	Freshwater	Estuarine	
		CoA carboxylase				■		■	■	■											
	Acifluorfen	Inhibition of protoporphyrinogen oxidase (PPO)		👤	👤								ND	ND	ND	ND	ND	ND	0.013	<0.001	ND
	Bromacil	Inhibition of photosynthesis at PSII								👤			ND	ND	0.120	<0.001	0.008	0.120	0.002	<0.001	0.22
	Fluometuron					👤							ND	ND	2.2	ND	ND	ND	0.004	<0.001	0.2
	Metribuzin		👤										0.2	ND	ND	ND	ND	0.190	4.83	4	ND
	Prometryn			👤	👤	👤		👤					ND	ND	0.78	ND	<0.001	ND	0.03	<0.001	ND
	Propazine												0.2	ND	ND	ND	ND	ND	3	4	0.2
	Propazine-2-hydroxy*		👤	👤	👤	👤	👤	👤	👤				ND	ND	ND	ND	ND	ND	0.011	0.005	0.02
	Simazine			👤						👤		👤	0.04	0.04	0.02	0.035	0.238	<0.001	0.543	0.100	0.7
	Terbuthylazine				👤						👤		ND	ND	ND	ND	ND	ND	0.008	ND	ND
	Terbutryn		👤							👤			<0.001	ND	<0.001	ND	<0.001	0.027	0.02	0.067	0.02
	Metolachlor	Inhibition of cell division	👤	👤	👤	👤	👤	👤	👤				**0.050**	**0.310**	**0.180**	0.004	**0.039**	**0.19**	**5.313**	**0.680**	**1.6**
	Terbutylazine	Inhibits root and shoot growth		👤	👤								ND	ND	ND	ND	ND	ND	0.002	0.108	ND
	Pendimethalin	Microtubule assembly inhibition	👤	👤	👤	👤	👤	👤	👤				ND	ND	ND	ND	ND	ND	3	4	1.2

			Registered associated land use (source)										Marine waters (including plume sampling)^{A}						Barratta^{B}		Herbert: freshwater^{C}
		Mode of Action	Sugar	Horticulture	Legume	Cotton	Rice	Sunflower	Mango/Lychee	Urban/industrial	Grazing	Forestry	Burdekin	Fitzroy	Mackay Whitsunday	Russell Mulgrave	Tully	Wet Tropics	Freshwater	Estuarine	
Insecticides	Bifenthrin	Axonic excitoxin: Inhibitor of key microsomal cytochrome P450 enzymes	♣	♣	♣	♣	♣	♣	♣	♣			ND	ND	ND	ND	ND	ND	3	4	ND
	Permethrin					♣				♣			ND	ND	ND	ND	ND	ND	<0.001	ND	ND
	Tetramethrin		♣	♣	♣	♣	♣	♣	♣	♣	♣		ND	ND	ND	ND	ND	ND	ND	ND	0.6
	Chloroxylenol (4-chloro-3,5-dimethylphenol)	Cane Toad control – unknown mechanism of action	♣	♣	♣	♣	♣	♣	♣	♣	♣	♣	ND	ND	ND	ND	ND	ND	ND	ND	0.22
	Fipronil	GABA-gated chloride channel antagonists				♣	♣	♣				♣	ND	ND	ND	ND	ND	ND	0.004	<0.001	ND
	Chlorpyrifos	**Inhibitor of acetylcholinesterase**	♣	♣	♣	♣	♣	♣	♣	♣	♣		ND	ND	<0.001	ND	ND	ND	0.001	<0.001	ND
	Diazinon			♣	♣	♣	♣			♣			<0.001	ND	<0.001	ND	ND	<0.001	ND	**0.014**	**0.157**
	Methamidophos		♣	♣	♣	♣	♣	♣	♣	♣	♣		ND	ND	ND	ND	ND	ND	0.973	ND	ND
	Phosphamidon												ND	ND	ND	ND	ND	ND	ND	0.108	ND
	DEET	Inhibitor of odorant receptors and gustatory receptors								♣			ND	0.63	ND	ND	ND	ND	ND	0.009	3.8
	Imidacloprid	Irreversible blockage of acetylcholine receptors	♣	♣	♣	♣	♣	♣	♣	♣	♣		0.007	<0.001	<0.001	0.004	**0.087**	**0.190**	**0.504**	0.02	**1.9**
	Imidacloprid urea												ND	ND	ND	ND	ND	ND	0.002	ND	ND

			Registered associated land use (source)										Marine waters (including plume sampling)^{A}						Barratta^{B}		Herbert: freshwater^{C}
		Mode of Action	Sugar	Horticulture	Legume	Cotton	Rice	Sunflower	Mango/Lychee	Urban/industrial	Grazing	Forestry	Burdekin	Fitzroy	Mackay Whitsunday	Russell Mulgrave	Tully	Wet Tropics	Freshwater	Estuarine	
Non-Pesticides	3,4 DiClAniline*	Herbicide production biproduct: Disruption of cell division	🕵										ND	ND	ND	ND	ND	ND	0.02	0.01	ND
	Tris (chloropropyl) phosphate isomers	Flame retardant											ND	ND	ND	ND	ND	ND	ND	ND	0.3
	Piperonyl Butoxide	Pesticide additive: synergist (inhibitor of cytochrome P-450 mono-oxygenases)								🕵			ND	ND	ND	ND	ND	ND	ND	ND	2.64
	2,6-Di-t-butyl-p-cresol (BHT)	Pesticide additive: Preservative (antioxidant)											ND	ND	ND	ND	ND	ND	ND	<0.001	0.2

*metabolite; NR: not reported OR below detection limit;
A: (3, 111, 130); B: (133); C: (124, 131-133)

4.5 Likely presence in the GBR and TS marine ecosystems

Alternate pesticides detected in GBR marine ecosystems can be derived from many different land use applications, although the predominant sources that contribute the highest loads and concentrations are from agricultural sources, particularly cropping lands (58, 126). Within the GBR catchment, the predominant land uses introducing alternate pesticides into the waterways include sugarcane, horticulture and broad acre cropping. Several pesticides may also be associated with use in urban areas and have been detected in WWTPs (123, 134), however, concentrations and loads tend to be much lower.

Currently within the GBR catchment area cropping and sugarcane cultivation are undertaken on 2,439,140 Ha and 1,478,032 Ha, respectively (135) using both irrigated and rain-fed methods. Water supply is the major factor limiting the further expansion of agriculture within the GBR catchment area. However, should new water sources become available it is foreseeable that cropping and sugarcane cultivation will expand further in the future (136).

Weed management in major GBR land uses such as sugarcane and cotton employ a variety of pre-emergent (i.e., trifluralin, pendimethalin, prometryn, fluometuron, metolachlor) and knockdown herbicides (glyphosate, 2,4-D, paraquat, diquat, pyrithobac-sodium and clethodim) and insecticides (bifenthrin, chlorpyrifos and imidacloprid) beyond the priority PSII herbicides (108). Broad leaf weed management on grazing pastures employs post-emergent herbicides (fluroxypyr, dicamba, MCPA, 2,4-D amine and 2,4-DB amine) (137) and while some of these herbicides have been detected in catchment monitoring programs they are typically not sourced to grazing lands (i.e. they receive wide application across other land uses). Paddock scale trials within banana plantations have shown that the herbicides glyphosate and glufosinate-ammonium have a high potential for off-farm transport by surface runoff (138). The general use herbicide imazethapyr (market name Spinnaker) may become an emerging pesticide of concern if use continues to increase in North Queensland cropping systems (Evan Shannon, BSES Ltd, pers. comm.).

In the sugar industry, legumes are increasingly being employed as a complementary or fallow crop for nitrogen fixation or to improve the physical, chemical and biological health of soils in areas previously used in monoculture cropping. A total of 32 herbicides, 27 insecticides and 9 fungicides are registered in Queensland (115) for common sugarcane rotation legume crops (maize, soyabeans, mungbeans), while only 10 herbicides and 5 insecticides were reportedly used (139). Of these herbicides and insecticides only 2,4-D (herbicide) had a ‘medium’ or higher mobility potential for surface water runoff, methomyl (insecticide), glyphosate, metolachlor, pendimethalin, acifluorfen (herbicides) all had ‘low’ potential for off-paddock movement, while the remaining pesticides were ranked as having ‘very low’ surface mobility potential (139). Several pesticides had toxicities of either ‘medium’ or greater to algae and/or *daphnia* sp. including paraquat, pendimethalin, diquat, s-metolachlor, methomyl, deltamethrin and thiodicarb. Of these pesticides, only methomyl (‘medium-high’ as low mobility with ‘very high’ toxicity to *daphnia* sp.) and pendimethalin (‘medium’ as low mobility with ‘high’ toxicity to algae) was assessed to have an overall risk of ‘medium’ or greater (139).

Cotton (which employs a similar herbicide suite to sugarcane) is currently emerging as a potentially significant crop across much of northern Australia, including the GBR catchments such as the Burdekin catchment. A major shift in pesticide management in cotton cropping has recently occurred with the introduction of genetically modified (GM) cotton (specifically glyphosate herbicide tolerance and toxicity to lepidopteran insect pests), which was licensed for northern Australia in 2006 (140). The emergence of GM cotton was initially predicted to greatly decrease the range of herbicides and insecticides required by cotton growers (140). The rapid emergence of glyphosate resistant weeds now sees herbicide resistance management strategies (particularly focussing on minimising glyphosate resistance) as a foundation of integrated weed management in cotton cultivation. Consequently, a wide variety of herbicides with different mode of actions are still utilised (Cotton Pest Management Guide 2015-16; CottonInfo (141)), and are regularly detected in the GBR catchment area. Frequent application of the same herbicides however, also occurs across a range of other industries such as sugarcane and horticulture, except for fluometuron which is registered for use in cotton only (109). Increased control requirements for insect pests such as mirids can be required in GM crops, with insecticides such as fipronil and dimethoate now used more heavily on GM crops than conventional cotton (140).

Aerobic rice systems (alternately referred to as upland, submerged–non-submerged rice, intermittent flooding or intermittent wet-and-dry rice; (142)) are being trialled or grown commercially in parts of northern Queensland, including in traditionally sugarcane dominated GBR catchments such as the lower Burdekin region. However, little specific agronomic or pest management data are available for growing aerobic rice in this area. Weeds are likely to be a critical pest management issue in aerobic rice (143), with grass control emerging as a key weed management issue in recent lower Burdekin rice growing experiences (Evan Shannon, BSES Ltd, pers. comm.). The main grass control herbicides in rice include pendimethalin (trade names including Stomp) and clomazone (trade names including Magister) for pre-emergent control and Cyhalofop-butyl (Barnstorm) for knockdown (post-emergent) control. Control of broadleaf weeds in rice includes herbicides such as dicamba and MCPA. Several of these herbicides (pendimethalin, dicamba, clomazone and MCPA) are detected in the GBR catchment area monitoring programs, but see application across a range of industries in addition to rice (109). Insect pests are a looming issue for rice management in Asia, and if similar challenges emerge in Australia, expected insecticide responses would likely include buprofezin, chlorpyrifos, cartap, fipronil, triazophos, and dimehypo (144, 145).

In the TS region, pesticide application tends to be on a localised scale and includes the application of chemicals in the management of weeds both in urban areas and on uninhabited islands throughout the region. Pesticide use is predominantly for the control of pests in urban areas (i.e. insects and vermin) and employs synthetic pryrethroids, organochlorines, organophosphates and carbamates (146). Weed (leuceana and lantana) management is also undertaken on affected islands where glyphosate was applied using spot spraying (J. Mellors, Torres Strait Regional Authority, pers.comm.), cut stump and low volume application methods in combination with manual control of weeds (i.e. hand slashing, grubbing and digging). Overall, pesticide application within the TS region is considered small scale and unlikely to have an impact on the local marine system.

4.6 Risk to the GBR and TS marine ecosystems

From the limited available data, we suggest that the current two alternate pesticides of most concern are metolachlor and imidacloprid, both due to their exceedances of water quality guidelines/trigger values in marine waters, and their wide usage across the GBR catchment area. Indeed, loads in the order of 500 kg of metolachlor and 270 kg of imidacloprid (exceeding several priority herbicides) have been reported for some rivers in the 2012/13 water year (110). These two alternate pesticides are predominantly sourced from sugarcane (metolachlor and imidacloprid), broadacre cropping (metolachlor) and cotton (metolachlor and imidacloprid).

Metolachlor concentrations in the GBR catchment and marine areas at times exceed the Australian freshwater low reliability trigger value of 0.02 µg/L (111, 124, 147, 148). Metolachlor is a chloroacetanilide herbicide that inhibits the biosynthesis of several plant components (149). Metolachlor and its breakdown products have been shown to have a slight to moderate toxicity to aquatic organisms including the crustacean *Daphnia magna*; LC50; LC50 > 1,000 mg/L over 24 and 48 hours (150), fish *Oncorhynchus sp;* LC50 = 15 mg/L over a 48 hour exposure and between 19 and 44 mg/L for 24 hour exposures (150) and induces developmental defects in the Pacific oyster (*Crassostrea gigas*) at concentrations as low as 0.1 µg/L (150-153). Concentrations of metolachlor have been measured in marine water samples collected adjacent to the Burdekin, Fitzroy, Mackay/Whitsundays, Russell Mulgrave, Tully and the Wet Tropics catchment areas with maximum concentrations of 0.05, 0.1, 0.18, 0.004, 0.039 and 0.19 µg/L, respectively (109, 111, 154). While no formal marine water quality guideline has been established, concentrations in the Burdekin, Fitzroy, Mackay/Whitsundays, Tully and the Wet Tropics catchment areas at times exceed the fresh water trigger value and were above the concentrations where abnormal Pacific oyster larvae development has been observed (153). As such, metolachlor concentrations at times may cause negative effects to local GBR species.

Imidacloprid is frequently detected in GBR waters at concentrations likely to pose some risk to GBR ecosystems (109, 111, 122) and loads in some rivers are higher than those of the priority PSII herbicides (110, 112). Imidacloprid is a neonicotinoid insecticide that has been banned for use in Europe for a two year period by The European Commission in December 2013 along with two other neonicotinoid insecticides (clothianidin and thiametoxam) (155). The European ban was put in place as a protective measure due to concerns that neonicotinoids are impacting upon bee colony health. To date studies on neonicotinoid toxicity has predominantly investigated with respect to terrestrial and fresh water invertebrates (reviewed in (156). Limited information is available with regard to both the presence and risk associated with neonicotinoids in marine systems. The European ban has brought a new focus on the monitoring and assessment of risks associated with neonicotinoids in the environment. Limited data are available on the toxicity of neonicotinoids on marine organisms, however some studies have shown that imidacloprid concentrations in the parts per trillion (ppt or ng/L) range have growth and reproductive effects in shrimp and crabs (157). While these studies were not conducted on species native to the GBR, it would be anticipated that local GBR species would show similar sensitives to exposures of imidacloprid as the study organisms. Imidacloprid has been detected in marine water samples collected adjacent to the Burdekin and the Wet Tropics catchment areas at concentrations of up to 0.19 µg/L (111), concentrations in the range for which growth and reproductive effects have been observed in non-indigenous crustaceans and as such it is anticipated that there may be some sub-lethal effects from imidacloprid exposure occurring within the GBR. Ecological values of 0.03, 0.1 and 0.3 µg imidacloprid /L in marine waters have been proposed for the protection of 99%, 95% and 90% of species, respectively; these values are more sensitive than the Canadian guideline developed in 2007 (157). Concentrations of imidacloprid in Australian waters at times exceed both the 99% and 95% protective concentrations not only in the GBR lagoon but also in freshwater reaches of certain GBR rivers (109).

A number of alternate pesticides and surfactants/additives detected within the GBR catchment area and lagoon are known endocrine disrupting compounds (EDCs) (e.g. herbicides pendimethalin and simazine; insecticides chlorpyrifos, fipronil and permethrin) (158). Kroon et al. (2015b) showed that estrogenic effects in estuarine and marine fish in the GBR were correlated with adjacent sugarcane land use. Specifially, the level of the biological marker for exposure of EDCs (liver vitellogenin transcription) in barramundi (*Lates calcarifer*) and coral trout (*Plectropomus leopardus* and *P. maculatus*) increased at sites with increased concentrations of ametryn, diuron, hexazinone, imidacloprid and simazine. These correlations were substantiated in subsequent laboratory experiments where juvenile barramundi were exposed to commercial herbicide and surfactant formulations (159, 160)

4.7 Discussion, recommendations and conclusion

A total of 50 alternate pesticides and associated additives have been detected in the GBR marine and fresh waters. Some of these pesticides have been detected at concentrations in GBR marine and estuarine waters which exceed water quality guidelines and hence may have detrimental effects on both fresh and marine organisms. Based on our analysis we suggest that the pesticides metolachlor and imidacloprid would on some occasions exceed ecologically relevant values within the estuary and inshore GBR lagoon, and have the capacity to induce negative effects on the biota including inshore/sub-tidal seagrass meadows and microphytobenthos (**Table 4-2**). Future land use change, regulation shifts and expansion of new commodities are beginning to and will continue to change the pesticide profile applied in the management of pests in North Queensland.

Table 4-2: Priority ranking of alternate pesticides, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Alternate pesticides (i.e. metolachlor and imidacloprid)	2	2	16	16	16	16	6

Recommendations for actions to best address this contaminant class are as follows:

1. Availability and inclusion of industry-specific usage data for pesticides would greatly inform monitoring programs, improve modelling outputs, and ultimately enhance the protection of downstream aquatic environments including the GBR WHA.
2. Monitoring programs must ensure that laboratory suites, where possible, are expanded to capture new and emerging pesticides.
3. Development of water quality guideline values (or more reliable values) for the two priority pesticides, and other alternative pesticides of potential concern.

4. Where insufficient ecotoxicological data are available it is recommended that studies on local species are undertaken:
    a. For the two priority pesticides, and other alternative pesticides of potential concern, currently being detected in surface waters;
    b. Prior to the approval of use of any new pesticide by the Australian Pesticides and Veterinary Medicines Authority (APVMA) to ensure the informed release of products.
5. Closer liaisons with industry to identify potential practice changes and likely shifts in product usage to ensure monitoring programs reflect actual pesticide application practices.
6. Expand pesticide Best Management Practice beyond current priority PSII herbicides and particularly so for the two priority pesticides, and other alternative pesticides of potential concern identified in this report.

5.0 PETROLEUM HYDROCARBONS

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5.1 Summary

Petroleum hydrocarbons comprise a very complex group of contaminants that have the potential to harm the marine environment, yet their presence in the GBR and TS marine ecosystems are not routinely monitored, nor are their effects on sensitive tropical species well understood. Here, we focussed on risks posed by the aromatic fraction, particularly the polycyclic aromatics hydrocarbons (PAHs), which are the most toxic petroleum hydrocarbon component to aquatic organisms and are monitored more often. The risks posed by PAHs to the GBR and TS marine ecosystems were assessed for the two most common, but contrasting, scenarios: (i) chronic exposure from contamination with terrestrial and port sources, and (ii) large acute petroleum spill events that result from shipping incidents.

The limited monitoring data available for PAHs indicated that contamination of sediments is highest in busy multi-use ports, followed by rivers with urban inputs, then island locations visited by small boats, and finally largely pristine offshore coral reefs. The sources of contamination within ports are spills of fuel during refuelling and cargo (e.g. coal which contains PAHs) during loading, direct discharge of burnt fuel and lubricants from ships and small boats, and accidental losses from coal stockpiles. Most contamination is likely to remain within port limits, but PAHs associated with coal dust can migrate to offshore areas. PAHs have only been detected at concentrations above national sediment water quality guidelines in highly disturbed port environments; however, the suitability of these national guidelines for application to the GBR WHA needs to be assessed.

Large (more than 4 tonnes) petroleum spills have not occurred within the GBR WHA, but recent risk assessments indicate spills in the order of thousands of tonnes are possible on a time scale of 10 to 100 years. The probability of large spills is increasing as shipping traffic increases, however this may be partially offset by improving navigation and other safety practices. Large spills in the GBR or TS regions could affect considerable areas of coral reef, seagrass meadow and mangrove habitats from nearshore environments to pristine offshore reefs, potentially taking decades to remediate and recover. As shipping traffic and coastal development increases along the GBR and TS, broader monitoring programs and studies on the bioavailability of PAHs and their effects on tropical biota are required to assess and manage risks to the environment.

5.1 Introduction

The GBR and TS marine environments may be at risk of two different types of exposure to petroleum hydrocarbons including:

1. chronic exposure from contaminated sediments associated with ports and large population centres, or from naturally occurring hydrocarbon seepage, and
2. acute exposure to oil, fuel and coal spills from ship collisions and/or groundings, e.g. the 2010 *Shen Neng* 1 oil spill in the southern GBR (161).

Marine organisms in the vicinity of any naturally occurring seepages may be well adapted to moderate concentrations of petroleum hydrocarbons (162). However, chronic exposure to contaminated sediments can have numerous detrimental effects on marine organisms including lethal and sub-lethal impacts, accumulation and alteration of habitat (163). Contaminated sediments close to the source are likely to pose the greatest risk to marine organisms; however, a recent GBR study reported contamination of sediments up to 40 nautical miles from potential coastal sources (164).

Hydrocarbon spills resulting from shipping incidents can occur along shipping routes in the GBR and TS marine environments or within port and harbour limits (165). In 2012–13, almost 11,000 movements of large commercial ships (>50 m) were monitored in the GBR and TS marine environments, with >87% berth of the 4,440 vessel arrivals at the four major ports (Gladstone, Hay Point, Cairns and Townsville) (166). In 2013–14, a total of 11,417 voyages comprising 2,910 large commercial ships were recorded through the GBR (166). Spills from incidents have been reported 879 times into Queensland ports and coastal waters since 2002[9], and in the tropics can cause decades-long impacts (167-169). The sources of some substantial spills, including 14,000 litres of diesel fuel spilled off Cape Tribulation in coastal waters in October 2013, remain unidentified.

Here we assess the existing monitoring data available for petroleum hydrocarbons in GBR and TS waters, their likely sources and the potential risk they pose to GBR and TS marine environments, and provide recommendations for future directions for monitoring, research and risk assessments.

5.2 Main classes of hydrocarbons

Hydrocarbons are compounds that contain carbon and hydrogen atoms in a vast array of molecular combinations. There are numerous natural sources of hydrocarbons in the marine environment, including natural seepage of petroleum formed over geological time periods from decaying plants and animals under pressure (170), and recent biogenic synthesis by microorganisms (171). The most common hydrocarbon contaminants are petroleum crude oils, fuels or other refined petroleum products, which contain various proportions of alkanes (paraffins), cycloalkanes (naphthenes) and aromatic hydrocarbons containing one or more aromatic rings (**Figure**).

Petroleum hydrocarbons generally have low solubilities in water and a large proportion of contaminants float on the seawater surface or become associated with sediments. Some oil can become entrained in the water column as oil droplets due to the wave action on oil slicks at the water surface, by high current velocities, or due to pressurised releases from underwater wellhead blowouts or pipeline ruptures (172).

Petroleum hydrocarbons that contain 1 – 8 carbon atoms are gases or highly volatile liquids, persisting for only short periods in the marine environment (hours to days), while higher molecular weight hydrocarbons are less volatile (see **Figure**) and can persist on/in seawater or sediments for days to months. Aromatic hydrocarbons, including monoaromatic hydrocarbons (MAHs) and especially polycyclic aromatic hydrocarbons (PAHs), are considered to be the most toxic petroleum hydrocarbon component to aquatic organisms (173). MAHs are more water soluble than saturated alkanes and PAHs, but 2- and 3-ringed PAHs are more acutely toxic, eliciting harmful effects at concentrations found in polluted

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[9] http://www.brisbanetimes.com.au/queensland/oil-spills-could-be-ecologically-disastrous-maritime-safety-qld-20160119-gm9c6s.html#ixzz3xpwYEUzq

waters (173, 174). Larger PAHs with 4 – 7 rings are more persistent and can be carcinogenic and mutagenic to marine species (175). Crude oils may also contain a variety of potentially toxic oxygen-, nitrogen- and sulphur-containing organic contaminants, such as phenols (176), water soluble acids and bases (177).

The present chapter primarily focusses on the occurrence and effects of different aromatic hydrocarbons from petroleum (**Table 5-1**) as these are the most toxic components and are more commonly monitored or reported in the field.

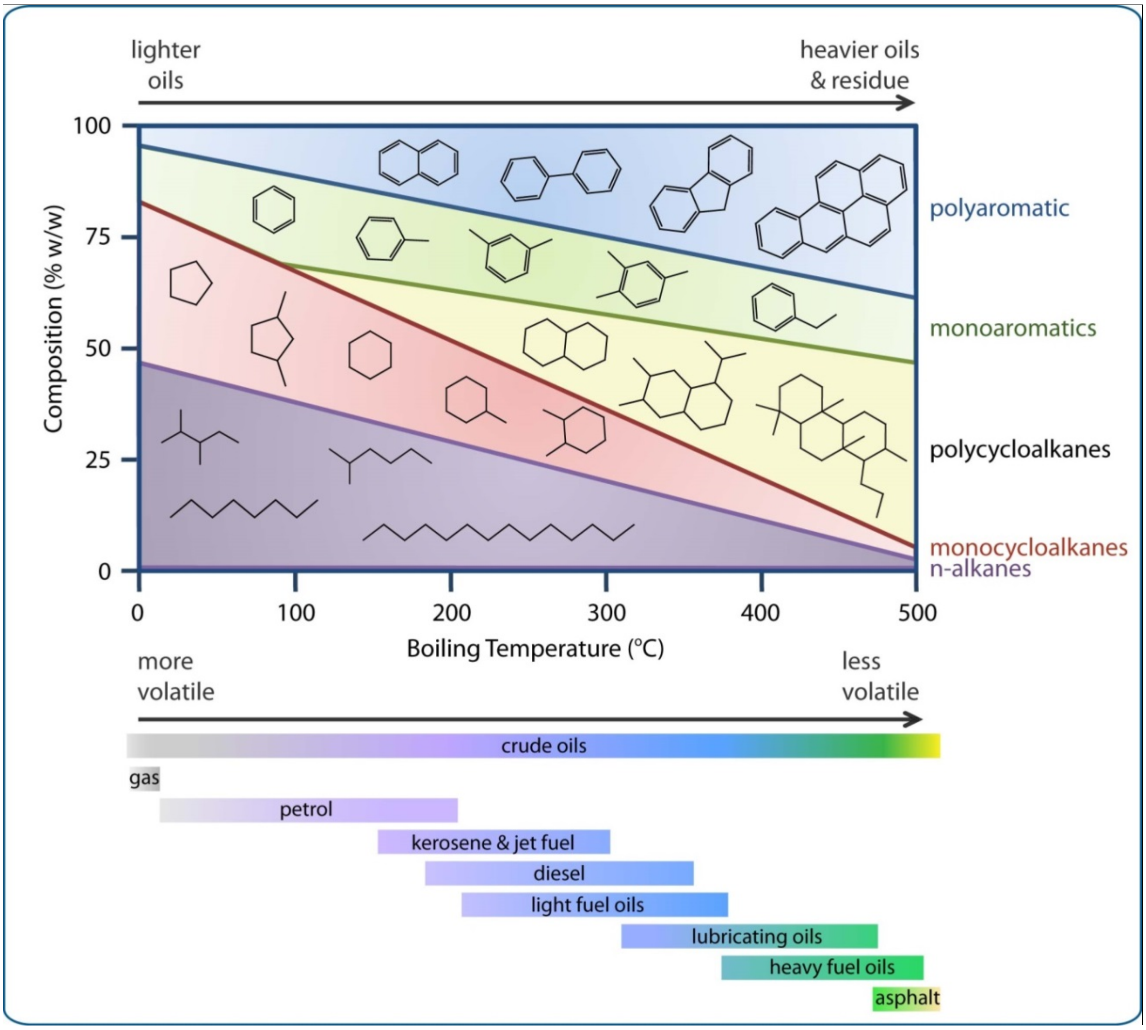

Figure 2: Distribution of hydrocarbon classes across the boiling range of petroleum crude oils and distillation fractions (adapted from Speight, 1999).

5.3 Presence, concentration and location in the GBR and TS marine ecosystems

There are no monitoring programs that routinely measure petroleum hydrocarbons across the GBR and TS marine environments. Instead, sources of relevant data include a handful of research publications (<10) and reports that describe results from short-term studies. These studies have reported total petroleum hydrocarbons (TPH), a sub-set of the more toxic PAHs (usually 16 US EPA priority PAHs), or have presented evidence of exposure in organisms via direct detection of PAHs or indirect measurements of metabolites or biomarkers for PAH exposure.

There are generally low concentrations of petroleum hydrocarbons associated with waters and sediments of the GBR that are distant from human activity. Total PAHs and aliphatic hydrocarbons are generally detected at concentrations below 1 µg l^{-1} and below 1 µg kg^{-1}, respectively (**Table 5-1**). These low background concentrations, along with the complexity in accurately measuring petroleum hydrocarbons from samples containing biotic hydrocarbons (from microalgae) (164), are the likely reasons for the paucity of monitoring data.

When petroleum hydrocarbons have been monitored, concentrations in sediments ranged from undetectable in offshore sites to low (total PAH < 40 µg kg^{-1}) at island locations, and high (total PAH up to 13,400 µg kg^{-1}) in busy ports (178, 179). PAHs were also detected in sediments of four rivers that flow into the GBR lagoon (180) and in surface sediments and in sediment traps at concentrations up to ~ 2,400 µg kg^{-1} from nearshore sites around Abbot Point/Mackay to offshore sites close to mid-shelf coral reefs (164).

Monitoring programs associated with dredging and port developments have measured TPH and PAH concentrations in sediments and assessed them against interim National Assessment Guidelines for Dredging (NAGD) (181, 182). Results from these studies have typically detected total PAH concentrations below guideline levels of 10,000 µg PAHs kg^{-1} (normalised to 1% organic carbon content) (**Table 5-1**).

Little monitoring of petroleum hydrocarbons has been undertaken following large fuel spills from shipping in the GBR. The exception has been a short monitoring program undertaken at nearshore sites following the 25 tonne heavy fuel spill from the *Global Peace*, which collided with a tugboat within Gladstone Harbour in 2006 (183, 184). The program measured total PAHs in sediments close to the spill at a maximum of 9,800 µg kg^{-1} (normalised to 1% OC) a month after the spill.

Petroleum hydrocarbons are often not detected in biota of contaminated sites as components such as PAHs can be rapidly metabolised (185). However, several field studies in the GBR region have identified PAHs or biomarkers for exposure in marine organisms, including fish, crabs, giant clams and sea cucumbers (53, 179, 180, 186-188)[10].

5.4 Likely presence in the GBR and TS marine ecosystems

The presence of petroleum hydrocarbon contamination in the GBR and TS marine environment is associated with runoff and discharge from industry and urban sources, vessel operations, shipping incidents, atmospheric deposition and natural sources (16, 24) (**Table 14-3**). Large oil extraction incidents such as the well-head blowout at the *Montara* platform

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[10] Indications of field exposure, uptake and metabolism of petroleum PAHs in fish (Barramundi) from the Johnstone River were revealed by the detection of fluorescent aromatic PAH metabolites in samples from this site. Fish from this site also had higher levels of other biomarkers for toxicant exposure (including PAHs), such as RNA damage, RNA:DNA ratios and EROD activity. Negri et al. (26) monitored organic contaminants in mud crabs from 11 GBR rivers over 2 years and only detected trace concentrations of PAHs in two pooled mud crab samples from the Johnstone and Pioneer Rivers. However, the detection of urinary metabolites of PAHs in mud crabs from 4 of these sites across a pollution gradient indicated biological availability and metabolism of petroleum-sourced PAHs (29). Trace concentrations of aliphatic hydrocarbons and PAHs have been detected in a range of GBR biota including giant clams, coral and sea cucumbers from offshore sites (19, 27, 28) but the scope of these studies was haphazard.

off north west Australia in 2009 (189) cannot occur as there is no oil exploration or extraction in the GBR or TS. Differences in sampling and reporting methods between studies make difficult any comparisons of hydrocarbon concentrations in marine sediments. When consistent sampling has been performed in diverse locations in the GBR, concentrations in the sediments of busy multi-use ports such as Townsville are highest, followed by rivers with urban inputs, then island locations visited by small boats and finally largely pristine offshore coral reefs (178) (**Table 5-1**).

The activities within large ports that contribute to contamination by PAHs and petroleum hydrocarbons include spills of fuel during refuelling and cargo (e.g. coal which contains PAHs) during loading, direct discharge of burnt fuel and lubricants from ships and small boats, and accidental loss from coal stockpiles (178, 190). The majority of petroleum hydrocarbon contamination in seawater around ports is likely to be associated with organic material in sediments, including coal particles (182), and most reports indicate that higher concentrations of PAHs are associated with sediments close to loading facilities of e.g. coal (191-193).

Most petroleum hydrocarbon contamination is likely to remain within port limits, but PAHs associated with coal dust have been detected up to 40 nautical miles from their potential source of Abbot Point near Mackay (164). PAHs have also been detected in the sediments and waters of river mouths in the absence of large vessel and industrial operations (180). For example, PAH concentrations were higher in river sediments from the Johnstone and Herbert Rivers compared to those in the Lockhart, Pascoe and Endeavour Rivers (**Table 5-1**) likely reflecting higher input from agricultural and urban sources. In tropical locations such as the GBR and TS, spikes in petroleum and natural sources of hydrocarbons may also occur after cyclones due to excess runoff (including hydrocarbons and nutrients) and resulting changes in biological carbon cycling in the ocean (194).

Offshore locations (reef and shoals) and coastal water bodies of the GBR and TS with no nearby ports or other industrial, urban or agricultural sources are not chronically contaminated with petroleum hydrocarbons (16). However, there is always a remote chance of catastrophic contamination due to large spills from shipping activities. Spills from large ships have included up to 4 tonnes of fuel oil from the *Shen Neng* 1, which ran aground on Douglas Shoal off Gladstone in 2010 (161), and the loss of ~25 tonnes of fuel oil from the *Global Peace* within Gladstone Harbour in 2006 (183, 184). Monitoring of the fate of oil from the *Shen Neng 1* spilt on the mid-shelf was not undertaken, while the highest concentrations measured in coastal sediments after the *Global Peace* spill were 9,800 μg kg^{-1} total PAHs (183). Notably, large spills on reefal or coastal systems of the GBR or TS could result in widespread habitat degradation and contamination lasting for decades (195).

Table 5-1: Main sources and available monitoring data for petroleum hydrocarbons in the GBR and TS marine ecosystems. All concentrations are in units of total PAHs μg kg sediment^{-1}. NA = not available. ND = not detected. ANZECC/ARMCANZ recommended sediment quality and upper sediment quality guideline values for total PAHs are 10,000 μg kg^{-1} and 50,000 μg kg^{-1}, respectively, normalised to 1% organic carbon (182). * Normalised to 1% TOC.

Main classes of emerging contaminant	**Main sources**	**NRM regions**						
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Petroleum hydrocarbons (chronic contamination of water and sediments)	Marine: Spills, leaks and discharge from vessels, ports, agriculture and urban sources	NA	Endeavour R. 37±37 (180) Pascoe R. 6.4 ± 3.9 (180) Lockhart R. < 2 (180)	Trace PAHs in water^{A,B} (180, 196) Johnson R. 187±171 (180) Herbert R. 11±6 (180) Up to 32 μg PAH kg^{-1} Hinchinbrook Is. (178) Green Is. Up to 32 (179)	Trace PAHs in water (179)^{C} Townsville Harbour Up to 13,400 (178) Ross R. Up to 184 (178) Burdekin R. Up to 19 (178) John Brewer Reef. < 0.02 (178) Abbot Point < 10,000* < 10 (191) <5 (192) Up to 83 (197)	Mackay, coast to shelf 23.5 – 2,389 (164)	Gladstone Harbour Up to 170 (178) Heron Is. Up to 21 (178) Port Curtis Up to 176 (198)	NA
Petroleum hydrocarbons (large spills from ships)	Marine: Spills, leaks and discharge from large ships >50 m	NA	NA	NA	NA	NA	Gladstone Harbour <105 – 9,800 (183).	NA

A. PAHs detected at trace concentrations in the water using passive samplers. Double Island, Fitzroy Is., High Is., Normanby Is., Russell Mulgrave R., Johnstone R., South Barnard Is., Dunk Is. (199).

B. PAHs detected in water grab samples from the Johnstone R. (10 ± 6 μg l^{-1}) and the Herbert R. (2.4 ± 1.3 μg l^{-1}) (180)

C. Up to 0.24 μg PAH l^{-1} detected in seawater at Green Is. (179)

5.5 Risk to the GBR and TS marine ecosystems

5.5.1 *Overall issues with assessing risks posed by petroleum hydrocarbons*

In order to estimate risks posed by petroleum hydrocarbons to GBR and TS marine environments it is necessary to understand both the probability of exposure and likely effects among a range of different organisms. Assessing these probabilities and effects are difficult for several reasons:

- Exposure can occur from large spills (via dissolved fractions, entrained droplets or smothering) or from chronic contamination (via ingestion or direct contact) (200).
- Concentrations of the more toxic MAH and PAH components of large oil spills are highly variable (temporally and spatially) in the water column and also greatly dependent on whether chemical dispersants are applied to dissipate the surface slick (201).
- Most of the petroleum hydrocarbon contamination data in the GBR and TS is from sediments (**Table 5-1**), but most toxicity data for tropical marine species has been derived from exposure to water-accommodated petroleum hydrocarbons (195, 202).
- Most ecotoxicology studies on tropical marine species have not reported measured concentrations of petroleum hydrocarbons, in particular the more toxic MAH and PAH components, and thus have limited utility in risk assessments (200).

5.5.2 *Chronic contamination of sediments*

The risks to GBR and TS biota posed by chronic contamination of sediments by petroleum hydrocarbons are uncertain. The highest concentrations of petroleum hydrocarbons (in particular PAHs) in the GBR and TS regions are within disturbed port environments (**Table 5-1**). Organisms most at risk are those living within the coastal sediments or particularly sensitive species in areas of moderate contamination. In general, the reported sediment concentrations of PAHs within the GBR and TS regions were lower than the interim NAGD sediment quality guideline value (SQGV) which is 10,000 µg PAHs kg^{-1} (normalised to 1% organic carbon content) (181, 182) (**Table 5-1**). Consequently, PAHs are considered a low risk to the highly disturbed port environment by port operators (191-193). However, SQGVs are derived from toxicity experiments mostly conducted with temperate and/or international species. Moreover, little is known about the bioavailability of PAHs associated with sediments or coal particles (182), and the effects of PAHs from contaminated sediments on local tropical marine species. The application of SQGVs within sensitive, high conservation value ecosystems of the GBR WHA may not be suitable and should be applied in the GBR and TS marine environments with caution.

5.5.3 *Large spills*

The probability of large petroleum hydrocarbon spills in the GBR and TS regions is determined by the amount of shipping traffic and the safeguards in place (such as pilotage, navigation aids, restricting traffic to designated lanes) to avoid incidents or to minimise the size or effect of spills when they occur (protected fuel tanks, response protocols) (203, 204). In recent years, approximately 11,000 movements of large commercial ships (>50 m) are monitored in the GBR and TS marine environments annually (166). Shipping movements within the GBR are highly managed, with designated routes, both inside the lagoon and between reefs to the outer routes in the Coral Sea (5). In the case of a collision or grounding, oil tankers could lose a tankful (over 10,000 tonnes) of refined or crude oil (204), coal carriers > 70,000 tonnes of coal (161), and large general cargo vessels up to 5,000 tonnes of fuel oil. So far there has not been a large oil spill into the GBR despite approximately one large ship grounding every 1-2 years since 1995 (5, 161, 203).

Det Norske Veritas (DNV) (165) estimated the probabilities of different types of oil spills in the GBR and TS regions by combining: (i) historical data of ship accidents within the region (ship-ship collisions, groundings, structural failure and fire/explosions while underway); (ii) likely amount of petroleum hydrocarbon spilt; and (iii) ship traffic frequency data of 2011/2012 and of predicted 2020 and 2032. Overall, DNV models indicated an annual expected loss of petroleum hydrocarbons from all ship spills within the study region of 418 tonnes, based on historical spill information and 2011/2012 shipping traffic data. The models also predicted that the chance of a single major oil spill (>20,000 tonnes) in the study region could be about 1 in 50 years, but this may increase depending on future traffic and safety regulations. Locations facing the highest risk of major oil spills are those where shipping traffic is highest including the West Torres Strait, North and Middle Inner Route, north of Yepoon and Hydrographers Passage. The DNV (165) risk assessment largely agreed with a previous risk assessment which indicated the locations at greatest risk were along the Inner Route of the Reef (north of Cape Flattery), the Port of Cape Flattery, Whitsunday Islands (mostly cruise shipping), Hydrographers Passage and the Great North East Channel (203).

In the tropical marine environment, sensitive receptors to spills include corals, seagrasses, mangroves, fish, marine mammals and birds (205-208). Each of those can be affected in different ways, depending on the nature of the exposure and their sensitivities; the effects may also be different from those studied in temperate species (202, 205, 208). One of the largest oil spills into shallow tropical reef environments occurred in 1968 when ~ 10,000 m^3 of medium crude was lost into the nearshore waters of the Caribbean coast of Panama (209). This spill had extensive long term effects on mangroves, seagrasses and corals (209), with very little evidence of recovery of coral reefs observed five years later (167). The early life stages of sessile invertebrates such as coral represent some of the most sensitive taxa to petroleum hydrocarbons, with toxic effects on coral larval settlement observed at total aromatic hydrocarbon concentrations as low as 64 $\mu g\ l^{-1}$ (210). As well as direct exposure of corals, fish and other organisms to hydrocarbons in the water column (168, 211), floating oil slicks can cause particular harm to reefs which emerge at low tide or by interacting with floating coral gametes during mass spawning (168, 212). Oil slicks can cause long-term contamination and mortalities in intertidal mangrove forests, where degradation rates are slow (169). Large floating slicks also have the potential to endanger waders and seabirds (213), as well as marine mammals that surface to breathe (214).

5.6 Discussion, recommendations and conclusion

The GBR and TS marine environments include large areas of coral reefs, shoals, seagrass beds and mangrove habitats that are not contaminated by petroleum hydrocarbons. On the other hand, the GBR and TS are immediately adjacent to petroleum hydrocarbon sources such as high-volume ports and the outflow of catchments affected by urban, agricultural and small vessel discharges. In addition, habitats along the entire length of the GBR and TS may be impacted by rare but potentially catastrophic oil spills from shipping incidents. The risk profiles for locations with chronically contaminated sediments need to be considered separately from the more unlikely but very serious scenario of large oil spill contamination.

At chronically contaminated sites, petroleum hydrocarbons (including the most toxic PAH fractions) are likely to be bound to the organic components of sediments or coal particles (182). Most of the limited monitoring data indicates that the highest concentrations of PAHs can be found adjacent to busy wharves such as those at Abbott Point, Townsville and Gladstone (**Table 5-1**). Maximum concentrations of PAHs of 13,400 µg kg^{-1} total PAHs (not normalised to organic carbon) (178) recorded in these ports may be higher than the interim Australian sediment quality guideline of 10,000 µg kg^{-1} (normalised to 1% OC) (182), but this is generally not the case in more recent studies (**Table 5-1**). Concentrations in some of the most polluted estuaries in China and Europe contain total PAHs in the rage of 200 – 10,000 µg kg^{-1} (215-217). PAH concentrations associated with coal particles in mobile sediments at concentrations of ~2,000 µg kg^{-1} were found in waters of the GBR MP (164), demonstrating the transport of moderate contamination from port activities into the GBR WHA.

The present qualitative assessment ranks potential impacts from large petroleum spills as a slightly lower risk to the marine environments of the GBR and TS than those of chronic contamination from port activities (**Table 5-2**). The GBR and TS regions have not encountered large oil spills so far but modelling of historical collisions, groundings and spill data indicates that a large spill is possible every ~50 years (165). This risk may increase over time as the ship traffic and transiting the GBR and TS is expected to increase by up to 2.5-fold over the next two decades (218), including passages of very large coal vessels and LNG tankers (166). The consequences of a large spill on sensitive coral, seagrass and mangrove habitats could be very severe and recovery can take decades (167, 169, 209).

Table 5-2: Priority ranking of main classes of petroleum hydrocarbons, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Petroleum hydrocarbons (Chronic contamination of water and sediments)	4	8	20	20	20	20	8
Petroleum hydrocarbons (Ship collisions and groundings)	16	16	16	16	16	16	16

Improving the assessment of risks posed to the GBR and TS marine environments requires:

1. more accessible routine monitoring data of PAHs in sediments from high-volume ports to more pristine habitats;
2. improved understanding of the bioavailability of PAHs in contaminated sediments (and from coal particles, potentially using passive samplers (182));
3. more data on the toxicity threshold concentrations of PAHs to key tropical species (coral, seagrass, mangroves and fish); and
4. a critical assessment of existing PAH water and sediment quality guidelines for application in the high conservation value habitats of the GBR and TS.

6.0 COAL PARTICLES

Authors: Kathryn L.E. Berry, Andrew P. Negri

6.1 Summary

Australia is currently the second largest exporter of coal in the world. In 2014 over 200 million tonnes of coal was transported through the GBR WHA. In addition, a series of mine and port developments are currently planned along the eastern coast of Queensland that will facilitate an estimated 4-fold expansion in coal exports by the end of the decade. The associated growth in shipping traffic through the GBR has raised concerns about increases in the likelihood of major incidents such the grounding of the coal carrier *Shen Neng 1* (2010). While shipping accidents may result in spills of up to 100,000 tonnes, some coastal habitats are already chronically exposed to particulate coal. Coal enters the marine environment via a range of mechanisms and is dispersed by currents throughout coastal and offshore ecosystems. Like suspended sediments, coal particles can reduce light penetration to the seabed, abrade and smother sessile benthic organisms, reduce feeding rates of filter feeders and respiration in a range of marine organisms. Unburnt coal is also a potential source of toxic polycyclic aromatic hydrocarbons (PAHs) and trace metals via leaching processes. Quantifying risks to the GBR and TS marine environments from coal exposure requires both an understanding of temporal and spatial concentrations as well as effect concentrations from particle and leachate exposure. While there is some recent data on threshold concentrations for fine suspended coal particles on mortality in corals and growth in fish and seagrass, there is limited publically available information on coal concentrations in the environment. In order to improve the assessments of risks posed by chronic contamination and large spills of coal to the GBR and TS marine environments, further research is needed including: (i) long-term monitoring of coal particles and associated hydrocarbon markers in coal ports and adjacent habitats in the GBR; (ii) improved modelling of coal particle transport to quantify spatial and temporal exposures of key habitats in the GBR marine environment, and (iii) further studies to quantify the lethal and sub-lethal impacts of coal on key GBR and TS taxa.

6.2 Introduction

Coal is a combustible, sedimentary rock comprising a heterogeneous mixture of carbon and organic compounds, with a smaller amount of inorganic material, including moisture and mineral impurities (219). Different types/ranks of coal are formed due to variations in the types of vegetation, conditions of formation and age, and are classified into four coal "ranks", which from low to high comprise: lignite, sub-bituminous, bituminous and anthracite (220). Each rank varies in chemical composition and thus their energy content, use, and the potential for biological effects are different (220).

Over the last three decades there has been a strong growth in Australia's mining sector due to global demand for coal and minerals. This growth has stimulated increases in coastal development, particularly related to port infrastructure and shipping activities (221). Australia is ranked 2nd in global seaborne coal exports, with the country's largest reserves (~34 billion tonnes) found within Queensland. There are more than 50 operating mines, and further large-scale thermal coal mines are proposed in the Surat and Galilee Basins (222). Generally, coal is transported by rail to the 5 major coal export terminals situated adjacent to the GBR WHA, namely Abbot Point, Hay Point (Dalrymple Bay and Hay Point Services Coal Terminals), and Gladstone (RG Tanna and Barney Point Coal Terminals) (**Figure**). These ports collectively exported close to 200 million tonnes (Mt) of coal by sea in 2014 (223), comprising 90% of the bulk transported (224) in the 11,417 voyages recorded through the GBR in 2013-2014 (166). The average annual ship traffic growth is forecast to increase annually 3-6%, potentially doubling by 2025 if demand continues and proposed large-scale mines and associated infrastructure progress (224, 225). Hence, the GBR and TS marine environments could be contaminated with coal particles that contain potentially toxic hydrocarbons and metals. The exposure and effects of both large spills and chronic coastal inputs on marine organisms, however, are largely unknown. This highlights the need for further investigation to improve risk assessments and management decisions for planning of development and emergency responses.

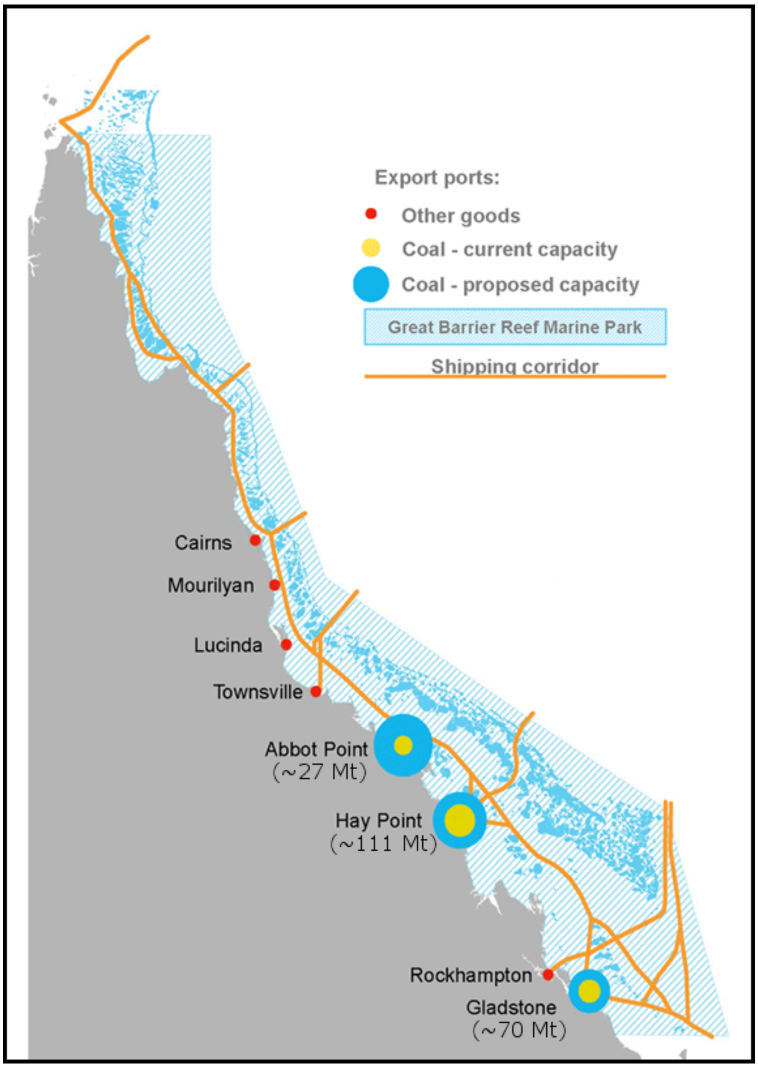

Figure 3: Shipping lanes and ports within the GBRMP. Coal ports are highlighted with yellow (current capacity) and blue (proposed capacity) circles. The numbers represent total exports in 2014. Image adapted from Parliament of Australia (226). Hay Point and Gladstone each have two coal terminals.

6.3 Main classes of coal contaminants

When coal particles enter the marine environment they can affect organisms due to their physical properties (block light, clog feeding and smothering), or by acting as a source of chemical contaminants (petroleum hydrocarbons, trace metals, acidity, and macro-nutrients) (220). Coal particles sourced from coastal stock piles and/or loading facilities likely add to the total suspended particulate matter in the GBR lagoon, although the relative contribution is uncertain at this stage. Coal is composed of variable amounts and combinations of organic and inorganic constituents such as polycyclic aromatic hydrocarbons (PAHs) and trace elements (e.g. cadmium and copper), respectively. Unburnt coal therefore is a potential source of these contaminants via leaching processes upon contact with water (227). The leaching and consequential effects on organisms are dependent on the coal type and its mineral impurities as well as the environmental conditions (220). Here, we largely present information on coal particles only; trace metals and hydrocarbons are presented in more detail in the '**Error! Reference source not found.**' and 'Petroleum hydrocarbons' chapters.

6.4 Presence, concentration and location in the GBR and TS marine ecosystems

Recent monitoring programs associated with dredging and port developments have measured sediment quality (including coal particles, PAHs and metals) within coal ports. While some monitoring programs at Abbot Point reported no coal particles in port sediments, others qualitatively noted coal fines in surface sediments of some samples (197). Sediment sampling of 13 samples at Abbot Point found varying sizes of coal particles in proximity of loading facilities (cited as (191) in (228)). Up to 45% of the sample surface material was coal below the coal-loading wharf, with concentrations of <1-7% outside the berth area. No coal was found at two reference sites 800 m east and west of the jetty (cited as (191) in (228)) (

Table 6-1), highlighting that larger particles are more likely to settle close to the source, while smaller particles will be dispersed with currents (229). Differences in the results of monitoring studies are likely due to differences in sampling methods (including small numbers of replicate samples), sites and analytical techniques. The presence of coal has been detected in water and sediments in port areas (above) and on beaches along the coast (K. Berry, AIMS@JCU, personal observation; **Figure**). However, there is limited recent and publically available data relating to coal particles in the broader GBR and TS marine ecosystems. Current research by AIMS@JCU is investigating the quantity of coal particles/dust found in sediment samples collected from ports (Gladstone and Hay Point), reefs (Whitsunday region) and beaches along the Queensland coast from Brisbane up to Thursday Island (TS).

Table 6-1: Main sources and available monitoring data for coal particles in the GBR and TS marine ecosystems. NA = not available.

Main classes of emerging contaminant	**Main sources**	**NRM regions**						
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay-Capricorn**	**Fitzroy**	**Burnett Mary**
Coal dust	Colliery waste from rivers, storage, loading and transport activities	NA	NA	NA	Abbot Point. Coal particles make up to 45% of sediment at coal ship berths. No coal > 800 m from jetty. (cited as (191) in (228))	NA	NA	NA
Coal particles	Shipping accidents	NA	NA	NA	NA	NA	NA	NA

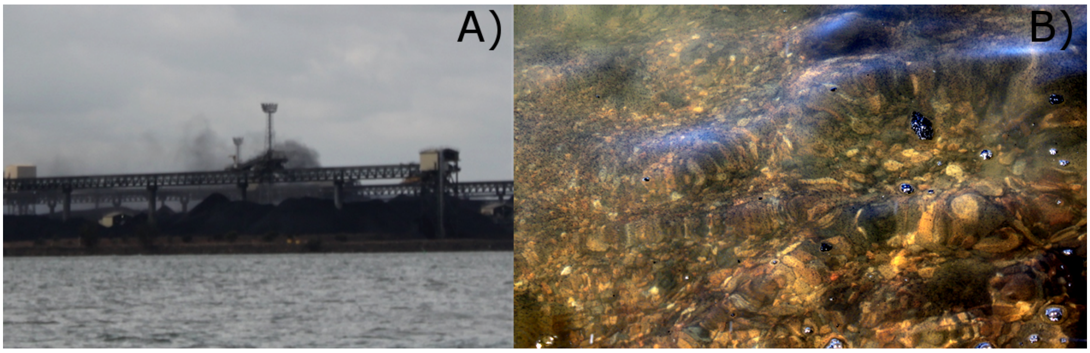

Figure 4: (A) Clouds of coal dust released from stockpiles and (B) particles partially coat the ocean surface after accidental spillage during a ship loading in Gladstone. Photo credit: Kathryn Berry, 2013.

Hydrocarbon markers for coal have been identified in sediments and sediment traps in the GBR lagoon, with the highest concentrations of ~2,000 µg/kg total PAHs detected closer to the coast (164). Detection up to 40 nautical miles offshore from coal terminals near Mackay (Hay Point and Dalrymple Bay) (164), indicates the potential for widespread transport within the GBR lagoon. Hydrocarbon markers are useful as an indicator of coal contamination and possibly the toxic PAHs that leach from coal (230). However, they are not necessarily quantitatively correlated with coal particle contamination due to differences in leaching rates, transport, and degradation.

PAH concentrations in Abbot Point were reported as low (<100 µg/kg) and below the ANZECC recommended sediment trigger value (see ‘Petroleum hydrocarbons’ chapter), with the exception of pyrene which was above detection limits ((191) as cited in (228)). Only two sampling locations were investigated in the study. Trace elements in sediments have been investigated at Abbot Point as parts of various environmental impact assessments ((191,

192) as cited in (228)). Arsenic and nickel had maximum sediment concentrations of 24.4 mg/kg and 34 mg/kg respectively (228), which exceed the ANZECC recommended sediment quality trigger values (41).

6.5 Likely presence in the GBR and TS marine ecosystems

Unburnt coal enters the marine 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 open coal stockpiles, accidental spillage, and coal carrier groundings (220).

Colliery waste generally enters river systems during major rainfall events when mines flood. The Fitzroy is the largest east draining river system in Australia and of the ~39 coal mines located within the Fitzroy Basin, all but two are permitted to discharge water under different environmental release conditions (231). Monitoring of the Fitzroy Basin after flood events in 2008 revealed that changes in salinity, heavy metal ion concentrations and acidity/alkalinity are the major water quality parameters of concern associated with coal mine discharge in the Fitzroy Basin (231). These parameters were detected at the furthest downstream monitoring station that was situated 20 km from the Fitzroy River mouth (232), suggesting that during major flood events it is likely that colliery waste will reach GBR waters.

Coal consistently enters the marine environment within ports adjacent to the GBR wherever coal is stockpiled, conveyed and transferred (**Figure**). The risk of chronic exposure in coastal marine systems is greatest near the large coal export ports (Abbot Point, Hay Point, Gladstone) (**Figure**). The likelihood of coal dust generation during offloading and transfer activities at Abbot Point was categorized as “almost certain” with a probability of 95-100% to occur throughout a year (233), with the potential for cumulative impacts to marine water quality considered possible ((191) as cited in (228)). Coal stockpiles along the GBR are not covered and heavy monsoonal rainfall can transport fine coal particles and leachate towards the ocean, potentially overflowing settlement ponds and sumps designed to minimize particle transport. Coal dust can also enter the marine environment directly from stockpiles during windy conditions (233). Fully enclosed conveyors are not used and dust plumes from conveyor offloading and accidental spillage during transfer is expected to occur during all operations year-round (233).

Once in the marine environment, larger coal particles will settle close to the input source, while smaller particles have the potential to be carried long distances by currents (229, 234). Oceanographic modelling predicted that coal particles on the ocean surface from coastal waters near Abbot Point would reach coral reefs off Mackay within three months under the influence of realistic wind conditions, tides and the East Australian current (235). In the UK, Canada and the U.S.A., sediments in proximity to coal sources have been found to contain 1-12% coal (dry weight) (229, 236-238). An unknown proportion of the chronic coal contamination of waters in Queensland ports is highly likely to migrate into GBR WHA waters; however, coal contamination is less likely in TS marine ecosystems due to their distance from coal port terminals.

Coal is carried by bulk carriers and comprises approximately ninety per cent of the cargo tonnage transported through the north-east region (166, 224). The bulk coal carrier *Shen Neng I* ran aground on Douglas Shoal in 2010 while carrying 68,000 tons of coal from the

Port of Gladstone, but no coal was released (161). International incidents have resulted in large quantities (up to 50,000 tons) of coal entering the marine environment, as during the salvage of the coal carrier MV *Smart* (South Africa, 2013). Options for salvaging large coal carriers that have run aground may include removing the cargo (and potentially dumping large quantities of coal) into the ocean to facilitate re-floating the ship and to avoid oil spills. Growth in shipping poses an increased risk of incidents and ship-sourced contamination (166) and, although rare, these large shipping spills may represent a substantial sources of marine contamination with unknown consequences for the GBR and TS marine environments.

6.6 Risk to the GBR and TS marine ecosystems

Understanding risks posed by coal particles to the GBR and TS marine ecosystems requires understandings of both potential exposures and effects on organisms. Within the GBR WHA, seagrass meadows, mangroves and coral reefs are situated in close proximity to coal ports and coal shipping lanes, respectively, and are likely to be three ecosystems impacted by chronic coal exposure and/or spillage from a coal carrier grounding. The TS region is transited by coal ships and is consequently also at risk of rare but potentially severe effects of coal spills from ship groundings or collisions.

The presence of coal particles in the marine environment has the potential to cause both physical and chemical impacts on GBR and TS marine organisms and ecosystems. Since coal particles may be present throughout the marine environment (as particles at the surface, within the water column, on/in the substrate; **Figure**), it has the potential to affect a wide range of organisms living within or transiting a contaminated habitat.

6.6.1 Effects of coal particles

Coal particles can affect aquatic plants in a variety of ways (**Table 14-4**). For example, suspended coal particles can be abrasive and cause damage to the leaves of the aquatic moss (*Eurhynchium riparioides*) and macroalgae *(Ulva lactuca*) after 3 weeks and eight days exposure, respectively (239, 240). In addition, exposure to coal dust reduced chlorophyll *a* production by aquatic moss (239). Accumulation of coal dust onto the upper and lower leaf/branch surfaces and trunks of mangroves growing around South Africa's largest coal-exporting port reduced photosynthesis (measured as carbon dioxide exchange and chlorophyll fluorescence) by 17-39% (241).

The effects of coal particles on marine fauna are variable (i.e. from behavioural to physiological and reduced survival), and are highly dependent on the concentrations of coal, the experimental design and duration of exposure (**Table 14-5**). Exposure of three taxa commonly found within the GBR (the hard coral *Acropora tenuis*, the reef fish *Acanthochromis polyacanthus*, the seagrass *Halodule uninervis*) to a range of coal concentrations over 28 d caused lethal effects in corals at concentrations as low as 38 mg l^{-1}. Suspended coal particles were not lethal to fish and seagrass; however, sub-lethal effects included reduced growth rates at concentrations of 38 and 73 mg l^{-1} respectively. Temperate Coho salmon (*Oncorhynchus kisutch*) was exposed to suspended coal particles resulting in a 96 hour LC_{50} of 7,000 mg l^{-1}, with mortalities only occurring at coal concentrations greater than 3,000 mg l^{-1} (242). Few fish were found to feed during the experiment; those that did feed contained coal particles in the alimentary tract. In dungeness crabs (*Cancer magister*), no mortalities were observed during a 22 day exposure to sediments containing coal, however behavioural changes were observed in terms of their burrowing (242, 243). The effects of coal mixed with sand on oxygen consumption and gill ventilation after 21 days exposure was found to be minimal, although coal was found deposited on the lamellae of the crabs (243).

Table 6-2: Priority ranking of main classes of coal particles, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay-Capricorn**	**Fitzroy**	**Burnett Mary**
Coal dust (Colliery waste from rivers, storage, loading and transport activities)	2	2	2	20	20	20	2
Coal particles (Ship collisions and groundings)	9	9	9	9	9	9	9

6.6.2 Effects of contaminants in coal leachate

Coal leaching experiments have applied a range of experimental techniques and coal types that are both likely to influence the results (**Table 14-5**). A coal carrier grounding scenario was experimentally simulated in the laboratory to investigate the potential for Bowen Basin coal to leach trace metals (60). Leaching of several metals was observed in seawater, with copper and manganese exceeding Queensland water quality guidelines (244) in undiluted leachate. There is limited evidence that PAH leachate from coal particles will be bioavailable (245), or that concentrations will exceed water quality guidelines or pose toxic threats (mutagenic or narcotic toxicity) to marine organisms. The effects of hydrocarbons, including PAHs in coal leachate, have been experimentally tested on some temperate marine and freshwater fish and molluscs (**Table 14-5**), but no relevant studies have been published on tropical species relevant to the GBR or TS marine environments.

6.6.3 Effects on ecosystem processes

Indirect effects of coal particles on marine ecosystems include alteration of the substratum composition, as well as the modification of predation and/or competition processes (220). Due to the high organic content in coal, the addition of coal to sediments can also contribute to anoxic and hypoxic conditions, which can also result in alterations to benthic communities (229). Secondary effects of coal particle deposition such as reduced larval survival, changes to population dynamics and potential flow-on effects to higher order consumers have also been hypothesized (229).

6.6.4 Environmental risk assessment

Estimating risks posed by coal to the GBR and TS environments (**Table 6-2**) requires an understanding of both the probability of exposure and likely effects amongst a range of different organisms. Assessing these probabilities and effects are difficult for several reasons: (i) exposure can occur from large spills (resulting from shipping accidents) or from chronic contamination (from loading and stockpiles in coal ports) and these need to be assessed separately; (ii) concentrations of coal particles and associated contaminants (PAHs and metals) are not regularly monitored and/or the data is not accessible; (iii) little modelling has been done to assess transport into the waters of the GBR Marine Park Area; and (iv) there is very little impact threshold data for coal particles (or PAHs and metals) on tropical species of high conservation value. Broadly, the likelihood of chronic coal contamination entering the environment at coal ports is high, while shipping accidents are far less likely to occur (but may have severe consequences) (**Table 6-2**). The risk associated with any coal contamination is dependent on the amount of dust/particles entering the ocean and the dispersion of these particles. The latter is still poorly quantified and is likely to be location-specific. Thus, the area affected will also be determined by the hydrodynamics at the contaminant-source area.

6.7 Discussion, recommendations and conclusion

Evidence from international literature and local studies demonstrates that the impacts of coal particles and leachate on marine organisms range from insignificant, to harmful effects on physiology and growth, and finally to mortality in some species (**Table 14-4**, **Table 14-5**). These impacts are highly dependent on the exposure duration, concentrations and types of coal, but no relevant information is available on any of these factors in the marine environments of the GBR or TS. Port developments report PAHs in sediments against national water quality guidelines as a proxy for coal contamination, but since coal particles themselves can be harmful to marine organisms, the development of guidelines for coal particles in the environment should also be considered.

The coastal water bodies near the five major coal shipping ports face the highest risk of chronic exposure from coal particles and leachate sourced from storage and loading facilities, and transport of these contaminants into the GBR WHA has been demonstrated using biomarker proxies (164). Understanding exposure of organisms to coal particles in the coastal water bodies of the GBR requires implementation of long-term monitoring programs of coastal habitats, including subtidal and intertidal zones. Re-suspension and sediment transport processes are complex (235) and are also not fully understood, making predictions of coal distribution arbitrary without accurate modelling and ground-truthing. It is therefore also important that hydrodynamic processes at point sources are investigated and combined with long-term monitoring data of the water column and substrate at input sources (i.e. ports and appropriate river mouths) along the GBR.

The expected increase in shipping of coal through the GBR and TS marine environments in coming decades (224, 225) may lead to an increased chance of accidental groundings and very large spills in coastal or reef habitats. Coal spills under these rare but serious circumstances are likely to result in simultaneous contamination of the marine environment with fuel oil (see ‘Petroleum hydrocarbons’ chapter) and antifoulants (see 'Antifouling paints' chapter), which may pose additional consequences for reefs, seagrass meadows and/or mangrove stands. Clearly more studies are needed on the potential impacts of both acute and chronic exposures to coal particles and to investigate the cause-effect pathways (chemical vs physical) on tropical marine species, including sensitive early life stages. This combination of new monitoring, modelling and effect research is essential in order to effectively assess the risk of increased coal exports and to develop more effective management and spill response plans.

7.0 PHARMACEUTICALS

Authors: Steven Melvin, Peta Neale, Jason van de Merwe, Frederic Leusch

7.1 Summary

The widespread global use of pharmaceuticals, combined with their high biological activity, poor removal from wastewater, and slow degradation, make them potential threats to aquatic environments. The principal sources of pharmaceuticals in the aquatic environment are WWTP effluent discharges and direct excretion of human waste. As such, the risk of pharmaceutical contamination in the GBR and TS marine ecosystems is limited to regions with high human population densities and in-water human activities (snorkelling, diving, etc.); that is, the Wet Tropics, Burdekin, Mackay-Whitsunday, Fitzroy and Burnett Mary NRM Regions. In this section, we compiled data from the literature on pharmaceuticals in WWTP effluents and receiving environments for the GBR and TS regions, and assessed the risks pharmaceuticals pose in aquatic environments based on toxicity data. We identified a paucity of monitoring data for pharmaceuticals in the GBR and TS ecosystems, so we extended our analysis to an Australia-wide dataset. Even at the national level there was limited information. Consequently, we compiled pharmaceutical prescription data for Australia and, combined with metabolism/ excretion data, sewage treatment removal and toxicity data we predicted the top 20 pharmaceuticals expected to be present in Australian WWTP effluent, and their likely risks. Our analysis of GBR and TS monitoring data identified 26 pharmaceuticals in WWTP effluent and surface water, with gemfibrozil, tramadol and venlafaxine potentially posing low risk to the GBR marine environments. A further 39 compounds were identified in WWTP effluent and receiving environments Australia-wide, with salinomycin, atorvastatin, and amitriptyline also posing some risk. Of the top 20 pharmaceuticals predicted to be in WWTP effluent based on prescription data, 15 have not previously been identified in WWTP effluent or receiving environments in Australia. Although there was no risk associated with most of these, there was no toxicological data available for irbesartan, sterculia or strontium ranelate. This chapter highlights the increased need for research efforts aimed at 1) more monitoring locations to include sampling in and around important receiving environments, including the GBR and TS marine environments, 2) measuring a broader range of compounds identified through national usage data, and 3) further toxicological assessments on pharmaceuticals for which information is limited.

7.2 Introduction

Pharmaceuticals are now widely recognised as emerging threats to aquatic animals and ecosystem health, and there is considerable international interest in characterising possible ecological risks associated with these compounds (246, 247). Vast quantities of a large number of pharmaceuticals enter natural aquatic waterways every day, primarily through the discharge of treated municipal sewage (248). Pharmaceutical concentrations are generally quite low in the aquatic environment, but most pharmaceuticals have been designed to be biologically active at low concentrations, and many studies have reported adverse effects in aquatic biota exposed to these compounds at low levels (249-251). While the majority of research on pharmaceutical toxicity has been directed at freshwater organisms, there is mounting evidence that suggests risks for marine organisms, too (252). In addition there has been a tendency for research to focus on well-studied compounds (253, 254), with limited information on the occurrence and effects of new and emerging pharmaceuticals. This highlights the need for a well-organised assessment of the risks that these compounds pose to highly valued marine environments, such as the GBR and TS. This chapter will 1) assess the risks of pharmaceutical contamination in the GBR and TS using existing occurrence and toxicity data, 2) predict emerging pharmaceuticals in this region using prescription data, and 3) identify knowledge gaps and sources of uncertainty to help direct future research in this area.

7.3 Main classes of pharmaceuticals

Pharmaceuticals comprise a broad range of medications used to treat various physical and mental illnesses, and are widely used to treat both humans and animals. Many different conventions are used for the classification of pharmaceuticals, including systems based on their biological modes of action, chemical structures, or intended use (255). Examples of some major pharmaceutical classes include: antibiotics, psychotropic drugs (e.g., anti-depressants and mood stabilisers), non-steroidal anti-inflammatory drugs (NSAIDs), fibrates, beta-blockers, anti-convulsants, and others. While it is often convenient to group contaminants into categories or classes, in this report it was possible to consider risks posed by individual pharmaceuticals, due to the small number of compounds for which there is available data.

7.4 Presence, concentration and location in the GBR and TS marine ecosystems

Limited monitoring data are available for pharmaceuticals in or around the GBR and TS marine ecosystems, and most of this is reported in treated domestic wastewater, rather than actual environmental concentrations. Only two studies were identified with data specifically relevant to the GBR and TS (123, 256), and these provided information for just 26 pharmaceuticals (**Table 7-1**). O'Brien *et al.* (123) focused on effluent from two WWTPs in Cairns, while Scott*, et al.* (256) focused on river water, including sites in northern Queensland. Most of the data was for the Wet Tropics, with a small amount of data for the Fitzroy and Burdekin regions. We found no monitoring data for the other NRM regions. Nevertheless, the available data represent the most highly populated areas of northern Queensland, which are expected to be the main sources of pharmaceuticals in the GBR region. In the majority of cases, pharmaceuticals measured in treated sewage were at concentrations between 10 and 500 ng/L. Exceptions include several pharmaceuticals observed in the Wet Tropics, including gabapentin (1.8 µg/L), hydrochlorothiazide (1.1 µg/L), iopromide (2.3 µg/L), tramadol (2.0 µg/L) and venlafaxine (1.2 µg/L) (123). In river water, paracetamol was reported in the Fitzroy region at 4.1 µg/L (256). Many of these measurements come from an individual sampling event, so the reliability of these concentrations as representative concentrations in these regions is limited. Nevertheless, the existing data reveals generally low concentrations of those pharmaceuticals that have been observed in treated sewage and river water in northern Queensland. Since many of these measurements represent concentrations prior to discharge, levels in the marine environment are expected to be lower.

Due to the lack of data directly relevant for the GBR and TS marine environments, we expanded our literature survey to include Australia-wide monitoring studies, as a means of obtaining broader national occurrence data for commonly used pharmaceuticals (**Table 7-2**). This identified a further 39 pharmaceuticals (65 in total) in Australian wastewater and receiving environments. It is likely that these additional pharmaceutical compounds could also pose risk to the GBR and TS regions. As such, the full list of 65 compounds was included in the pharmaceutical risk assessments (**Figure**).

Table 7-1: Main sources and available monitoring data (ng/L) for pharmaceuticals in the GBR and TS marine ecosystems. WWTPs = waste water treatment plants.

Pharmaceutical compound (class)	**Main sources**	**NRM regions**						
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Atenolol (beta-blocker)	WWTPs			140-360[a]				
Carbamazepine (anticonvulsant)	WWTPs			380-860[a]	17-569[b]			
Cephalexin (antibiotic)	WWTPs			190-450[a]				
Codeine (analgesic)	WWTPs			150-310[a]				
Desmethyl diazepam (psychotropic)	WWTPs			10-20[a]				
Diclofenac (NSAID)	WWTPs			60-260[a]				
Erythromycin (antibiotic)	WWTPs			40-180[a]				
Frusemide (diuretic)	WWTPs			40-280[a]				
Gabapentin (anticonvulsant)	WWTPs			1000-1800[a]				
Gemfibrozil (fibrate)	WWTPs			20-70[a]	5[b]			
Hydrochlorothiazide (diuretic)	WWTPs			350-1100[a]				
Indomethacin (NSAID)	WWTPs			20-40[a]				
Iopromide (contrast media)	WWTPs			50-2300[a]				
Metoprolol (beta blocker)	WWTPs			90-160[a]				
Naproxen (NSAID)	WWTPs			95-270[a]; 5[b]				
Oxazepam (psychotropic)	WWTPs			230-440[a]				
Oxycodone (analgesic)	WWTPs			50-90[a]				
Paracetamol (NSAID)	WWTPs			38[b]	6[b]		4060[b]	
Phenytoin (anticonvulsant)	WWTPs			40-73[a]; 5[b]	53-57[b]			
Primidone (anticonvulsant)	WWTPs			30-180[a]	14[b]			
Sulfamethoxazole (antibiotic)	WWTPs			170-380[a]	22-67[b]			
Salicylic acid (NSAID)	WWTPs			31-47[b]	20-42[b]		22-31[b]	
Temazepam (psychotropic)	WWTPs			110-240[a]				
Tramadol (analgesic)	WWTPs			420-2000[a]				
Trimethoprim (antibiotic)	WWTPs			32-130[a]				
Venlafaxine (psychotropic)	WWTPs			330-1200[a]				

Bold compounds were identified as potential risks based on calculated hazard quotients (HQs ≥ 1).

[a]O'Brien *et al.* (123); [b]Scott*, et al.* (256)

7.5 Likely presence in the GBR and TS marine ecosystems

The most likely sources of pharmaceuticals in the GBR and TS marine ecosystems are from WWTPs' effluents discharging into rivers that flow in the region. Therefore, the distribution of the human population and locations of WWTPs would influence the presence of pharmaceuticals in the GBR and TS regions. The current population of northern Queensland, Australia, exceeds 1.2 million people (257), with the majority of this population in Townsville (189,000 people), Cairns (169,000), Mackay (122,000), Rockhampton (118,000), Maryborough (100,000) and Bundaberg (94,000). Conversely, less than 5,000 people live in the Torres Strait region. There are over 50 operational wastewater treatment plants in coastal north Queensland that discharge into rivers that are connected to the GBR marine environment (258). Pharmaceuticals in the GBR and TS are therefore most likely adjacent to these population centres and point-source discharge sites. However, dilution following WWTP discharge is likely to be significant, greatly reducing pharmaceutical concentrations in the GBR and TS marine environments. For example, data for Sydney Harbour revealed relatively low (ng/L) concentrations of all measured compounds despite its proximity to a major urban centre (259). This could be taken as evidence that concentrations of pharmaceuticals in the marine environments will generally fall below concentrations expected to pose a significant risk to wildlife. However, this only considers inland urban sources and assumes that wastewater represents the only source for pharmaceuticals in the GBR and TS marine environments.

Due to the global value of the GBR as an important recreational and commercial area, pharmaceutical inputs could conceivably also arise from large commercial, military and recreational vessels, commercial fishing and tourism boats. Sources related to the tourism industry are particularly important and may prove to be relevant sources of pharmaceuticals in high use areas. Approximately two million people visited the GBR in 2014 (260), and human waste therefore represents a potential source of untreated waste in areas of in-water activities (e.g., snorkelling areas). In addition, the discharge of treated and untreated sewage from vessel septic tanks could add to the pharmaceutical loads in the GBR. However, it is unclear whether these sources have the potential to introduce sufficient pharmaceutical loads in the GBR to cause an environmental risk. Aquaculture and agricultural activities in north Queensland also present possible sources of pharmaceuticals, but limited information exists concerning sources other than domestic sewage.

To complement the limited monitoring data for pharmaceuticals in the GBR and TS, we prioritised pharmaceuticals likely to be found in WWTP effluent based on Australian prescription data, following methods described by King et al. 2015 (261). Briefly, the total mass of each pharmaceutical prescribed in Australia (in 2011) was calculated from Department of Health medicine data. The top 20 pharmaceuticals were then further investigated for metabolism/excretion in the human body and removal during sewage treatment (**Table 7-3**). In cases where metabolism/excretion and/or WWTP removal data was not available, the worst case scenario (100% excretion and 0% WWTP removal) were used in the calculations. From this approach, a predicted effluent concentration was calculated for each of the top 20 pharmaceuticals prescribed annually in Australia. This revealed a further 15 pharmaceuticals that had not previously been identified in Australian WWTP effluent or receiving environments. Furthermore, the four highest predicted effluent concentrations were all >10 µg/L, considerably higher than any other pharmaceutical concentrations previously reported in WWTP effluent or river water Australia-wide. While there are some uncertainties to this approach (*e.g.*, that all prescribed medications are consumed), predicted concentrations of the five pharmaceuticals that have also been reported in Australian WWTP effluent were similar to literature concentrations (**Table 7-2**, **Table 7-3**). This approach also highlights the fact that there are a number of pharmaceuticals likely to be in WWTP effluent that are currently not being monitored, and are potentially posing some risk to aquatic systems, particularly those for which toxicity data are limited.

Table 7-2: Main sources and occurrence data (ng/L) for pharmaceuticals identified through Australia-wide literature survey. Bolded compounds were identified as potential risks based on calculated hazard quotients (HQs ≥ 1). HQs were derived by dividing the reported or predicted concentration by the predicted no-effect concentration, using the most sensitive toxicity data obtained through ECOSAR.

Compound	CASRN	Class	Reported concentration (ng/L)		
			Wastewater Effluent	Rivers	Harbours
Amitriptyline	50-48-6	Antidepressant	6.1-74[b]	62 (max)[a]	
Amoxicillin	26787-78-0	Antibiotic	50 (max)[c]; 30 (max)[d]	200 (max)[c]	
Atenolol	29122-68-7	Beta blocker	94-695[b]; 300-600[e]; 140-360[f]	133 (max)[a]	
Atorvastatin	134523-00-5	Statin	5.4 - 85[b]; 20[e]		
Carbamazepine	298-46-4	Anticonvulsant	288-676[b];80-550[e]; 380-860[f]; 158-3205[h]; 1970 (max)[i]	682 (max)[a]	2.7 (max)[g]
Cefaclor	53994-73-3	Antibiotic	1800 (max)[c]; 60 (max)[d]	200 (max)[c]	
Cephalexin	15686-71-2	Antibiotic	250 (max)[c]; 210[e]; 190-450[f]	100 (max)[c]	
Chlortetracycline	57-62-5	Antibiotic	250 (max)[c]; 5 (max)[d]	600 (max)[c]	
Ciprofloxacin	85721-33-1	Antibiotic	720 (max)[d]	1300 (max)[c]	
Citalopram	59729-33-8	Antidepressant	20-80[e]		
Clindamycin	18323-44-9	Antibiotic	70 (max)[c]; 5 (max)[d]	10 (max)[c]	
Cloxacillin	61-72-3	Antibiotic	700 (max)[c]		
Clozapine	5786-21-0	Antipsychotic	12-59[b]	90 (max)[a]	
Codeine	76-57-3	Analgesic	400[e]; 150-310[f]		9.5 (max)[g]
Desmethyl diazepam	1088-11-5	Antianxiety	10-20[f]		
Diazepam	439-14-5	Antianxiety	6.1[b]	8 (max)[a]	
Diclofenac	15307-86-5	NSAID	38-272[b]; 10-90[e]; 60-260[f]; 550 (max)[i]		
Doxycycline	564-25-0	Antibiotic	150 (max)[c]; 40 (max)[d]	400 (max)[c]	
Enrofloxacin	93106-60-6	Antibiotic	50 (max)[c]; 10 (max)[d]	300 (max)[c]	20[e]
Erythromycin	114-07-8	Antibiotic	20[e]; 40-180[f]		
Fluoxetine	54910-89-3	Antidepressant	12-20[b]	22 (max)[a]	36 (max)[g]
Frusemide (Furosemide)	54-31-9	Diuretic	60[e]; 40-280[f]		
Gabapentin	60142-96-3	Anticonvulsant	50-3900[e]; 1000-1800[f]		
Gemfibrozil	25812-30-0	Fibrate	20-342[b]; 120-450[e]; 20-70[f]; 2860 (max)[i]	213 (max)[a]	
Hydrochlorothiazide	58-93-5	Diuretic	30-140[e]; 350-1100[f]		
Ibuprofen	15687-27-1	NSAID	20-457[b];1660 (max)[i]: 4.6-120[j]	44 (max)[a]	
Indomethacin	53-86-1	NSAID	20[e]; 20-40[f]		
Iopromide	73334-07-3	Contrast media	7600[e]; 50-2300[f]		10 (max)[g]
Ketoprofen	22071-15-4	NSAID	20-104[b]; 630 (max)[i]; 3.1-20.7[j]		

Lincomycin	154-21-2	Antibiotic	300 (max)[c]; 60 (max)[d]; 40[e]	50 (max)[c]	
Meprobamate	57-53-4	Antianxiety	8.2[b]		
Metformin	657-24-9	Antidiabetic	486-3710[b]; 90-160[f]		
Metoprolol	51384-51-1	Beta blocker	50-230[e]		
Monensin	17090-79-8	Antibiotic	20 (max)[c]	150 (max)[c]	
Nalidixic acid	389-08-2	Antibiotic	450 (max)[c]	750 (max)[c]	
Naproxen	22204-53-1	NSAID	36-483[b]; 500[e]; 95-270[f]; 1910 (max)[i]; 1.6-179[j]	347 (max)[a]	
Norfloxacin	70458-96-7	Antibiotic	250 (max)[c]; 40 (max)[d]	1150 (max)[c]	
Oleandomycin	3922-90-5	Antibiotic	150 (max)[c]	20 (max)[c]	
Omeprazole	73590-58-6	Proton pump inhibitor	5.2-9[b]	5 (max)[a]	
Oxazepam	604-75-1	Antianxiety	50-80[e]; 230-440[f]		
Oxycodone	76-42-6	Analgesic	10[e]; 50-90[f]		
Oxytetracycline	79-57-2	Antibiotic	70 (max)[c]; 20 (max)[d]	100 (max)[c]	
Paracetamol	103-90-2	Analgesic	8.2-102[b]; 17000[e]	7150 (max)[a];	67 (max)[g]
Penicillin G	61-33-6	Antibiotic	300 (max)[c]	250 (max)[c]	
Penicillin V	87-08-1	Antibiotic	2000 (max)[c]; 80 (max)[d]	10 (max)[c]	
Phenytoin	57-41-0	Anti-seizure	47-146[b];10-120[e]; 40-73[f]	145 (max)[a]	
Praziquantel	55268-74-1	Anthelmintic	10[e]		
Primidone	125-33-7	Anticonvulsant	54-205[b]; 20[e]; 30-180[f]	259 (max)[a]	
Propranolol	525-66-6	Beta blocker	10[e]		8.9 (max)[g]
Roxithromycin	80214-83-1	Antibiotic	500 (max)[c];100 (max)[d]; 40[e]	350 (max)[c]	
Salicycilic acid	69-72-7	Analgesic	16-46[b]	1530 (max)[a]	
Salinomycin	53003-10-4	Antibiotic		150 (max)[c]	
Simvastatin	79902-63-9	Statin	31[b]		
Sulfamethoxazole	723-46-6	Antibiotic	200 (max)[c]; 320 (max)[d]; 10-80[e]; 170-380[f]	2000 (max)[c]	
Sulfasalazine	599-79-1	NSAID	150 (max)[c]; 10 (max)[d]	30 (max)[c]	
Sulfathiazole	72-14-0	Antibiotic	600 (max)[c]; 5 (max)[d]	40 (max)[c]	
Temazepam	846-50-4	Sedative	30-110[e]; 110-240[f]		
Tetracycline	60-54-8	Antibiotic	20 (max)[c]; 30 (max)[d]	80 (max)[c]	
Tramadol	27203-92-5	Analgesic	80-270[e]; 420-2000[f]		5.8 (max)[g]
Triamterene	396-01-0	Diuretic	5.1-51[b]		
Trimethoprim	738-70-5	Antibiotic	45-313[b]; 250 (max)[c]; 70 (max)[d]; 20-120[e]; 32-130[f]	657 (max)[a]; 150 (max)[c]	
Tylosin	1401-69-0	Antibiotic	3400 (max)[c]; 65 (max)[d]	60 (max)[c]	
Venlafaxine	93413-69-5	Antidepressant	100-270[e]; 330-1200[f]		32 (max)[g]
Verapamil	52-53-9	Calcium channel blocker		36 (max)[a]	

NSAID: nonsteroidal anti-inflammatory drug

[a]Scott, *et al.* (256); [b]Leusch, *et al.* (262); [c]Watkinson, Murby, Kolpin and Costanzo (263); [d]Watkinson, Murby and Costanzo (264); [e]French *et al.* (265); [f]O'Brien *et al.* (123); [g]Birch, Drage, Thompson, Eaglesham and Mueller (259);[h]Allinson*, et al.* (266); [i]Ying, Kookana and Kolpin (267); [j]Hashim and Khan (268).

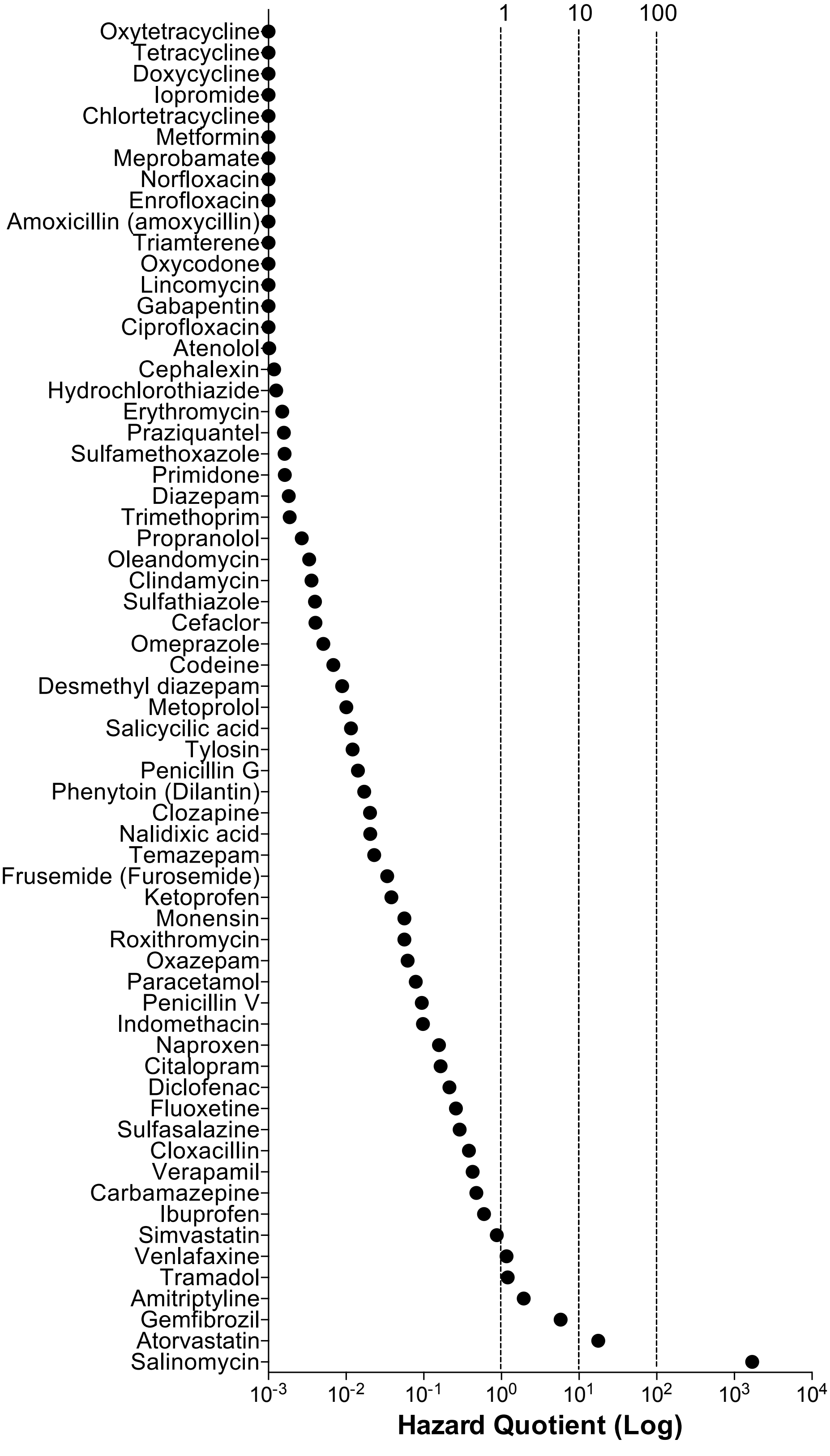

Figure 5: Ranked hazard quotients (HQs) for pharmaceuticals identified in Australian WWTP effluent and receiving environments, derived by dividing the reported or predicted concentration by the predicted no-effect concentration, using the most sensitive toxicity data obtained through ECOSAR. HQ <1 indicates no risk, 1 ≤ HQ < 10 represents a low risk, 10 ≤ HQ < 100 signifies a high risk, and HQ ≥ 100 indicates expected adverse effects.

Table 7-3: The top 20 most prescribed pharmaceuticals in Australia (by mass), including predicted concentrations in WWTP effluent (based on metabolism/excretion and WWTP removal) and hazard quotients (using ECOSAR toxicity data).

Compound	Mass prescribed (kg/yr)	Predicted concentration in WWTP effluent (ng/L)	HQ
Paracetamol	560,281	7,572	<1
Macrogol	369,728	18,033	<1
Metformin	126,869	19,437	<1
Lactulose	115,274	56	<1
Sodium valproate	44,868	66	<1
Irbesartan	27,549	338	N/A
Sterculia	21,815	12,061	N/A
Strontium ranelate	18,831	11,568	N/A
Calcium carbonate	18,414	1,131	N/A
Amoxicillin	17,615	2,207	<1
Celecoxib	15,223	71	<1
Atorvastatin	12,652	4	<1
Levetiracetam	9,442	3,828	<1
Naproxen	9,298	571	<1
Lithium carbonate	8,917	5,478	<1
Venlafaxine	8,319	206	<1
Sorbitol	7,789	574	<1
Gliclazide	7,530	142	<1
Clopidogrel	6,866	26	<1
Quetiapine	6,765	172	<1

7.6 Risk to the GBR and TS marine ecosystems

Although pharmaceutical monitoring data in the GBR and TS regions were largely limited to the Wet Tropics (123), the compounds identified in this area are likely to be present in other areas of north Queensland with similar population densities (i.e. Burdekin, Mackay-Whitsunday, Fitzroy and Burnett Mary). In addition, the pharmaceuticals identified in WWTP effluent and receiving environments at other locations in Australia are likely to be present wherever WWTP effluent is being discharged, although confirmation that these compounds are present in the GBR and TS cannot be established. At the other end of the scale, Torres Strait and Cape York, with a very small human population and few WWTPs, are unlikely to face any risk from pharmaceuticals in the marine environments. The spatial extent of the pharmaceutical risk would also be similar in the areas with higher population and WWTP numbers, with the presence of pharmaceuticals likely limited to coastal areas, and/or localised offshore areas with high prevalence of in-water tourism activities (e.g. snorkelling, diving). Perhaps the Wet Tropics, which hosts the most visitors to the GBR annually, would be at a slightly higher risk of pharmaceuticals via the additional source of direct discharge from human waste.

Hazard quotients (reported or predicted concentration divided by the predicted no-effect concentration, i.e. PNEC) were used to quantify the risks associated with pharmaceutical contaminants in the GBR marine environment. Pharmaceutical concentrations specific to the GBR were used where available, followed by data from other WWTPs in Australia and the predicted WWTP effluent concentrations, in cases where there was no data specific to the GBR. Toxicity estimates for all compounds were obtained from the US EPA Eco-toxicological Quantitative Structure Activity Relationship (ECOSAR) profiler (http://www.epa.gov/oppt/newchems/tools/21ecosar.htm). Acute toxicity estimates for fish, daphnia and algae were used to calculate PNECs for all pharmaceuticals by applying a 1,000x uncertainty factor, as per the guidelines outlined by the European Commission Guidance Document on Risk Assessment (269). Due to the scarcity of information directly relating to the GBR and TS marine environments and the uncertainty surrounding sources other than domestic wastewater, we applied an additional assessment factor of 10× to ensure that the HQs erred on the side of environmental protection. Pharmaceuticals were grouped according to the established framework (270, 271), where HQ <1 indicates no risk, 1 ≤ HQ < 10 represents a low risk, 10 ≤ HQ < 100 signifies a high risk, and HQ ≥ 100 indicates that adverse outcomes are expected (**Figure**).

Only three compounds identified in the GBR were considered to pose risk to the marine environment (**Figure** ; **Table 7-4**), all with 'low risk' HQs: gemfibrozil (HQ = 5.8), tramadol (HQ = 1.2), and venlafaxine (HQ = 1.2). While these HQs have been calculated largely from Cairns WWTP effluent concentrations, the risks are expected to be similar in all other GBR NRMs outside of Torres Strait and Cape York (as explained above). In addition, our consideration of national monitoring data resulted in salinomycin (HQ = 1700), atorvastatin (HQ = 18), and amitriptyline (HQ = 1.9) also being identified as potential risks (**Figure** ; **Table 7-4**), but whether these compounds are actually found in the GBR and TS marine ecosystems remains uncertain. Although none of the top 20 pharmaceuticals predicted to be in WWTP effluent posed a risk to the GBR marine environment (**Table 7-4**; all HQs<1), the risks of three of these compounds (irbesartan, sterculia or strontium ranelate) could not be assessed due to lack of toxicity data.

Table 7-4: Top 9 pharmaceuticals prioritised on risk to GBR marine environments (a), and priority ranking of highest risk pharmaceuticals based on a qualitative risk assessment in the GBR and TS marine ecosystems (b). Risk was considered similar to all NMRs except for TS and Cape York NRMs; no risk was considered in the latter due to low population and WWTP numbers. Priority order: (1) confirmed presence in GBR and HQ>1; (2) confirmed presence in Australia (but not GBR) and HQ>1; and (3) predicted in Australian WWTP effluent >1 µg/L and no available toxicity data. See Table 14-6 for detailed risk assessment scores.

(a)

Contaminant	Risk category	HQ
Gemfibrozil Tramadol Venlafaxine	Confirmed present in GBR WWTP effluent; HQ>1	5.8 1.2 1.2
Salinomycin Atorvastatin Amitriptyline	Not in GBR; present in Australia; HQ>1	1700 18 1.9
Irbesartan Sterculia Strontium ranelate	Predicted in Australian WWTP >1 µg/L; no available toxicity data	N/A N/A N/A

(b)

Main classes of emerging contaminant	NRM regions						
	Torres Strait	Cape York	Wet Tropics	Burdekin	Mackay-Capricorn	Fitzroy	Burnett Mary
Pharmaceuticals Gemfibrozil, Venlafaxine, Tramadol	4	4	20	20	20	20	20

It is important to note that the HQs were calculated based on WWTP effluent concentrations, with an additional 10× uncertainty factor applied, so actual risks following dilution in the marine environment may be significantly lower. Nevertheless, numerous studies have demonstrated that sub-lethal outcomes from exposures to low concentrations of pharmaceuticals can often have implications for higher-level biological processes (e.g., survival, health and population fitness) (272, 273). This highlights the need for more research surrounding the sources, fate, and effects of emerging pharmaceutical contaminants in marine environments.

7.7 Discussion, recommendations and conclusion

Our survey of the literature confirms the recognised difficulty in predicting the relative risks posed by pharmaceuticals compared to other anthropogenic contaminants entering marine environments, due to paucity of monitoring and toxicity data (274). Pharmaceutical risks have been well studied for freshwater environments (275), but marine ecosystems have been largely ignored due to the assumption that dilution would greatly reduce the risk. Considering the value of the GBR and TS marine ecosystems, it might be expected that Australian research be at the forefront of global efforts. In contrast, a recent review of worldwide pharmaceutical risks to marine environments demonstrates the extremely limited monitoring data available for Australia compared to other parts of the world (274). We were able to identify more studies and data for a greater number of pharmaceuticals than that review, but still conclude that data are limited.

Researchers are only beginning to recognise the sensitivity of coral reef ecosystems to pharmaceuticals and other contaminants that are widely used by humans. Risks may be even greater considering the likelihood of complex mixtures associated with wastewater discharge (251, 276). However, the overall conclusion from our survey of the literature and subsequent risk assessment is the need for better monitoring of pharmaceutical contaminants in the GBR and TS marine environments. Prior to commencing sampling and pharmaceutical screening with broad chemical analysis, it would be prudent to further develop a short-list of potentially high-risk compounds using predictive methods for risk prioritisation (261, 277). We performed the first step in the identification of priority pharmaceuticals relevant for inclusion in monitoring programs targeting the GBR and TS marine environments, by basing risks estimates on prescription data, metabolism and excretion data (pharmacokinetics), and removal during sewage treatment. This strategy will help avoid the pitfalls of the Matthew Effect (commonly known as the ‘bandwagon effect’), where available monitoring and toxicity data influences and biases future research activities (253). Once a comprehensive suite of pharmaceuticals has been identified for monitoring using this process, collaboration on regional, national and international scales will be necessary to generate a comprehensive database of compounds posing a risk to marine environments, and particularly the high value GBR and TS.

8.0 PERSONAL CARE PRODUCTS

Authors: Rai Kookana, Mike Williams, Frederieke Kroon

8.1 Summary

The presence of personal care products (PCPs) in consumer products is virtually ubiquitous. From plasticisers in plastics to preservatives in cosmetics, PCPs are present in products that we apply to our bodies, consume with our food or that have become highly useful in our day to day life. PCPs can therefore be released into sewage when we excrete or wash them from our body or are used to wash our bodies with, from which they can then pass through WWTPs to varying degrees. PCPs that are applied dermally, such as in cosmetics or sunscreens, can also be directly washed from our bodies into the environment.

Currently, there is little available data relating to concentrations of PCPs in the GBR and TS regions. Sources of PCPs in the GBR and TS marine environment are most likely to occur in areas of higher population density where greater volumes of WWTP discharge will occur. The greatest inputs are therefore likely to occur in urban locations of the Wet Tropics (e.g. Cairns), Burdekin (e.g. Townsville), Fitzroy (Rockhampton and Gladstone), Mackay Whitsunday (e.g. Mackay) and Burnett Mary (e.g. Bundaberg) natural resource management (NRM) areas of the GBR and TS. Also, reefs adjacent to these population centres, especially in the Wet Tropics NRM, would also be exposed to a range of dermally applied PCPs. With a large degree of uncertainty relating to concentration, fate and effects of PCPs (especially data relevant to the GBR and TS region), a potentially high degree of toxicity identified for a number of PCPs (including triclosan) highlighted in this report and the broad diversity of chemicals classified as PCPs, it is recommend that a more detailed assessment of PCPs within the GBR and TS NRM areas adjacent to urban centres is warranted.

8.2 Introduction

A wide range of organic compounds are used by human populations as PCPs e.g. cosmetics, creams, soaps and shampoos. PCPs are chemicals generally used on the human body to alter odour, appearance, touch or taste as active ingredients of cosmetics, toiletries or fragrances (278). Due to their widespread use, these products are considered high volume products (produced in thousands of tons), which are released into waste streams from population centres or at sites associated with human activities (e.g. tourism or recreation activities), sometimes with little or no transformation of the PCP occurring before release into the environment.

PCPs are receiving increasing attention globally due to their potential ecotoxicological effects on aquatic and terrestrial organisms (278). Many PCPs are persistent (e.g. artificial sweeteners, x-ray contrast agents), bioaccumulative (e.g. synthetic fragrance musks and some UV filters) and toxic (e.g. antimicrobials), thus making them of concern for their potential impacts on the health of aquatic ecosystems. In addition PCPs can also have subtle, yet profound, effects such as endocrine disruption (89).

Daughton and Ternes (1999) expressed their concerns about pharmaceuticals and PCPs (PPCPs) as follows:

"*Subtle effects, from low concentrations of bioactive PPCPs, whose continual expression over long periods of time in certain nontarget populations, could lead to cumulative, insidious, adverse impacts that would otherwise be attributed to natural change/ adaptation or ecologic succession—any "signal" would be lost among the noise. Current comprehensive environmental risk assessments and epidemiologic studies do not factor in exposures/body burdens from PPCPs and therefore may be flawed by over simplicity*."

Pharmaceuticals in the GBR and TS region are covered in the 'Pharmaceuticals' chapter; here we only consider PCPs.

8.3 Main classes of personal care products

PCPs represent a broad class of chemicals that are present in a large array of consumer products and are generally intended for external use, although a number are also present in food products. Because of the broad range of applications for PCPs, they are also represented by a broad range of classes of compounds, both in terms of function and physicochemical properties. Some of the common classes of PCPs, with an example of an active ingredient associated with the class, include:

- Surfactants and their transformation products (e.g. nonylphenol, quaternary ammonium compounds)
- Disinfectants and antimicrobials (e.g. triclosan, parabens)
- Insect repellents (e.g. DEET)
- Musks and fragrances (e.g. galaxolide, tonalide)
- UV filters (e.g. benzophenone, octocrylene)
- Plasticisers (e.g. Bisphenol A (BPA), Diethylhexylphthalate (DEPH), phthalates)
- Anticorrosives (e.g. benzotriazoles)
- Artificial sweeteners (e.g. acesulfame, aspartame)

8.4 Presence, concentration and location in the GBR and TS marine ecosystems

Currently, there is little data available on PCPs in the GBR and TS regions. One study has reported concentrations of five PCPs released from two WWTPs in Cairns, located in the Wet Tropics NRM area (**Table 8-1**). Two of the PCPs, acesulfame and iopromide, were detected at low μg/L concentrations in the WWTP effluent stream, which is consistent with stormwater and WWTP effluent concentrations measured in other studies not located in the GBR and TS region (265, 279). Acesulfame is an artificial sweetener used in a wide variety of food products and due to persistence within WWTPs and the environment, it has often been used to track both intentional and unintentional WWTP discharges (279, 280). Iopromide is also highly resistant to degradation during wastewater treatment and its high dosage rates for its use as an X-ray contrast agent means that it is often detected at relatively high concentrations in WWTP effluents (265, 281).

Table 8-1: Main sources, available monitoring and ecotoxicity data and hazard quotients for personal care products in the GBR and TS marine ecosystems. WWTP = waste water treatment plant.

Main classes of emerging contaminant	**Main sources**	**NRM regions**							**Other[#] (ng/L or kg)**	**NOEC^ (ng/L)**	**HQ[$]**
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**			
Acesulfame	WWTP	-	-	<LOR-4400[1]	-	-	-	-	20,000 (max) (WW)[a]	$7.2x10^{9}$ (EC_{50})[b]	$3x10^{-3}$
Benzalkonium Cl	WWTP	-	-	-	-	-	-	-	<LOR-865 (WW)[c]	41,000 (EC_{50})*[d]	21
Benzophenone 3	WWTP dermal	-	-	-	-	-	-	-	2.5-175 (WW)[e]	132,000*[f]	0.13
Benzotriazole	WWTP	-	-	-	-	-	-	-	3,900 (max) (WW)[a]	$1x10^{7}$ [g]	0.04
Bisphenol A (BPA)	WWTP	-	-	-	-	-	-	-	40±17 (SW)[h]	100,000[j]	0.04
Propylparaben	WWTP dermal	-	-	-	-	-	-	-	218 (max) (WW)[k]	$9.9x10^{6}$ [k]	0.002
Caffeine	WWTP natural			<LOR[1]					130±28 (WW)[k]	$5.2x10^{6}$ *[k]	0.003
DEET	WWTP dermal	-	-	-	-	-	-	-	490 (SW)[l]	$3.7x10^{6}$ *[m]	0.013
DEHP	WWTP dermal plastics natural	-	-	-	-	-	-	-	644±253[h] (SW)	109,000[n]	0.6
Galaxolide	WWTP dermal	-	-	-	-	-	-	-	2,000 (max) (WW)[a]	470,000 (EC_{50}) [e]	4.2
Iopromide	WWTP	-	-	<LOR-2300[1]	-	-	-	-	7,600 (max) (WW)[a]	>$1x10^{9}$ (EC_{50}) *[o]	<0.008
Nonylphenol	WWTP	-	-	-	-	-	-	-	335±96[h], 614-2,991[p](WW) 48±7[h], 287-2,058[p] (SW)	130,000[j]	2.3
Triclosan	WWTP	-	-	<LOR-30[1]	-	-	-	-	23-434 (WW)[q], 5,000-27,000 (sed)[r]	19,100 (EC_{50}) [e] 60,000 (sediment EC_{25}) *[e]	23 (water) 450 (sediment)

[#]data from other Australian WWTPs; ^ no observable effect concentration or EC_{50} values (where applicable), lowest values have been reported with PNEC values obtained by dividing NOEC values by an AF; *ecotox data from freshwater species; [$]hazard quotient (PEC/PNEC), PNEC obtained using AF=100 (NOEC) or 1000 (EC_{50})

References: [1](123), [a] (265), [b] (282), [c] (283), [d] (284), [e] (285), [f] (286), [g] (287), [h] (288), [j] (289), [k] (290), [l] (291), [m] (292), [n] (293), [o] (281), [p] (294), [q] (295), [r] (296) The stimulant caffeine, widely found in beverages and also naturally present in many plant species, was not detected in the WWTP effluent samples, which may be attributable to its lability during wastewater treatment (297). Caffeine has been detected, however, at concentrations ranging up to low μg/L in Australian stormwater and surface waters, including SE Queensland (279, 290). This indicates that there is potential for caffeine to be discharged at least into near-shore environments close to areas of higher urban density.

Triclosan, an antimicrobial commonly found in products such as toothpaste and detergents, was measured at concentrations up to 30 ng/L, which is within the same range found in other Australian WWTPs (295, 296). Since triclosan is a hydrophobic compound, it associates to a higher degree with suspended solids and sediments and higher concentrations are usually measured in sediments, relative to the water column (296).

8.5 Likely presence in the GBR and TS marine ecosystems

With PCPs largely associated with use in consumer products, rates of release into the environment are expected to be associated with population centres and, in particular, due to releases from WWTPs. However, diffuse entry into the environment of PCPs present in dermally-applied cosmetics, sunscreens and insect repellents is also likely (285). The population density of urban centres in the GBR and TS region is less than other coastal regions in Australia, based on the population size and geographic area (257). There are over 50 operational wastewater treatment plants in coastal north Queensland that discharge into rivers that are connected to the GBR marine environment. The current population of northern Queensland exceeds 1.2 million people (257), with the majority of this population in Townsville (189,000 people), Cairns (169,000), Mackay (122,000), Rockhampton (118,000), Maryborough (100,000) and Bundaberg (94,000). Conversely, less than 5,000 people live in the Torres Strait region. Near-shore discharges from WWTPs are therefore likely to be greatest from these urban centres. These urban centres are also likely to be important staging points for visitors to offshore reefs, where direct inputs of PCPs may be important.

An Australia-wide survey of four PCPs (caffeine, propylparaben, triclocarban and triclosan) included monitoring surface waters from unspecified locations within a number of GBR and TS NRM areas (**Table 8-1**) (290). Despite the locations not being specified, it would be reasonable to assume that the measured concentrations and frequencies of detection in this survey would be indicative of what may have been found in the GBR and TS NRM areas. With population densities in the GBR and TS region lower than those found in other coastal regions of Australia (e.g. regions surrounding state capitals), the lower end of the measured ranges in this study are likely to be most applicable to the GBR and TS regions. Mean concentrations of triclocarban, triclosan and propylparaben, all antimicrobial compounds, were below their respective limits of reporting (LOR), which were all 10 ng/L (290). The 95th percentile of triclosan and propylparaben were reported as 24 and 20 ng/L and they were measured in 25 and 12%, respectively, of the 285 samples collected. Since these were surface water samples, which would have undergone at least some degree of dilution, the concentrations of triclosan are in broad agreement with what has been measured in other areas of Australia (265, 295). No previous reports of the preservative propylparaben are known to have been reported in Australia, although with its high volume of use in cosmetics and food products (along with a range of other parabens) and its high frequency of detection in other countries, its presence would be expected albeit at low (e.g. ng/L) concentrations (298).

Other data were available for other PCPs (e.g. alkyphenols, triclosan, artificial sweeteners, DEET etc.) from WWTPs located in other regions of Queensland and Australia (**Table 8-1**). This data can be used for estimating the potential loading of PCPs in WWTP effluents and receiving waters, assuming similar population levels service by and removal efficiency of the WWTPs. Other antimicrobials, preservative, insect repellents, plasticizers, UV filters and fragrances were also detected in these studies at concentrations ranging from ng/L to low μg/L.

With the number of organic chemicals used in cosmetics, cleaning products, food products, plastics and other consumer products, however, the number of PCPs entering at least the near-shore environment through WWTP and stormwater discharges would be vastly greater than has been currently documented through targeted chemical analysis. Furthermore, with the personal application of consumer products (such as sunscreens, insect repellents and skin care products), the number of PCPs directly entering the marine environment would be considerably greater than outlined in **Table 8-1**. The loads and associated concentrations (dependent on e.g. loadings of PCPs in consumer products, their application rates and their fate once released into the environment) is much harder to quantify although it would be reasonable to expect they would be similar to measured PCPs.

8.6 Risk to the GBR and TS marine ecosystems

Previous studies assessing the ecological risks of PCPs generally use a hazard quotient (HQ) approach, where the highest measured (or predicted) concentrations (MEC or PEC; see **Table 8-1**) are compared with the lowest concentrations where no effect (PNEC) is expected to occur (285). Assessment factors (AFs) are often applied to ecotoxicity data to make ecological risk assessments more conservative and therefore more likely to identify potential risks (269) . In this case, an AF of 1000 was applied to EC_{50} values and an AF of 100 was applied to no-observable effect concentration (NOEC) data, since these represent the most conservative case. Many of the derived PEC and PNEC data (**Table 8-1**) have a great deal of uncertainty related to them (e.g. concentrations of PCPs in marine waters, use of freshwater or short-term ecotoxicity data) and the HQ values reported are therefore indicative only of potential risks.

PCPs identified as having HQ >1 include the antimicrobial quaternary ammonium surfactant benzalkonium chloride (HQ=21), the musk fragrance galaxolide (4.2), a nonionic surfactant by-product nonylphenol (2.3) and the antimicrobial triclosan (23 water; 450 sediment). Algae are found to be particularly sensitive to the antimicrobials benzalkonium chloride and triclosan, with EC_{50} values reported for *Pseudokirchneriella subcapitata* and *Navicula pelliculosa*, respectively. The affinity of triclosan to sediments and its reported toxicity to the freshwater benthic organism *Hyalella azteca*, however, would suggest that there are also potential risks to benthic organisms (**Table 8-1**). A risk assessment for triclosan has previously been conducted by the Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) (299). This risk assessment derived values from a number of international freshwater-based studies for assessment of risks to the marine environment. The PNEC value used in the NICNAS report was less conservative than the value we derived, which was 50 ng/L for aquatic organisms (compared with our value of 19.1 ng/L) and 200 ng/L for sediment dwelling organisms (compared with 60 ng/L) (**Table 8-1**). PEC values for the NICNAS report were also less conservative, with surface water concentrations predicted to be <10 ng/L. Our PEC took into account the worst-case measured Australian

WWTP effluent concentration of 434 ng/L (**Table 8-1**). If the highest WWTP concentration from a Cairns WWTP effluent (30 ng/L) was used instead, an HQ of 1.5 would still be arrived at, while using the NICNAS PNEC of 50 ng/L would lead to an HQ of 0.6.

Benzalkonium chloride, galaxolide and nonylphenol (similar to triclosan) also have a high affinity for sediments and particulate matter. Benzalkonium chloride has had high concentrations measured in the mg/kg range in marine sediments in the USA (300) although this strong association with sediment has been found to reduce the benthic toxicity of other quaternary ammonium surfactants (301). This has also been found to be the case with galaxolide (302). Although the environmental concentrations of nonylphenol are somewhat mitigated by biodegradation and association with sediments, there is still concern relating to its presence in the environment such that its use has been banned in the EU and it is strictly monitored in Canada and Japan (303).

Other PCPs with a HQ between 0.1 and 1 included the UV filter benzophenone 3 (0.13) and the plasticizer DEHP (0.6). Benzophenone 3 (or oxybenzophenone) is found in many cosmetics and sunscreens for its UV filtering properties and its presence in PCPs has been found to contribute to bleaching in coral (304). In this particular study it was postulated that benzophenone 3 (and other UV filters present in the sunscreen) were acting through enhancing susceptibility of zooxanthellae to viral infections. Another study has found that high concentrations of benzophenone 3 (1 mg/L) can shield other chemicals present in solution from UV photolysis (305) but whether this could plausibly have a similar shielding mechanism (as per increased coastal sediment loads) at low doses in the environment requires further investigation. Even with an unclear mode of action, benzophenone 3 (along with other UV filters and preservatives used in sunscreens and cosmetics) is significant in that it can directly enter the marine environment in close proximity to communities of coral reefs. Estimates of loads entering the marine environment in such a manner could be broadly undertaken based on visitor numbers which are collected for the entire GBR and TS region by GBRMPA (http://www.gbrmpa.gov.au/visit-the-reef/visitor-contributions/gbr_visitation/numbers). The number of visitors estimated to have visited the reef (based on tourist operator logs) was around 700 per day in 2014, with more than 97% of these visitations occurring around Cairns, within the Wet Tropics NRM area. An analysis of release of sunscreens following application, suggested around 5 g of sunscreens can be released into the environment per application, with two applications per day commonly undertaken (304). With the maximum permissible sunscreen composition of organic UV filters being 15% (http://www.tga.gov.au/publication/australian-regulatory-guidelines-sunscreens-args), the maximum release per person would be around 150 mg released from 10 g applied sunscreens, or ~100 g of active ingredient per day around a highly visited reef near Cairns (assuming all 700 people visited the same reef). The final concentrations of UV filters derived from sunscreens and cosmetics is dependent on the volume of water surrounding a reef, where a more concentrated visitor zone would increase the risk. Recommended applications of sunscreens, however, would be expected to lead to a high extent of dilution in the marine environment, although it is notable that sunscreen concentrations of 10 μL/L were found to have significant effects on coral bleaching (304). While the risk of propylparaben was considered to be relatively low (**Table 8-1**), other parabens used as preservatives in sunscreens can have a significant effect on coral bleaching (304).

The plasticizer DEHP also had an HQ between 0.1 and 1 (HQ=0.6). DEHP is a weakly estrogenic compound but its presence in a considerably broad range of consumer products means that it also widely distributed throughout the aquatic environment, including sediments (306). Other PCPs with known effects on the endocrine system, otherwise known as endocrine disrupting chemicals (EDCs), include BPA and nonylphenol. While each of these PCPs individually are only likely to have a weak effect on endocrine function in exposed aquatic organisms, around 800 chemicals are known to interfere with normal endocrine function (89). This makes exposure to EDCs highly likely from a complex mixture such as WWTP discharges.

Based on the limitations of evidence available to make a highly certain assessment of risks relating to PCPs in the GBR and TR region, it is still possible to identify areas where higher risks are possible and further assessments should be focussed on these areas. Since the principal route of PCP entry into the marine environment is through WWTP discharges, areas with higher population densities are therefore more likely to have higher PCP loads. Without considering tidal influences and other potential transportation mechanisms (e.g. association with sediments or suspended particulate matter) within the marine environment, the most important NRM areas for further assessments are the Wet Tropics, Burdekin, Fitzroy and Burnett Mary and, in particular, nearshore environments close to urban centres and WWTP discharges within these NRM areas (**Table 8-2**). Some of the PCPs applied to the skin (e.g. UV filters, preservatives and insect repellents; **Table 8-1**) may also enter the marine environment following dermal release in tourist hotspots, including popular reef viewing areas. Such PCPs have been assessed as having a potentially greater area of influence (**Table 8-2**), although the potential for adverse effects is dependent on the PCP.

Table 8-2: Priority ranking of personal care products, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. Only those personal care products with a score >10 are shown. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Benzalkonium Cl	3	3	12	12	12	12	12
Benzophenone 3	12	12	30	30	30	30	30
Bisphenol A	4	4	10	10	10	10	10
DEHP	8	8	20	20	20	20	20
Galaxolide	4	4	16	16	16	16	16
Triclosan	4	4	16	16	16	16	16

While HQ values reported for a number of PCPs were close to or >1, indicating a potential risk in the marine environment, PEC and PNEC values to derive the HQ were highly conservative (**Table 8-1**). For example, PEC values were usually based on WWTP effluent concentrations, which do not account for substantial dilution when released into the marine environment, while PNEC values were at concentrations orders of magnitude higher compared than experimentally observed effects following application of AFs. Despite such qualifications, the required data to make more certain risk assessments of the identified PCPs are not available, especially with respect to data pertinent to the marine environment within the GBR and TS regions.

8.7 Discussion, recommendations and conclusion

Estimating the risks for the PCPs identified in **Table 8-1** are dependent upon a number of assumptions, which are necessary *in lieu* of the knowledge gaps that exist in relation to concentrations, fate and effects of the PCPs. This is not only true for the GBR and TS region but also for Australia, as well as globally. Where HQ values were within an order of magnitude of 1, adjustment of input factors relating to PEC or PNEC (e.g. concentrations, levels of dilution, assessment factors) made a considerable difference as to whether the case for a perceived risk is stronger (HQ>1) or weaker (HQ<1).

Despite the variability in HQ values for triclosan, it has previously been found by NICNAS to have a high to very high risk for a number of aquatic organisms, including bacteria, algae, invertebrates and fish (299). Extrapolation of the risk of triclosan from the freshwater to the marine environment, however, was considered to reduce the potential risks to an acceptable level due to high dilution when it is discharged from a point source, usually in WWTP effluents (14). A number of critical gaps were identified in this risk assessment, including a paucity of data relating to concentrations of triclosan (and its metabolites) in WWTP effluents or in the environment in Australia. Furthermore, there are notable knowledge gaps relating to the ecotoxicity of triclosan (and its metabolites) to aquatic species and this is particularly the case for species residing in Australia (299). Considering the high potential for triclosan (and its metabolites) to bioaccumulate, the toxicity of triclosan at ng/L concentrations, the poorly defined fate of triclosan within the marine environment and the lack of knowledge relating to the concentration, fate and effects of triclosan relevant to the GBR and TS regions, it is apparent that a more detailed analysis of triclosan is required.

The likelihood of consequences assessment indicated a number of other PCPs with a higher rating than triclosan (**Table 8-2**). This was mainly related to their likely release into a broader geographic area than the principally WWTP-derived triclosan. The PCPs galoxolide and benzophenone 3 can be dermally applied in products such as sunscreens, fragrances and other cosmetics, which can then be released *in situ* in tourist hotspots on the reef. DEHP is not only used in cosmetics but it also has extremely widespread use in plastics and is considered a priority substance by NICNAS (307), along with a number of other phthalates (see http://www.nicnas.gov.au/chemical-information/pec-assessments). The use of the antimicrobial preservative propylparaben in cosmetics means it could also be more widespread than WWTP-derived PCPs. Based on available information, it has a considerably lower degree of known toxicity (**Table 8-1**) despite related parabens being found to potentially affect coral bleaching (304). Future assessments of potential risks of PCPs in the GBR and TS regions should therefore focus on the more highly populated urban areas, where greatest volumes of WWTP discharges occur, within NRM regions identified as having a higher priority (**Table 8-2**). Tourist hotspots, where release of dermally-applied PCPs could also occur, should also be identified within these NRM regions and available tourist visitation data in this respect provides useful guidance for this.

With little monitoring data for PCPs in the GBR and TS regions (or indeed, globally) it is difficult to confidently derive PECs for HQs and the need for local, targeted monitoring campaigns would be an important step in reducing this uncertainty. The lack of certainty related to PECs, in combination with a lack of understanding of the effects of PCPs in the marine environment, means that HQs derived from currently available information are likely to have a high degree of uncertainty associated with them. With a number of the PCPs identified in this report having a concerning degree of ecotoxicity associated with them, however, it would be prudent to undertake a more detailed assessment of both distribution and potential ecotoxicological effects of PCPs within the GBR and TS regions. Distribution throughout the environment could be related to factors such as tidal flow and sediment transport in the proximity of WWTPs (for particle associated PCPs). Monitoring of PCPs that are considered to be a lower risk, such as artificial sweeteners, have proved to be a useful approach for tracking WWTPs in aquatic environments (280). A more detailed review of effects on marine organisms could include, where possible, derivation of species sensitivity distributions to give greater confidence in PNEC values. This will ensure a greater degree of certainty and confidence can be assigned to such compounds for any mitigation strategies, including derivation of appropriate water quality guidelines.

PCPs as a class of compounds, however, are an extremely diverse array of chemicals with a similarly broad range of physicochemical properties with many PCPs having little or no information relating to their ecological fate or effects. In the process of prioritising PCPs for further assessment, identification of PCPs with a greater amount of available data could be used as a surrogate for other PCPs with, for example, similar physicochemical properties, environmental release pathways or modes of action. Based on the current lack of understanding relating to PCPs, not only regionally but also globally, such a task would also require considerable collaborative efforts on a regional to global scale to properly target PCPs of greatest concern and collate suitable concentration, fate and effects data.

9.0 NANOMATERIALS

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9.1 Summary

The use of engineered nanomaterials (NMs) in consumer products over the last decade has rapidly increased, with a likely increase in environmental exposures following post-consumer use discharges. The principal sources of NMs in the environment are expected to come from wastewater treatment plant (WWTP) effluents, as well as direct release of NM-containing consumer products. This would suggest that higher risks from NMs would be apparent in areas with higher population densities in the GBR (GBR) and Torres Strait (TS) regions, which would include areas in the Wet Tropics (e.g. Cairns), Burdekin (e.g. Townsville), Fitzroy (Rockhampton and Gladstone), Mackay Whitsunday (e.g. Mackay) and Burnett Mary (e.g. Bundaberg) natural resource management (NRM) areas. Visitors to reef zones are highest adjacent to these population centres.

There is currently no information, however, relating to concentrations of NMs in the GBR and TS regions. Also, available peer-reviewed literature relating to the fate and effects of NMs in marine ecosystems is limited, with many exposure scenarios unlikely to represent the marine ecosystem within the GBR and TS regions due to lower population pressures and mitigating effects of the marine environment on concentrations of NMs in the water column (e.g. dilution). Finally, demonstrated effects of NMs on individual organisms or indeed communities of organisms are also unclear and, therefore, characterising risks in the GBR and TS regions are highly uncertain.

9.2 Introduction

The use of engineered nanomaterials (NMs), or materials measuring 1 – 100 nm in at least one dimension, in consumer products has dramatically increased in the last decade (308). The knowledge relating to the consequences of their release into the environment, however, has advanced at a much slower rate. Because of the surface to area ratio of NMs, they are likely to be highly reactive once released into the environment which makes the characterisation of their environmental fate and effects all the more critical. In relation to the marine environment, NMs in consumer products have raised concerns relating to their potential effects on coral and phytoplankton (308-311).

9.3 Main classes of nanomaterials

The majority of NMs in use relate to applications in personal care products, the majority of which are metal and metal oxide NMs (310, 312). Silver (Ag) nanomaterials have a wide range of applications due to their antimicrobial properties, while titanium oxide (TiO_2) and zinc oxide (ZnO) nanomaterials are used in cosmetics and sunscreens due to their effective UV screening properties. Cerium oxide (CeO_2) nanomaterials are used as a diesel fuel additive, while carbon nanomaterials (fullerenes) are by-products of combustion processes.

9.4 Presence, concentration and location in the GBR and TS marine ecosystems

There is currently no available monitoring data relating to NMs in the GBR and TS marine ecosystems (**Table 9-1**).

Table 9-1: Main sources and available monitoring data for nanomaterials in the GBR and TS marine ecosystems.

Main classes of emerging contaminant	**Main sources**	**NRM regions**						
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Ag	WWTPs (personal care products)	NA*	NA	NA	NA	NA	NA	NA
TiO_2	WWTPs, recreation (cosmetics, sunscreens)	NA	NA	NA	NA	NA	NA	NA
ZnO	WWTPs, recreation (cosmetics, sunscreens)	NA	NA	NA	NA	NA	NA	NA
CeO_2	Transport run-off (diesel exhaust)	NA	NA	NA	NA	NA	NA	NA
Carbon-based (e.g. fullerenes)	WWTPs, combustion	NA	NA	NA	NA	NA	NA	NA

*NA = data not available

9.5 Likely presence in the GBR and TS marine ecosystems

Since the majority of nanomaterials sourced from human activities are primarily associated with wastewater discharges (313), the presence of wastewater treatment plants (WWTPs) and populations that are serviced by the WWTPs are likely to give the best indication of the potential loads entering the marine environment. There are over 50 operational wastewater treatment plants in coastal north Queensland that discharge into rivers that are connected to the GBR marine environment (258). The current population of northern Queensland exceeds 1.2 million people (257), with the majority of this population in Townsville (189,000 people), Cairns (169,000), Mackay (122,000), Rockhampton (118,000), Maryborough (100,000) and Bundaberg (94,000).

The majority of available data on the environmental concentrations of NMs are based on predicted environmental concentrations (PECs) based on modelling (314). Measured environmental concentrations (MECs) of nanomaterials are rare, with a small number of papers reporting MECs for nano-Ag, nano-TiO_2 and fullerenes. Nano-Ag was measured in WWTP effluent in Boulder, Colorado (population ~100,000) at a concentration of 100 ng/L (315). An MEC of 5.7 μg/L of colloidal TiO_2 was measured in WWTP effluent serving ~324,000 people, while 1.6 μg/L of TiO_2 was measured in WWTP effluent from a Canadian town of population ~100,000 (316). MECs of C60 and C70 fullerenes in Spanish wastewater effluent were below 5 ng/L for WWTPs serving between 135,000 – 424,000 people (317).

These reported MECs are generally comparable with PECs derived from modelling (318). Considering the populations serviced by WWTPs in the GBR and TS regions, a conservative assumption that centres with the highest population (e.g. Townsville) are serviced by a single WWTP, the expected concentrations of NMs would be similar to MECs reported in literature. Discharge into the nearshore environment would be expected to greatly mitigate these concentrations due to both dilution effects and the tendency of NMs to agglomerate appreciably in saltwater (314). Also, wastewater treatment is likely to reduce the toxicity of NMs through agglomeration, association with particulate matter or transformation to less toxic species, such as Ag_2S (313, 319).

Another potentially important source of NMs in the marine environment is through direct release of NMs from applied personal care products, including sunscreens and deodorants, during recreational activities (314, 320, 321). For example, an analysis of the release of TiO_2 release into an enclosed marine bay (0.016 km^2, average depth 1.5 m) estimated ~4 kg of nano-TiO_2 could be released each day, leading to approximate concentrations of 0.3 mg/L nano-TiO_2 (320). It is likely that the assumptions made in this analysis are also likely to be substantially mitigated within the GBR and TS regions (*see* Risk to the GBR and TS marine ecosystems). Run-off during storm events of nano-CeO_2 released from diesel exhaust are estimated to make sporadic and short-term contributions to near shore concentrations (up to 300 ng/L), although long-term loadings are expected to be negligible (322).

Dissolution of NMs, resulting in the free metal ion in solution, association of NMs in solution with either other NMs or naturally occurring particulate matter (aggregation) and formation of less-reversible clusters of NMs (agglomeration) are likely to dominate the environmental fate of NMs and mitigate their potential risks in the aquatic environment (313, 323).

9.6 Risk to the GBR and TS marine ecosystems

A number of studies have assessed the potential effects of NMs in marine organisms, including coral, algae, macro-invertebrates and fish, although there is considerably less data available compared with studies relating to effects of NMs in freshwater organisms (324). Furthermore, this data is further confounded based on the difficulty of characterising the fate of NMs within the marine environment. In general, the majority of studies assessing effects in marine organisms have focussed on sub-lethal effects, such as stress response or immune system function, with implications for effects on higher organism or population function being less clear (314, 324). For example, expression of proteins, such as heat shock protein (HSP), superoxide dismutase (SOD) and metallothionein (MT), related to an organism's response to a stressor have been demonstrated to be affected in marine annelids, bivalves and fish (321, 325).

The effects of NM exposure are often driven by the dissolution of the metal (oxide) NM and subsequent exposure of the organism to, for example, Ag^+, Cu^{2+} or Zn^{2+} (314). Therefore the dissolution of NMs into free ions in the marine environment may give an indication of their potential toxicity. Fate of wastewater-derived NMs, however, suggests aggregation and agglomeration in the marine environment is more likely to occur, due to high ionic strength and presence of organic matter in the near-shore environment. This may have important implications for filter feeders, such as bivalves, or sediment particle feeders, such as polychaetes and gastropods, although noted effects were generally sub-lethal (314, 324).

Exposure concentrations also tend to be at levels not expected in marine environments, especially when mitigating effects such as agglomeration are taken into account (324). For example, nano-TiO_2 was found to induce partial bleaching (14% reduction of zooxanthellae numbers) and a five-fold increase in HSP expression at concentrations of around 100 μg/L in the Caribbean coral, *Montastraea faveolata* (326). Furthermore, these effects were only noticeable after the 7th day of exposure but not after 2 or 17 days of exposure (320, 326).

Further analysis of sunscreen-derived nano-TiO_2, demonstrated oxidative stress in marine phytoplankton due to the nano-TiO_2 mediated production of hydrogen peroxide (H_2O_2), which is plausible under environmental conditions (320). Assumptions made in this estimate include 10,000 people visiting the studied bay (average depth 1.5 m) each day, with each visitor applying 36 g of sunscreen containing ~5% w/w nano-TiO_2. Total visitor numbers to the GBR region are generally less than this, with monthly data collected during 2014 suggesting numbers of visitors ranging from around 135,000 – 225,000 for the entire GBR region, or approximately 4,500 – 7,500 visitors per day (http://www.gbrmpa.gov.au/visit-the-reef/visitor-contributions/gbr_visitation/numbers). The number of visitors directly visiting the reef was considerably less than this, with visitor numbers ranging from 15,000 – 26,000 per month (500 – 850 per day). A conservative assumption of all of these people visiting the same area of reef has visitor numbers, and therefore nano-TiO_2 loads, already at least an order of magnitude less than the Spanish study. Furthermore, with the average depth of the reefs around 35 metres in the nearshore environment (http://www.gbrmpa.gov.au/about-the-reef/facts-about-the-great-barrier-reef) the extent of dilution would again decrease the TiO_2 loads by at least another order of magnitude. These mitigating effects would be expected to reduce the potential production of H_2O_2 to levels less than estuarine and nearshore waters with high loadings of organic matter (320).

Effects of NM exposure in marine organisms have been demonstrated and clearly cannot be ignored, in terms of potential risks to filter and particle feeders or corals. Based on existing evidence, however, the environmental risks due to the presence of NMs are likely to be low in GBR and TS regions, mainly due to the limited exposure potential throughout the region. Although evidence is currently limited, potential effects on marine organisms cannot be discounted in near-shore or tourist hotspots but a comprehensive understanding of this risk is pending collation of further knowledge relating to both the fate and effects of NMs in marine environments.

Near shore activities, such as WWTP discharges, are largely linked to population centres and tourist activity, including direct visits to reef-viewing areas, are likely to be the main exposure pathways of NMs into the GBR and TS marine environment. The largest populations of the GBR and TS regions are found in the Burdekin, Fitzroy, Burnett Mary and Wet Tropics, with respective populations of around 200,000. Major population centres in these regions include Cairns (Wet Tropics), Townsville (Burdekin), Rockhampton and Gladstone (Fitzroy) and Bundaberg and the Fraser Coast (Burnett Mary). The Mackay and Whitsunday region also has a population around 150,000, with Mackay and Whitsunday being major population centres for this region. As many of these population centres are important centres for visiting the reef, these regions have been identified as being higher priority areas for NM exposure (**Table 9-2**).

Table 9-2: Priority ranking of nanomaterials, based on a qualitative risk assessment, in the GBR and TS marine ecosystems. See Table 14-6 for detailed risk assessment scores.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Ag	4	4	8	8	8	8	8
TiO_2	4	4	8	8	8	8	8
ZnO	4	4	8	8	8	8	8
CeO_2	2	2	4	4	4	4	4
Carbon (e.g. fullerenes)	2	2	4	4	4	4	4

9.7 Discussion, recommendations and conclusion

Currently there is no information relating to concentrations of NMs in the marine environments of the GBR and TS regions. Although effects have been demonstrated in marine organisms exposed to NMs, exposure concentrations leading to adverse outcomes are unlikely to occur in the GBR and TS regions. Also, demonstrated effects have generally not included whole organism or population-level effects, making potential risks difficult to define. This is especially so considering the poor understanding of the fate of NMs in the marine environment and the likely mitigating effects on the concentrations of NMs in the water column. Furthermore, while there is literature published on the fate and effects of NMs in marine ecosystems, most of these studies are based on theoretical assessments or conducted under conditions that might not reflect the conditions prevailing within the GBR and TS regions. For example, population pressures are not as high within these regions, compared with scenarios relating to freshwater environments in the northern hemisphere where the majority of research in this area has been undertaken.

Release of NMs into the marine environment will correspond closely with population centres, where WWTPs and direct inputs of NM-containing personal care products (e.g. sunscreens) are likely to be the principal pathways into the marine environment. Current knowledge would suggest that there would be substantial mitigation of NM concentrations in the water column due to high ionic strength of seawater and dilution effects. This will limit potential risks to areas close to where NMs are initially released into the marine environment, including nearshore water bodies adjacent to areas of higher population density and marine ecosystems receiving high numbers of visitors (e.g. reefs).

Areas within the GBR and TS have therefore been identified as potentially constituting a greater risk based on population centres and areas of the reef close to these population centres, where higher human activity is likely to occur. These include Cairns (Wet Tropics), Townsville (Burdekin), Rockhampton and Gladstone (Fitzroy), Bundaberg and the coast surrounding Fraser Island (Burnett Mary) and Mackay (Mackay Whitsunday).

Aquatic NM research has predominantly focussed on freshwater systems; further knowledge on the fate and effects of NMs in the marine environment is required, especially in light of the increasing use of NMs in consumer products and the increasing population centres at a number of locations within the GBR and TS region.

10.0 ANTIFOULING PAINTS

Authors: Frederieke Kroon, Jeffrey Tsang

10.1 Summary

An 'antifouling system' (or antifoul) is defined as '*a coating, paint, surface treatment, surface, or device that is used on a ship to control or prevent attachment of unwanted organisms*'. Antifouling paints for use on ships' hulls generally contain pigments (e.g. copper, iron or zinc oxides), and booster biocides to increase their efficacy. In the marine ecosystems of the GBR, both pigments (copper, zinc) and biocides (tributyltin (TBT), Diuron, Irgarol 1051) have been detected; Irgarol 1051 is not registered for use in Australia. No monitoring information on antifouling components could be found for (i) TS marine ecosystems, and (ii) booster biocides other than TBT, Diuron, and Irgarol 1051. Other booster biocides (Sea-Nine 211, Dichlofluanid, Chlorothalonil) have been detected in water and sediment samples in ports, marinas and estuaries around the world, and may also be present in the TS and GBR marine ecosystems. Locations where concentrations of metals and TBT have exceeded ANZECC/ARMCANZ water quality and sediment quality guidelines include sites of ship groundings and coastal harbours (Abbott Point, Cairns, Gladstone, Hay Point, and Townsville). Anchorage areas for bulk cargo and other trading vessels are also likely to contain elevated levels of metals and biocides, but monitoring information is not available for these areas. With shipping extending out into mid-shelf and offshore waters of the GBR and TS along shipping lanes and around tourist and fishing areas, chronic exposure is likely to occur continuously throughout the year in all four water bodies of the marine environment. Consequently, chronic contamination of water and sediments is likely to be of higher risk to the TS and GBR marine environments than acute exposure following ship collisions and groundings. This indicates that current management arrangements, which do not consider the risk of routine shipping operations and associated leaching or loss of antifouling paints, may need to be re-assessed and associated research recommendations are provided.

10.2 Introduction

An 'antifouling system' (or antifoul) is defined as '*a coating, paint, surface treatment, surface, or device that is used on a ship to control or prevent attachment of unwanted organisms*' (327). Antifouling paints for use on ships' hulls have traditionally contained copper as pigment given its toxicity to a large number of marine organisms (328, 329). Copper is still being widely used in antifouling paints although its application is being increasingly regulated following concerns about environmental impacts (330). After the 1950s, organotins such as tributyltin (TBT) were added as booster biocides to antifouling paints to increase their efficacy (328-330). The environmental impacts of TBT were first recognised in the early 1980s (330), following declines in oyster production in France (331), and marked increases in the degree of imposex (i.e. induction of male sex characteristics in female gastropods) in the U.K. (332). These impacts and others (25, 329, 333-338) resulted in the adoption of the International Convention on the Control of Harmful Anti-Fouling Systems on Ships (the AFS Convention) in 2001 (327). The Convention entered into force in September 2008, however, it is likely that TBT is still being used in developing or less developed nations (334, 335, 339). In Australia, the Convention is being enacted under the Protection of the Sea (Harmful

Anti-fouling Systems) Act 2006 (340). This Act stipulates that (i) organotin compounds that act as a biocide in an antifouling system are not to be applied to a ship in Australia, and (ii) non-complying ships are not to enter or remain in shipping facilities (i.e. a port, a shipyard, or an offshore terminal) in Australia (340).

The AFS Convention resulted in the development and application of new booster biocides for use in antifouling paints (328-330, 338, 341-343). Controlled laboratory exposure to these new biocides has demonstrated toxicity to a range of marine organisms, including diatoms, cyanobacteria, dinoflagellate, seaweed, seagrass, sea anemone, coral, polychaete tubeworm, sea urchin, barnacle, amphipod, copepod, brine shrimp, mussel, and fish (344-356). This includes endocrine disrupting effects in male fish exposed to the active ingredient used in the commercial antifoulant Sea-Nine 211, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) (346). Indeed, the acute toxicity of some of these biocides, such as copper pyrithione (CuPT) and Irgarol, can be higher for some marine organisms than TBT (344). Several of these new biocides have been detected in coastal and marine environments around the world, including Chlorothalonil, copper (from copper pyrithione), Dichlofluanid, Diuron, Irgarol 1051, Sea-Nine 211, and zinc (from zinc pyrithione) (343, 351, 353, 354, 357-365). Concentrations of booster biocides in marine environments, such as marinas, harbours, coastal waters, mooring areas, and ship groundings, can exceed the predicted no effect concentrations derived from laboratory exposures (343, 345, 351, 353, 357, 362, 364).

10.3 Main classes of antifouling paints

Antifouling paints generally contain pigments such as oxides of copper (CuO), iron (FeO) or zinc (ZnO), and previously also arsenic and mercury (328, 329). Organic booster compounds (i.e. biocides) are added to antifouling paints to improve their efficacy (328, 329). The organotin TBT was used as a booster biocide globally from its introduction in the early 1960s until the adoption of the AFS Convention in 2001 (327). Currently, around eighteen compounds are used as antifouling biocides around the world, namely Benzmethylamide, Chlorothalonil, Copper pyrithione (CuPT), DCOIT (Sea-Nine 211), Dichlofluanid, Diuron, Fluorofolpet, Irgarol 1051, Mancozeb, Polyphase, TCMS pyridine, TCMTB, Thiram, Tolylfluanid, Triphenylborane-pyridine, Zinc pyrithione (ZnPT), Zineb, and Ziram (328-330, 341, 343, 353). The APVMA has:

- registered several of these booster biocides, including for the State of Queensland, for:
    - antifouling (CuPT, Dichlofluanid, Diuron, Thiram, ZnPT, Zineb),
    - fungicide (Chlorothalonil, Mancozeb, Zineb, Ziram),
    - algicide and herbicide (Diuron), or
    - mixed function pesticide (TBT).
- approved several of these booster biocides as an active constituent (Chlorothalonil, CuPT, Dichlofluanid, Mancozeb, TCMTB, Thiram, Tolylfluanid, Zineb, ZnPT, Ziram) (115).

Searches in November 2015 for Benzmethylamide, DCOIT (Sea-Nine 211), Fluorofolpet, Irgarol 1051, Polyphase, TCMS pyridine, and Triphenylborane-pyridine in the APVMA's Public Chemical Registration Information System database returned empty (115); these biocides are thus considered not registered for use in Australia. Recent work has examined the use of ZnO and CuO nanoparticles in antifouling paints (366, 367); the risk of nanomaterials to the GBR and TS marine environments is assessed in the 'Nanomaterials' chapter.

10.4 Presence, concentration and location in the GBR and TS marine ecosystems

Components of antifouling paints, including pigments, TBT, and other booster biocides, have been detected in the marine ecosystems of the GBR region (**Table 10-1**) (39, 127, 161, 365, 368-370). Most of these studies, however, are >10 years old. Recent monitoring programs with information on pigments and TBT were identified were identified through the project team's knowledge and in collaboration with NESP TWQ project 3.8 (27). Out of those identified, the Port Curtis Integrated Monitoring Program (PCIMP) was the only program making their monitoring dataset available for our project. For the other programs, we relied on monitoring data presented in environmental investigations and EIS documents for the ports of Abbot Point, Cairns, Hay Point and Townsville (29, 31, 32, 198, 371). Here, we only present data on pigments (i.e. metals) that was collected as part of (i) specific surveys for antifouling components, and (ii) ship-groundings; a comprehensive overview of monitoring data for copper and zinc, and other metals, is presented in Chapter '**Error! Reference ource not found.**'. No monitoring information on antifouling components could be found for (i) TS marine ecosystems, (ii) ship collisions, and (iii) booster biocides other than TBT, Diuron, and Irgarol 1051.

10.4.1 Pigments

In a 1999 survey for antifouling components, copper was detected in sediment at commercial harbours, mainland marinas, and mooring sites at both mid-shelf islands and the outer reef, with concentrations above ANZECC/ARMCANZ sediment quality guidelines (65 mg/kg) (41) in some commercial harbours and mainland marinas (369). Concentrations of copper and zinc in sediment at ship grounding scars are several magnitudes higher than ANZECC/ARMCANZ sediment quality guidelines (zinc: 200 mg/kg) (12, 41, 161, 368, 369).

10.4.2 Biocides

In a 1999 survey, TBT was detected in sediment at commercial harbours and mainland marinas, including exceedances of ANZECC/ARMCANZ sediment quality guidelines, but was below detectable levels in sediment at mooring sites at mid-shelf islands and the outer reef (369). In 1992, butyltins were also detected in muscle and liver tissue from silver trevally (*Caranx sexfasciatus*), stripey (*Lutjanus earponotatus*), black pomfret (*Apolectus niger*) and squid (*Loligo chinensis*), collected around Townsville (370).

More recent monitoring programs, associated with dredging and port developments, have demonstrated that TBT is still present in the water column and/or sediment in the harbours of Abbot Point, Cairns, Gladstone, Hay Point and Townsville (29, 31, 32, 39, 198, 372). In Trinity Inlet (Cairns Port), the 95% upper confidence limit (UCL) for TBT from 2001 to 2013 (26.3 µg Sn/L) (31) exceeded the ANZECC/ARMCANZ water quality guidelines (0.006 µg Sn/L) (41). Concentrations in sediment pore water from the Cairns Port were reported to be below these guidelines (31, 32). For sediment samples, the most recent EISs reported 95% UCLs for TBT within the NAGD value of 9 µg Sn/kg (normalised to 1% organic carbon, dry weight) (181, 182) for Abbot Point (373), and Hay Point (29); 95% UCL for TBT was not presented in the Townsville EIS (32). In Port Curtis, TBT was detected in a small number of sediment samples collected in February 2012 with no exceedances of the NAGD value (198). In contrast, 95% UCLs for TBT have exceeded the NAGD value consistently in the Cairns Port dredging areas from 2005-2009 (95% UCL 40.8 µg Sn/kg), and again in 2011 (95% UCL 26.5 µg Sn/kg) (31). The available monitoring information shows that maximum concentrations of individual sediment samples have exceeded the NAGD value in all ports (29, 31, 32, 373, 374), except Gladstone (198).

Ship groundings in the GBR have resulted in TBT concentrations in water and sediments that are several magnitudes higher than the ANZECC/ARMCANZ guidelines (12, 161, 368, 369).

Bioaccumulation of TBT in oysters has been reported in Rosslyn Bay (Keppel Island), Cairns Port, and Gladstone Port (374). Enrichment of TBT in oysters and mud whelks has been documented in certain areas around Port Curtis (39), including concentrations that exceed those known to be linked to imposex in gastropods (39). Food standards for TBT do not exist in Australia (49).

Diuron contamination of GBR marine waters is chronic, widespread and year-round (127). While sugarcane land use in the adjacent catchment is the main land-based source of Diuron (58), application or leaching from antifouling paints is likely to contribute Diuron in some locations (127, 356, 375, 376). Indeed, Diuron has been regularly detected in sediment in Cairns Port with a maximum concentration of 5.00 µg/kg (31). A comprehensive overview of monitoring data for Diuron is presented in the ‘Alternate pesticides’ chapter.

Chlorothalonil has not been detected in flood plumes and marine waters off the five NRM regions bordering the GBR, with the only detection occurring in creeks and rivers in the Wet Tropics NRM region (Chapter ’Alternate pesticides’). Given the location, and its registered use as fungicide in various agricultural land uses (377), it is most likely that the source is not ship - but agriculture based.

Despite Irgarol 1051 not being registered for use in antifouling paints in Australia (115), the biocide was detected in seagrass tissue in four of the five locations sampled along the GBR coast in 1997 (365). The concentrations detected were considered to be potentially toxic to seagrass by Scarlett *et al.* (365).

10.5 Likely presence in the GBR and TS marine ecosystems

The main sources of antifouling components in the GBR and TS marine ecosystems are ships, mainly large commercial, military and recreational vessels, commercial fishing and tourism boats. In 2012–13, almost 11,000 movements of large commercial ships (>50 m) were monitored in the GBR and TS marine environments, with >87% berth of the 4,440 vessel arrivals at the four major ports (Gladstone, Hay Point, Cairns and Townsville) (166). In 2013–14, a total of 11,417 voyages comprising 2,910 large commercial ships were recorded through the GBR (166). Shipping traffic was projected to increase by ~1.7-fold for 2020 and ~2.6-fold for 2032 (based on 2011–12 numbers) (218, 224); forecast traffic levels have decreased since then (378). In addition to increases in vessel numbers, average vessel size of bulk carriers are projected to increase from 2011 to 2025 (224). The combined increases in vessel movements and vessel sizes will increase the likelihood of antifouling components being released along shipping lanes in the marine environments of the GBR and TS regions.

Table 10-1: Main sources and available monitoring data for components of antifouling paints in the GBR and TS marine ecosystems, for (a) water samples (in µg/l), (b) sediment samples (in mg/kg dry weight for metals, and µg/kg dry weight for biocides), and (c) biota samples (in mg/kg wet weight for metals, and ng/kg wet weight for biocides). Concentrations for tributyltin (TBT) in water, sediment and biota samples are µg Sn/L, µg Sn/kg dry weight, and ng Sn/kg wet weight, respectively. NA = not available, UCL = upper confidence limit; bold numbers indicate exceedances of ANZECC/ARMCANZ water and sediment quality guidelines (41, 182), and Generally Expected Levels for metal contaminants (49). Maximum residue limits (MRL) for seafood are not listed for booster biocides in the Australia New Zealand Food Standards Code (Standard 1.4.2) (379).

(a)

Main classes of emerging contaminant		**Main sources**	**NRM region**							**Trigger value**	
			Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**	**95%**	**99%**
Pigments	Copper	Commercial and recreational shipping	NA	NA	Sudbury reef (**193**)[a]	NA	NA	NA	NA	1.3	0.3
	Iron	Commercial and recreational shipping	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Zinc	Commercial and recreational shipping	NA	NA	Sudbury reef (**146**)[a]	NA	NA	NA	NA	15	7
Biocides	Diuron	Commercial and recreational shipping; Agriculture	NA	NA	Cairns Port (<0.005 µg/L)[b]	NA	NA	NA	NA	NA	NA
	Tributyltin (TBT)	Commercial and recreational shipping	NA	NA	Sudbury reef (**43**)[a] Cairns Port (95th UCL **2.5-26.3**)[b]	Townsville Port (<0.005)[c]	NA	Port Curtis (mean <0.012*, max **0.02**)[d]	NA	0.006	0.0004

* Standard deviation or standard error not presented in Jones et al. (39).

[a] (12), [b] (31), [c] (32), [d] (39)

(b)

Main classes of emerging contaminant		Main sources	NRM region							Trigger value	
			Torres Strait	Cape York	Wet Tropics	Burdekin	Mackay Whitsunday	Fitzroy	Burnett Mary	Low	High
Pigments	Copper	Commercial and recreational shipping	NA	NA	Sudbury reef (**972–21,700**)[a] Sudbury reef (**1,180**)[b] Port Douglas Marina (9 ± 5)[c] Low Isles (20 ± 1)[c] Agincourt Reef (20 ± 2)[c] Cairns Port (**70** ± 61)[c] Yorkey's Knob (33 ± 1)[c] Fitzroy Island (20 ± 2)[c] Michaelmas Reef (20 ± 1)[c]	Townsville Port (**113** ± 105)[c] Breakwater Marina (**72** ±7)[c] Magnetic Island (11 ± 8)[c] Kelso Reef (22 ± 1)[c]	Abel Point Marina (**95** ± 18)[c] South Molle Island (12 ± 8)[c] Bait Reef (21 ± 0)[c]	Douglas Shoal (<detection-**152,300**)[f]	NA	65	270
	Iron	Commercial and recreational shipping	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Zinc	Commercial and recreational shipping	NA	NA	Sudbury reef (**1,170–19,400**)[a] Sudbury reef (**1,570**)[b]	NA	NA	Douglas Shoal (<detection-**22,000**)[f]	NA	200	410
Biocides	Diuron	Commercial and recreational shipping; Agriculture	NA	NA	Cairns Port (95% UCL 1.24, max 3.84)[h]	NA	NA	NA	NA	NA	NA

	Tributyltin (TBT)	Commercial and recreational shipping	NA	Heath Reef (**7,500 - 340,000**)[c]	Sudbury reef (<1-**17,000**)[a] Sudbury reef (**160,000**)[b] Port Douglas Marina (<1)[c] Low Isles (<1)[c] Agincourt Reef (<1)[c] Cairns Port (<1–**1,275**)[c] Cairns Port (95% UCL <0.5-**40.8**)**[h] Cairns Port (**72-470**) **[k] Yorkeys Knob (<1–5.5)[c] Fitzroy Island (<1)[c] Michaelmas Reef (<1)[c]	Townsville Port (<1–**18**; <0.005)[c] Townsville Port (<0.5-**221.6**)[d] Breakwater Marina (<1–4.2)[c] Magnetic Island (<1)[c] Kelso Reef (<1)[c] Abbot Point (<0.05-**21.1**)[i]	Abel Point Marina (<1)[c] South Molle Island (<1)[c] Bait Reef (<1)[c] Port of Hay Point (<0.05-**36.32**)[j]	Port Curtis (mean 50*, max **655**)[e] Douglas Shoal (<detection-**545,000**)[f] Port Curtis (<0.5 – 2.0)[g] Rosslyn Bay (1.8–5.0) **[k] Gladstone (<0.5-1.9)**[k]	NA	9.0***	70

*Standard deviation not presented in Jones et al. (39); ** Normalised to 1% organic carbon (31); ***Normalised to 1% organic carbon, dry weight (182)

[a] (368), [b] (12), [c] (369), [d] (32), [e] (39), [f] (161), [g] (198), [h] (31), [l] (373), [j] (29), [k] (374)

(c)

Main classes of emerging contaminant		Main sources	NRM region							Generally Expected Levels (median)	Generally Expected Levels (90th percentile)
			Torres Strait	Cape York	Wet Tropics	Burdekin	Mackay Whitsunday	Fitzroy	Burnett Mary		
Pigments	Copper	Commercial and recreational shipping	NA	NA	NA	NA	NA	NA	NA	5	30
	Iron	Commercial and recreational shipping	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Zinc	Commercial and recreational shipping	NA	NA	NA	NA	NA	NA	NA	130	290
Biocides	Irgarol 1051	Commercial and recreational shipping	NA	NA	Michaelmas Cay, green algae (0)[a] Yule Pt, seagrass (0.3 ± 0.1)[a] Ellie Pt, Trinity Bay, seagrass (6.6 ± 0.3)[a]	NA	Oyster Bay, South Molle Island, seagrass (20.3 ± 24.2, max 48)[a] Hervey Bay, seagrass (3.2 ± 0.2)[a]	NA	NA	NA	NA
	Tributyltin (TBT)	Commercial and recreational shipping	NA	NA	Cairns Port, oysters (44-92)[c]	Townsville, fish/squid muscle (< 3.0-47), fish liver (1.2-570)[b]	NA	Rosslyn Bay, oysters (42-59)[c] Gladstone, oysters (23-37)[c] Clinton Coal Wharf and Fisherman's Landing, oysters (300-700) [d] Calliope River mouth, mud whelk (>500)[d]	NA	NA	NA

[a] (365), [b] (370), [c] (374), [d] (39)

Anchorages for bulk cargo and other trading vessels near the five major ports are either designated by navigational charts (Cairns, Gladstone, Hay Point), or directed to anchor by the port's Regional Harbour Master (Abbot Point, Townsville) (380). The total anchorage area for all the five ports adds up to 2,881 km^2, ranging from 14 km^2 at Gladstone inner anchorage to 1,573 km^2 at Hay Point (380). The most heavily used anchorage area is off Hay Point with 720 ships proceeding to anchor each year, with 2 to 3 ship calls per day for an average stay of 19 days (380). At this anchorage, up to 60 ships can be anchored at any one time, and ships can be at anchor for up to two months (380).

Leaching and release of antifouling components from large commercial vessels will occur while underway along shipping lanes, while at anchor at anchorage areas, and while at berth in port. We could not find any information on the presence of concentrations of antifouling components in water or sediment along shipping lanes or anchorage areas; for ports see the previous section. Based on a total copper leach flux of around 0.8 kg to 3.2 kg per day for an average bulk carrier for GBR coal ports (218), some rough estimates can be made on the presence of copper, e.g. for the most heavily used anchorage area off Hay Point. Assuming a scenario of 60 ships at anchor every day for a year, this would translate into a release of 17,520 to 70,080 kg of copper into the Hay Point anchorage area. Assuming all copper leachate settles onto the seabed of this anchorage area, this would translate into the accumulation of copper at 11 to 45 mg/m^2 per year. Whether this presents a risk to marine organisms will depend on the chemical form (i.e. speciation) of copper rather than its total concentration. The most bioavailable and toxic form of copper is its free ion, which readily binds to organic compounds or suspended particles in the marine environment (381); this generally attenuates its toxicity. In anoxic marine sediments copper will likely form insoluble sulfides (382), which are not readily bioavailable or toxic. However, ingestion of sediment particles by benthic feeders may leach copper (and other metals) in acidic juices of their intestines. Unlike contaminants such as TBT, metals such as copper will not degrade with time and likely to accumulate in marine sediment. This can be a potential source of toxic metals if disturbed (e.g. dredging, ship movement, anchorage activity, and cyclonic events). When metal concentrations in water or sediment samples exceed trigger values, its speciation and bioavailable concentration should be assessed to determine if there is a risk to marine organisms (383).

In 2012–13, 83,000 privately registered recreational vessels and 485 commercial trawlers were operating in the GBR and TS regions (166). In addition, commercial marine tourism in the GBR is predominantly vessel based, with >80% of day visits in 2013 concentrated in the Cairns and Whitsunday Planning Areas (5). Leaching and release of antifouling components from these vessels is likely to be much less than that of large commercial vessels. However, in high use areas such as marinas and ports this could still be locally significant and contribute to the overall load of metals and biocides (369).

In catastrophic cases, release of antifouling components can occur during ship collision and grounding. In the GBR WHA, the number of reported collisions and groundings has ranged from zero to five per year since 1985 (5). All reported collisions were between ships and smaller vessels, while groundings include those within designated port areas (5). The catastrophic effects of groundings of large vessels, and associated release of antifouling components including TBT, on the GBR marine environment were evident in the groundings of the *New Reach* in 1999, the *Bunga Teratai Satu* in 2000, and the *Shen Neng* in 2010 (12, 161, 368, 369, 384, 385).

10.6 Risk to the GBR and TS marine ecosystems

Many scientific reports have described and reviewed the occurrence and effects of antifouling paints on marine species and ecosystems (333, 338, 341, 353, 364, 386). The booster biocide TBT has received particular attention (25, 328-338). In contrast, little information is available on the effects of alternatives to organotin compounds on aquatic organisms and ecosystems (353). The most recent review from 2004 (353) found that:

- several alternative booster biocides are now being detected in water and sediment samples from around the world, including Irgarol 1015, Diuron, Sea-Nine 211, Dichlofluanid, and Chlorothalonil;
- ecotoxicological data are available for Irgarol 1051, Diuron, as well as Sea-Nine 211, with few or no data available for other biocides;
- concentrations of biocides in the aquatic environments were generally not high enough to have acute toxic effects on higher species; however, this review did not consider ship collisions or groundings; and
- potential chronic effects of biocide concentrations present in the aquatic environment were generally unknown.

In the TS and GBR marine ecosystems, shipping related risks, such as groundings, anchoring, and persistent and chronic release of antifouling formulations, have known and potential impacts on matters of national environmental significance and Outstanding Universal Value (OUV) (166). Next, we identify areas where higher risks are possible, based on studies conducted following the 2004 review with a particular focus on tropical marine species and ecosystems. Specifically, we examine (i) the probability of exposure to antifouling paints, and (ii) the likely effects of the antifouling paints on marine organisms and ecosystems (**Table 10-2**).

Table 10-2: Priority ranking of main classes of antifouling components, based on a qualitative risk assessment, in the GBR and TS marine ecosystems

Main classes of emerging contaminant	**NRM region**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Pigments & Biocides (Chronic contamination of water and sediments)	16	16	30	30	30	30	40
Pigments & Biocides (Ship collisions and groundings)	18	18	18	18	18	18	18

10.6.3 Probability of exposure to antifouling paints

In the GBR and TS marine ecosystems, the probability of exposure to antifouling paints is related to the presence of ships, mainly large commercial vessels, military and recreational vessels, and commercial fishing and tourism boats. Acute exposure to extremely high concentrations of antifouling metals and TBT in both water (12) and sediment (12, 161, 368, 369) have occurred in areas of ship groundings along the GBR. The effects of antifoul contamination may spread well beyond the ship grounding site depending on the mixing of local waters. The grounding of the *Bunga Teratai Satu* in 2000 was followed by extensive mitigation efforts to reduce the levels and extent of antifouling contamination (385). In contrast, the *Shen Neng* caused the largest ship grounding scar on the GBR; the site has not been cleaned up (5) despite severe contamination with copper, zinc and TBT (161). Ongoing monitoring has not occurred at any ship grounding site in the GBR or TS to determine the long-term impacts of antifoul contamination, the effectiveness of any clean-up operations, and/or the potential for recovery of reef ecosystems. Under current management arrangements in the GBR WHA, groundings of large vessels are predicted to occur possibly once in 10 years (5).

Chronic exposure is likely to occur in areas frequented by ships, primarily in ports and marinas, at anchorage areas, at moorings, and along shipping lanes. Recent monitoring data on antifouling contamination indicate that chronic exposure to antifouling components occurs at all five major ports (Abbot Point, Cairns, Gladstone, Hay Point and Townsville (29, 31, 32, 198, 371, 372). It is likely that anchorage areas and moorings, and to lesser extent shipping lanes, are also chronically exposed to antifouling components; however, no recent monitoring data exists for these locations in the GBR and TS marine environments. Shipping occurs primarily in enclosed and open coastal waters, but extends out into mid-shelf and offshore waters along shipping lanes and around tourist and fishing areas (5). This is particularly evident in the Burnett-Mary NRM region, where shipping traffic is concentrated across all these four water bodies (Fig. 5.23 in (5)).

10.6.4 Likely effects of antifouling paints on marine organisms and ecosystems

Toxicity of antifouling paints to reef organisms such as hard and soft corals was observed near the grounding scar of the *Bunga Teratai Satu* on Sudbury Reef (385). Laboratory exposures to copper, zinc and TBT concentrations detected at GBR ship grounding sites found significant reduction in coral fertilisation and larval metamorphosis (9, 10, 75), coral recruitment (12), and major mortality of newly settled and coral branchlets (387). These results indicate that such exposures in the field may threaten the recovery of the resident coral community for many years unless the paint is removed (12, 387).

Acute exposure to Irgarol 1015 concentrations reflecting those detected in Caribbean marinas, harbours and coastal waters showed a reduction in photosynthesis of corals (351). Similarly, significant inhibition of photosynthesis was observed in zooxanthellae exposed to environmentally relevant concentrations of Diuron and Irgarol 1015 (355). More recent ecotoxicological tests on sub-tropical marine organisms showed that the effects of CuPT were comparable to that of TBT, while Irgarol 1015 was more toxic to autotrophic species than TBT (344).

Chronic, longer-term exposures to antifouling components can have toxic and sub-lethal effects in marine organisms. Similar to acute exposures, corals are sensitive to longer term exposures to low concentrations of TBT throughout their life history (352, 384). Chronic photo-inhibition was observed in coral recruits and adults exposed to Diuron and Irgarol 1051 for 4–14 days in laboratory experiments (356). Accumulation of butyltin compounds have been detected in shellfish and fish collected from Asian, European and Canadian harbours and marinas (25), and can result in endocrine disruption in molluscs and fishes (388). Around Port Curtis, TBT enrichment has been reported in oysters (*Saccostrea* spp.) and mud whelks (*Telescopium telescopium*), including concentrations that exceed those known to be linked to imposex in gastropods (39). Indeed, the occurrence of imposex in the whelk *Morula marginalba* in certain areas of Port Curtis was up to 43% (389). The occurrence of imposex can be particularly high in areas with commercial shipping, with 100% imposex reported in the gastropod *Thais orbita* in coastal waters around Perth (390). The implications for gastropod (and fish) populations have not been examined, nor the impacts of potential bio-accumulation along marine foodwebs. A recent study in Hong Kong found organtin compounds in seafood at concentrations that may be of concern to human consumption (391).

10.7 Discussion, recommendations and conclusion

Components of antifouling paints, including metals, TBT, and other booster biocides, have been detected in the marine ecosystems of the GBR region (**Table 10-1**) (39, 127, 161, 365, 368-370). Recent monitoring programs, associated with dredging and port developments, have demonstrated that TBT is still present in the water column and/or sediment in the harbours of Abbot Point, Cairns, Gladstone, Hay Point and Townsville (29, 31, 32, 39, 198, 372). Given its phase-out, the entry of TBT into the environment should eventually disappear but will remain a legacy issue for some time yet (166). Specifically, degradation of TBT will take longer in anoxic compared to oxic sediments, which may be an issue for dredging or other sediment disturbances. Diuron and Irgarol 1015 have also been detected in areas exposed to shipping (31, 365), and their ecotoxicological effects may be on par, if not worse than those of TBT (344, 351, 355). While monitoring information for most other biocides currently used is not available for the region, overseas studies (353) (353) suggest that at least some of them are likely to be present, including in ports and marinas. No monitoring information on antifouling components could be found for TS marine ecosystems.

Groundings of both large (>50 m) and small (<50 m) vessels, including the dislodging of antifoulants, are two of the 41 threats considered to the GBR region's values (5). At the site of ship groundings, the impact of exposure to antifouling paint components is likely to be detrimental to marine organisms and ecosystems, at least in the short term (161, 368, 385). Unless antifouling paint residue is removed from the grounding site, such acute and extreme exposures may threaten the recovery of the resident coral community for many years (12, 387). The lack of monitoring at GBR grounding sites following clean-up (385) or no clean-up (161) means that the long-term impacts of exposure to extreme concentrations of antifouling components are currently unknown.

The risk of routine shipping operations, and associated leaching or loss of antifouling paint components, are deemed negligible and not considered under current management arrangements (5). Our review indicates that chronic contamination of water and sediments is of higher risk to the TS and GBR marine environments than acute exposure following ship collisions and groundings (**Table 10-2**). This is because chronic exposure is likely to occur continuously throughout a year in all four water bodies of the marine environment, with shipping extending out into mid-shelf and offshore waters along shipping lanes and around tourist and fishing areas (5). Chronic exposure in harbours such as Port Curtis has resulted in accumulation of TBT in oysters and mud whelks (39), and occurrence of imposex in the whelk *Morula marginalba* (389). Furthermore, our review suggests that antifouling compounds may accumulate at very high levels at anchorage areas such as those off Hay Point.

To improve the assessment of risks posed by antifouling paints to the GBR and TS marine environments, we recommend:

1. develop a more comprehensive understanding of the presence, location and potential sources of antifouling paints by bringing together existing monitoring datasets held by governments and government agencies, Port authorities, universities, research organisations, engineers and consultants (*sensu* (392);
2. determine whether leaching of antifouling components at GBR anchorage areas poses an identifiable risk to the OUV of the GBR (166);
3. examine the effects of chronic exposure to antifouling compounds, including TBT, on marine biota in areas of high shipping traffic;
4. determine the presence and concentrations of booster biocides other than TBT in water, sediment and biota, including seafood, of high-volume ports; and
5. determine the toxicity threshold concentrations of booster biocides other than TBT to key tropical species (coral, seagrass, mangroves and fish).

11.0 MARINE DEBRIS, INCLUDING MICROPLASTICS

Authors: Frederieke Kroon, Marji Puotinen

11.1 Summary

Marine debris (or marine litter) is defined as '*any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment*'. Marine plastic pollution is generally divided into macroplastics (e.g. fishing nets, plastic packaging) and microplastics (plastic particles <5 mm in diameter). Macroplastic is ubiquitous along the coastlines and in coastal and marine waters of all seven NRM regions, with 81% of ~1.8 million anthropogenic items collected during beach clean-ups from 2008 to 2015 being plastic. Microplastic contamination has only recently been reported for the coastal and marine environments of the study area, with maximum concentrations of up to 40,000 – 80,000 pieces per km^2 reported between Shoalwater Bay and Townsville in February 2013. Source attribution shows that marine debris is derived from marine and land-based sources, but the relative contribution of likely sources such as large commercial, military and recreational vessels, commercial fishing and tourism boats, aquaculture installations, discharges of (untreated) municipal sewage and storm water, industrial facilities, coastal tourism involving recreational visitors and beach-goers, and riverine transport of waste from landfills and other inland sources, is unknown. The large number of likely sources does suggest the potential for widespread and chronic exposure of the GBR and TS marine environments, which is supported by data from beach clean-ups on the GBR and TS coasts and islands. Both entanglement in, and ingestion of marine debris, have been reported for marine species in the study area including turtles, cetaceans, dugong, and seabirds, and are likely to affect many more species. Given the high likelihood of occurrence in all seven NRM regions, the potential impact at a wider scale, and the presence in most if not all water bodies, marine plastic debris receives one of the highest scores in the qualitative risk assessments conducted as part of this study.

11.2 Impacts of marine debris on marine environments

Marine debris (or marine litter) is defined as '*any persistent, manufactured or processed solid material discarded, disposed of or abandoned in the marine and coastal environment*' (393). Larger marine debris, such as derelict fishing gear, can entangle or entrap a wide range of marine species (394). Ingestion of smaller particles may block feeding and digestive processes and expose organisms to associated chemical contaminants (395, 396). The impacts of marine debris is of particular concern for species that are already threatened, vulnerable, endangered, or critically endangered (394, 397). However, whether marine debris entanglement and ingestion ultimately result in reduced reproductive fitness and population size is difficult to determine. Marine ecosystems can be affected by marine debris pollution through changes of habitat and species assemblages, dispersal of marine organisms, introduction of invasive species, and alteration of marine food webs (398). The effects of marine plastic pollution on fisheries have not been well studied globally, although microplastic ingestion has been documented in wild-caught fisheries species (395, 399-402), and accumulation of chemical contaminants from marine plastics in fish has been reported in laboratory studies (403-405). The potential flow-on effects on fisheries sustainability and human health, however, are currently unknown.

11.3 Main classes of marine debris

Marine plastic pollution is generally divided into macroplastics (e.g. fishing nets, plastic packaging) and microplastics (plastic particles <5 mm in diameter) (406, 407) In the GBR and TS regions, 81% of ~1.8 million items of marine debris collected in a total of 1,121 beach clean-ups from 2008 to 2015 comprised plastic, with the remainder being classified as foam (6%), glass and ceramic (4%), rubber (4%), and metal (3%) (408, 409). These results are consistent with the finding that approximately three-quarters of marine debris along the Australian coastline is plastic, with the remainder comprising glass and metal (24%), and cloth (1%) (410). In addition, most floating debris in Australian coastal and offshore waters is plastic (410). Widespread contamination of Australian coastal and marine waters with microplastics was recently reported by Hardesty *et al.* (410) and Reisser *et al.* (411), including in remote marine environments of North-Western Australia (412). The terms 'primary' and 'secondary' microplastics refers to particles being either specifically manufactured for particular applications (e.g. industrial 'scrubbers', plastic powders, plastic nanoparticles, and resin pellets; micro-beads in personal care products), or produced as a result of fragmentation from larger items. This distinction can be used to pin-point sources of marine plastic pollution and target measures for mitigation. Globally, the presence of oceanic microplastics has been identified as an emerging issue of international concern (406).

11.4 Presence, concentration and location of marine debris

Marine debris has been detected along the coastlines and in coastal and marine waters of all seven NRM regions in the study area (**Table 11-1**) (408, 410, 411, 413, 414). The presence of marine debris in the GBR Marine Park was first documented in the scientific literature in 1997 (413). This survey of twelve sand cays and continental islands along the Cape York Peninsula found items made of plastics (mostly soft-drink bottles, kitchen and laundry detergent containers), polystyrene (mostly small fishing net floats and fragmented packing cases), rubber (mostly thongs), and glass (mostly drink bottles, light globes). Recent monitoring programs with information on marine debris and microplastics were identified through the project leader's knowledge and collaboration with NESP TWQ project 3.8 (27). The *Australian Marine Debris Initiative* of the Tangaroa Blue Foundation made their monitoring dataset available for our project, which includes data collected by *Eco Barge Marine Debris Cleanup and Monitoring (Eco Barge)*. For other known monitoring programs (e.g. CSIRO's survey of marine debris (410)), we relied on results presented in reports and journal papers.

11.4.1 Macroplastics and other marine debris

The Australian Marine Debris Database (AMDD) records a total of 1,121 beach clean-ups across the 7 NRM regions from January 2008 to October 2015 (408) (**Figure**)[11]. A total of 1,781,068 anthropogenic items were collected, primarily consisting of those classified as plastics (1,440,383; 81%); items classified as foam (6%) and rubber (4%) that potentially

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[11] These beach clean-ups were not conducted using a randomized design for site selection, potentially biasing the data towards high abundance of marine debris as clean-ups are more likely to occur in locations with marine debris than those without.

Table 11-1: Main sources and available monitoring data for main classes of marine debris in the GBR and TS marine ecosystems.

Main classes of marine debris	**Main sources**	**NRM region**						
		Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Macroplastics (e.g. fishing nets, plastic packaging)	Merchant shipping, ferries and cruise liners; fishing vessels; military fleets and research vessels; pleasure craft; aquaculture installations	Beach clean-ups (mean 78 items ± 91 SD 100 m^{-1}; 59% of total items; n=43)[e]	Sand cays and continental islands (mean 8 ± 10 SD 100 m^{-1}; 20% of total items; n=15)[a] Beach clean-ups (mean 398 ± 1,037 SD 100 m^{-1}; 84% of total items; n=60)[e]	Beach clean-ups (mean 69 ± 185 SD 100 m^{-1}; 69% of total items; n=365)[e]	Beach clean-ups (mean 597 ± 1,385 SD 100 m^{-1}; 87% of total items; n=25)[e]	Beach clean-ups (mean 1,558 ± 2,219 SD 100 m^{-1}; 91% of total items; n=80)[e]	Beach clean-ups (mean 296 ± 398 SD 100 m^{-1}; 85% of total items; n=29)[e]	Beach clean-ups (mean 31 ± 23 SD 100 m^{-1}; 58% of total items; n=4)[e]
Other marine debris (glass, metal, cloth)	Merchant shipping, ferries and cruise liners; fishing vessels; military fleets and research vessels; pleasure craft; aquaculture installations	Beach clean-ups (mean 33 ± 65 SD 100 m^{-1}; 25% of total items; n=43)[e]	Sand cays and continental islands (mean 2 ± 1 SD 100 m^{-1}; 6% of total items; n=15)[a] Beach clean-ups (mean 25 ± 79 SD 100 m^{-1}; 5% of total items; n=60)[e]	Beach clean-ups (mean 19 ± 35 SD 100 m^{-1}; 19% of total items; n=365)[e]	Beach clean-ups (mean 44 ± 43 SD 100 m^{-1}; 6% of total items; n=25)[e]	Beach clean-ups (mean 27 ± 30 SD 100 m^{-1}; 2% of total items; n=80)[e]	Beach clean-ups (mean 35 ± 65 SD 100 m^{-1}; 10% of total items; n=29)[e]	Beach clean-ups (mean 17 ± 19 SD 100 m^{-1}; 33% of total items; n=4)[e]
Microplastics (i.e. particles < 5mm diameter)	**Primary** - industrial 'scrubbers', plastic powders, plastic nanoparticles, resin pellets; micro-beads in personal care products **Secondary** – fragmentation of larger items	Surface waters* (20,000 - 40,000 pieces km^{-2})[b], (1,500 - 3,500 pieces km^{-2})[c]	Surface waters* (1,000 - 40,000 pieces km^{-2})[b], (1,500 - 7,500 pieces km^{-2})[c]	Surface waters* (1,000 - 40,000 pieces km^{-2})[b], (3,500 - 7,500 pieces km^{-2})[c]	Surface waters (1,000 - 80,000 pieces km^{-2})[b], (2 fragments ~11,000 L^{-1})[d]	Surface waters (40,000 - 80,000 pieces km^{-2})[b]	Surface waters (5,000 - 20,000 pieces km^{-2})[b]	NA

* different concentrations reported for same surveys in associated reports; reported particles predominantly small fragments < 5mm diameter. [a] (413), [b] (410), [c] (411), [d] (414), [e] (408); data from [a] and [e] have been standardized to 100m beach length for all beaches ([a]), and beach clean-ups covering lengths of 100-1,000 m ([e]).

contain plastics (409) would increase this percentage to 90% (408). Hardesty *et al.* (410) reported that the density of marine debris is relatively low along the GBR coast compared to other sections of the mainland, based on surveys across 172 coastal sites around Australia.

Using the AMDD records, the amount and proportion of plastic in marine debris was standardized to 100m beach following the international literature (415-418), for a total of 606 beach clean-ups with beach lengths ranging from 100 – 1,000m. The standardized data revealed that plastics were the most abundant item in marine debris within all seven NRM regions ranging from 58% to 91% of total items (**Table 11-1**). Specifically, plastics were most abundant by item and by proportion in the Mackay-Whitsunday (91%), Burdekin (87%), Cape York (84%) and Fitzroy (85%) NRM regions, ranging from an average of 398 to 1,558 items per 100 m^{-1} of beach cleaned. Other marine debris (glass, metal, cloth) comprised a relatively large proportion of the marine debris in the Burnett Mary (33%), Torres Strait (25%), and Wet Tropics (19%) NRM regions.

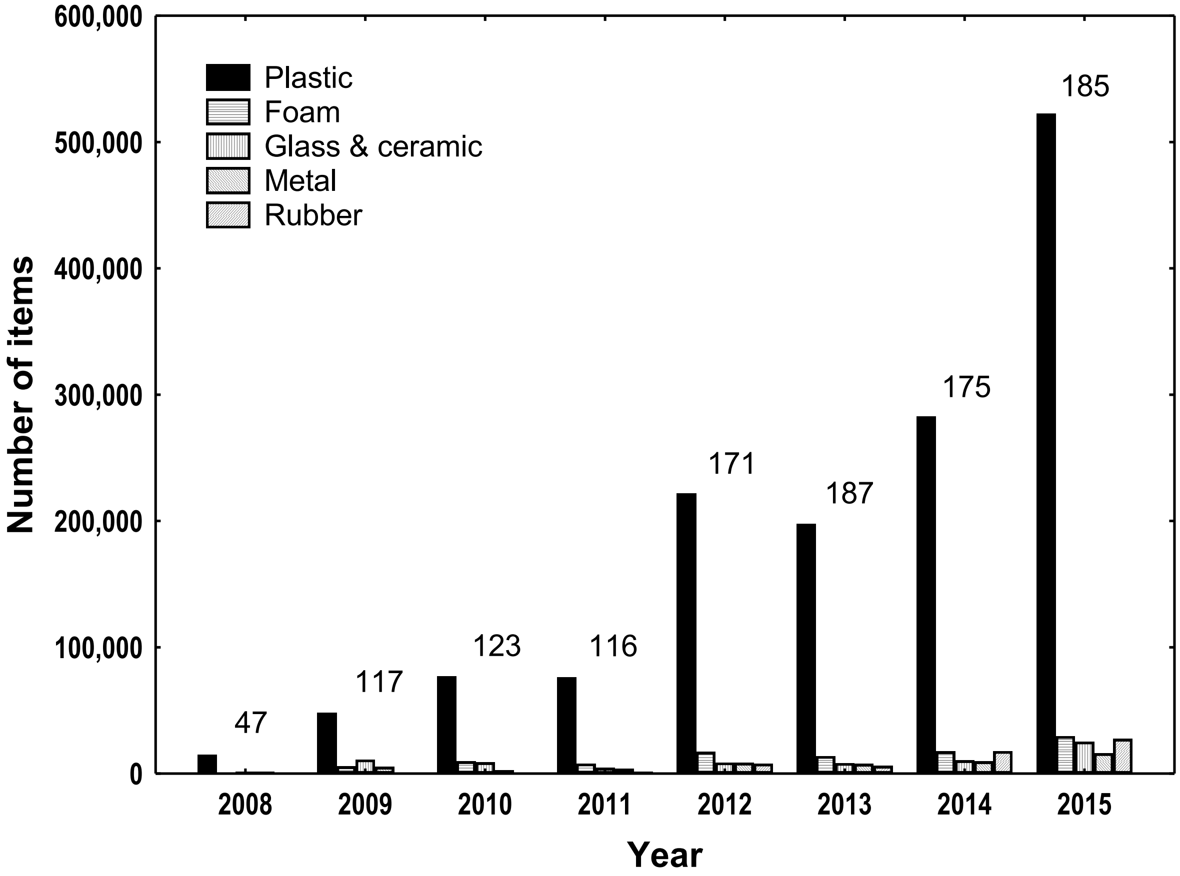

Figure 6: Number of anthropogenic items collected in beach clean-ups in the 7 NRM regions encompassing the GBR and TS marine ecosystems, from January 2008 to October 2015. Number of beach clean-ups for each year is given. Note that the length of individual beaches cleaned is not consistent across years, potentially explaining some of the inter-annual differences.

11.4.2 Microplastics

Within the study area, microplastic contamination has only recently been reported for the coastal and marine environments (**Table 11-1**) (410, 411, 414). Microplastics were first reported in surface waters of the GBR, at concentrations ranging from 1 – 80,000 pieces per km^2, during surveys in September 2012 and February 2013 (410). The highest concentrations (40,000 – 80,000 pieces per km^2) were recorded between Shoalwater Bay and Townsville in February 2013 (410). A journal publication from this work only reports the microplastic results along Cape York and Torres Strait, at concentrations of 1,500-7,500 pieces per km^2 (411). A subsequent study found microplastic contamination in waters adjacent to Orpheus and Pelorus Islands in the central GBR, at concentrations of up to two plastic fragments (size 100–500 µm) per ~11,000 L seawater (414). A pilot study examining the potential presence of microplastics in the AIMS' zooplankton collection has identified plastic fibres and particles in samples collected in the outer reef waters of the Swains in 2012 (Prof P. Sobral, pers. comm., Universidade Nova de Lisboa, Portugal). It is likely that contamination with secondary microplastics is, and will continue to be widespread, given the prevalence of marine plastic pollution in the study area. Relative to secondary microplastics, the proportion of primary microplastics is likely to be small given the relatively low population density in the GBR and TS regions.

11.5 Likely presence in the GBR and TS marine ecosystems

A global review on marine debris found that the '*majority of sea or ocean-based sources of marine litter come from merchant shipping, ferries and cruise liners; fishing vessels; military fleets and research vessels; pleasure craft; offshore oil and gas platforms and drilling rigs; and aquaculture installations*' (393). For example, lost and discarded fishing gear, both recreational and commercial (including aquaculture), contributes almost 20% of plastic debris in the oceans (419). This despite the fact that the disposal of plastics into the sea is completely banned under *Annex V* of the *International Convention for the Prevention of Pollution from Ships 1973* (420). The same review found that the primary sources of land-based marine debris are '*municipal landfills (waste dumps) located on the coast, water bodies such as rivers, lakes and ponds that are used as illegal dump sites, riverine transport of waste from landfills and other inland sources, discharges of untreated municipal sewage and storm water, industrial facilities, medical waste, and coastal tourism involving recreational visitors and beach-goers*' (393). In addition, microplastics such as fibres from clothing and microbeads from cosmetics are known to be present in treated sewage discharge (406). All these sources, except oil and gas platforms and drilling rigs, are present in the study region and are likely to contribute to the marine debris load. The relative contribution of each of these potential sources, however, is currently unknown.

Similarly to international studies, source attribution shows that marine debris in Australia is derived from marine and land-based sources, with relative attribution depending on the location (410, 413, 421). In the GBR and TS regions, only a few projects have specifically examined the sources of marine debris pollution (410, 413, 421). Most of the marine debris found on islands and cays in the Far Northern Section of the GBR is likely derived from oceanic and local shipping sources (413). On the other hand, high concentrations of marine debris recorded in the GBR lagoon between Shoalwater Bay and Townsville in February 2013 were associated with large flooding events (410) due to Ex-Tropical Cyclone Oswald (422), and thus most likely derived from land-based sources. The paths of many satellite-tracked global drifters suggest that the South Pacific and Coral Sea are at least a contributing source of marine debris washing up on the GBR and TS marine ecosystems (421). Information on sources of microplastics in the GBR and TS regions is limited (411, 414). Both studies identified these microplastics primarily as secondary, with fragments most likely derived from single-use disposable packaging and fishing equipment (411, 414).

11.6 Risk to the GBR and TS marine ecosystems

Many scientific reports have described and reviewed the effects of marine debris on species, ecosystems and fisheries (393, 406), with the occurrence and impacts of microplastics receiving particular attention in recent years. Most of these studies (>90%) report on the effects of plastics on individual species in both field collections and controlled experimental systems (394). The most recent reviews from 2015 (394, 406) found that:

- Marine debris is pervasive and has been documented in marine habitats, organisms and ecosystems around the world;
- Knowledge of the nature and extent, and impacts, of marine debris remain poorly understood;
- Whether marine plastic entanglement and ingestion ultimately result in reduced reproductive fitness and population size is difficult to determine; and
- Marine plastic pollution should be considered as one of the many threats to marine species and thus contributing to the overall cumulative impacts.

In the TS and GBR marine ecosystems, risks related to marine debris have known and potential impacts on matters of national environmental significance and OUV (5, 423). Next, we identify areas where higher risks are possible, based on studies conducted following the 2015 reviews with a particular focus on tropical marine species and ecosystems. Specifically, we examine (i) the probability of exposure to marine debris, and (ii) the likely effects of marine debris on marine organisms and ecosystems (**Table 11-2**).

Table 11-2: Priority ranking of main classes of marine debris, based on a qualitative risk assessment, in the GBR and TS marine ecosystems.

Main classes of marine debris	**NRM region**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Macroplastics (e.g. fishing nets, plastic packaging)	60	60	45	45	45	45	30
Other marine debris (glass, metal, cloth)	24	24	18	18	18	18	12
Microplastics (i.e. particles < 5mm diameter)	60	60	45	45	45	45	30

11.6.3 Probability of exposure to marine debris

In the GBR and TS marine ecosystems, the probability of exposure to marine debris is likely to be related to the presence of large commercial, military and recreational vessels, commercial fishing and tourism boats, aquaculture installations, discharges of (untreated) municipal sewage and storm water, industrial facilities, coastal tourism involving recreational visitors and beach-goers, and riverine transport of waste from landfills and other inland sources. To the best of our knowledge no monitoring has been conducted in the GBR and TS regions to specifically link marine debris to any of these sources, and their relative contribution is unknown.

Chronic exposure to marine debris is likely to occur in areas frequented by ships, primarily in ports and marinas, at anchorage areas, at moorings, and along shipping lanes. It is likely that anchorage areas and moorings, and to a lesser extent shipping lanes are also chronically exposed to marine debris. Shipping occurs primarily in enclosed and open coastal waters, but extends out into mid-shelf and offshore waters along shipping lanes and around tourist and fishing areas (5). Furthermore, commercial marine tourism in the GBR is predominantly vessel based, with >80% of day visits in 2013 concentrated in the Cairns and Whitsunday Planning Areas (5). Chronic exposure is also likely to occur at a more local scale in the vicinity of sewage, storm water, aquaculture, and industrial discharges. Discharges from these sources occur along the GBR coast, with, for example, over 50 operational wastewater treatment plants discharging into rivers that are connected to the GBR marine environment (258) (see Chapters 7.0, 8.0, and 9.0 for more detail).

Land-based sources are likely to contribute to marine debris in the GBR and TS environments through riverine transport of waste, particularly during flood events in the wet season. For example, high concentrations of marine debris recorded in the GBR lagoon between Shoalwater Bay and Townsville in February 2013 were associated with large flooding events (410) due to Ex-Tropical Cyclone Oswald (422), and thus most likely derived from land-based sources.

Overall, given the wide range of potential sources of marine debris it is likely that exposure in the GBR and TS ecosystems is widespread and occurs year-round. This is supported by data from repeated beach clean-ups at the same site showing marine debris to be present year-round, with strong seasonal variation (**Figure**).

11.6.4 Likely effects of marine debris on marine organisms and ecosystems

Both entanglement and ingestion have been reported for marine species in the TS and GBR marine ecosystems including turtles, cetaceans, dugong, and seabirds (423). In northern Australia more generally, mortality for a range of species following entanglement in marine debris has been reported including turtles, dolphins, dugong, sea snakes, sharks, pelicans, and various fish species including barramundi and sharks (424). Several Australian studies have documented ingestion of plastic particles by marine species, including seabirds on North Stradbroke Island (425), Lord Howe Island (426), and Heron Island (427), turtles from South East Queensland (428), and tropical hard corals in laboratory experiments (414). High levels of ingested plastic in seabird fledglings was associated with increased contaminant loads (426). Based on evidence from overseas (395), the impacts are likely to be much more widespread and include many more marine species than currently documented. Ecosystem

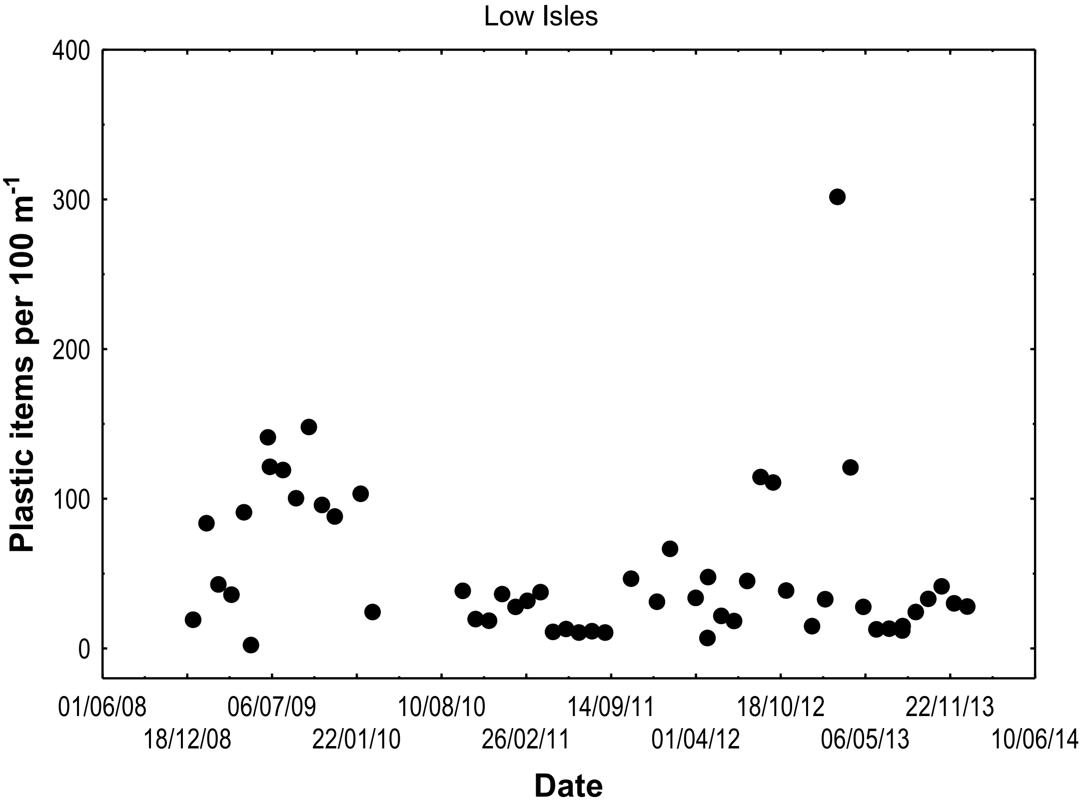

Figure 7: Number of plastic items in beach clean-ups, standardized to 100 m beach length, conducted at Low Isles from 2008 to 2014.

effects on the GBR and TS marine environments have not been examined, although micro-organisms and invertebrates have been detected on floating marine plastic in GBR waters (429), indicating a new dispersal pathway for marine organisms. Furthermore, damage by marine debris such as derelict fishing line was found to increase the occurrence of coral disease on the GBR (430). We are not aware of any Australian studies on the potential impacts of marine debris on fisheries, and potential flow-on effects on fisheries sustainability and/or human health.

11.7 Discussion, recommendations and conclusion

Marine debris has been found along the coastlines and in coastal and marine waters of all seven NRM regions in the study area (**Table 11-1**) (408, 410, 411, 413, 414). Recent monitoring programs demonstrated that plastics comprise on average 81% of total items, ranging from 58% to 91% depending on the NRM region (408). Microplastic contamination has only recently been reported for the region's coastal and marine environments (**Table 11-1**) (410, 411, 414). The timeframe for complete mineralisation of plastic in the marine environment is unknown but estimated to range from months to millennia (397, 431, 432), depending on a combination of environmental factors and the properties of the polymer (406). Such persistence makes plastic pollution of the GBR and TS marine environment a long-term issue, particularly considering the projected exponential increase of plastic production (433).

The size and composition of marine debris determine the pathways that lead to detrimental effects. For example, derelict fishing gear is comparatively large and can entangle or entrap a wide range of marine species (394, 434). Across northern Australia, mortality for a range of species following entanglement has been reported including turtles, dolphins, dugong, sea snakes, sharks, pelicans, and various fish species including barramundi and sharks (424). Ingestion of smaller particles, including micro-plastics, may block feeding and digestive processes and expose organisms to associated chemical contaminants (395-397). Plastic ingestion has been documented for a large range of marine species, including detritivores, deposit feeders, planktivores, filter-feeders and suspension-feeders (395), and has been particularly well studied in seabirds (432, 435).

To improve the assessment of risks posed by marine debris, including microplastics, to the GBR and TS marine environments, we recommend:

- develop a more comprehensive understanding of the presence, location and potential sources of marine debris by bringing together existing datasets held by governments and government agencies, universities, research organisations, industry, NGOs and community groups (*sensu* (392);
- determine the presence, concentrations and potential impacts of microplastics in discharges from coastal sewage treatment plants;
- examine the persistence of marine debris, particularly marine plastics, in tropical marine environments (including microbial breakdown);
- determine whether marine debris, including microplastics, pose an identifiable risk to the OUV of the GBR; and
- examine the effects of marine plastic pollution on commercial, recreational and indigenous fisheries, and potential flow-on effects on human health.

12.0 DEVELOPMENT OF PESTICIDE WATER QUALITY GUIDELINES

Authors: Olivia King, Michael Warne, Rachael Smith

12.1 Summary

Pesticide water quality guidelines were developed for four pesticides, namely 2,4-D (436), Metribuzin (437), Imazapac (438), and Isoxaflutole (439, 440), following the revised process to derive Australian and New Zealand guidelines for toxicants in fresh and marine waters (6) (Table 12-1).

Table 12-1: Toxicity default guideline values (µg/L) developed for four pesticides following the revised process to derive Australian and New Zealand guidelines for toxicants in fresh and marine waters (6).

Pesticide	**Reliability**	**Aquatic ecosystem**	**High conservation value systems (99% species protection)**	**Slightly to moderately disturbed systems (95% species protection)**	**Highly disturbed systems**	
					(90% species protection)	**(80% species protection)**
2,4-D	Low	Marine	26	169	393	985
Metribuzin	Moderate	Freshwater and Marine	1.6	2.9	3.7	4.9
Imazapic	Low	Freshwater and Marine	2.2	3.7	4.6	5.9
Isoxaflutole	Low	Freshwater	0.15	0.79	1.7	3.9
	Moderate	Marine	0.51	0.93	1.3	2.2

The associated reports have been submitted by DISTI to the relevant agencies for consideration of national endorsement as part of the revision of the Australian and New Zealand guidelines.

13.0 DISCUSSION, RECOMMENDATIONS AND CONCLUSIONS

Our study assessed the qualitative risk of nine emerging contaminants to the GBR and TS marine ecosystems. Based on expert knowledge from the project team and international studies, the project team and stakeholders agreed to assess the risk of heavy/trace metals and metalloids, alternate pesticides, petroleum hydrocarbons, coal particles, pharmaceuticals, personal care products (PCPs), nanomaterials (NMs), antifouling paint components, and marine debris including microplastics (Table 2-2). Additional potential emerging contaminants were identified, including (i) radio-active material; (ii) unexploded ordnance, explosive ordnance waste, and a wide range of dumped war materials; (iii) thermal pollution; and (iv) perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) contained in firefighting foam. An initial scan revealed available and/or accessible information appeared to be even less than for the other nine emerging contaminants, precluding the project team from including these four additional categories of emerging contaminants in the risk assessment.

Our assessments have provided an improved understanding of the status of the GBR and TS marine environments and potential sources of emerging contaminants. Based on the qualitative risk assessment, a subset of personal care products (Benzophenone 3), chronic antifouling contamination, marine plastic debris (macro- and microplastics) were identified as priorities (Figure).

The UV filter Benzophenone 3 can be dermally applied in products such as sunscreens, fragrances and other cosmetics. It scored highest of all the PCPs due to the (i) expected year-round release via WWTPs and *in situ* in tourist hotspots on the reef, (ii) potential for moderate impacts such as coral bleaching at low concentrations (304), and (iii) potential presence in more than one water body. Our study estimated a potential load of Benzophenone 3 released at a highly visited reef near Cairns, suggesting that the maximum release would be around ~100 g of active ingredient (i.e. UV filters) per day. The final concentrations of UV filters derived from sunscreens and cosmetics are dependent on the volume of water surrounding a reef, where a more concentrated visitor zone would increase the risk. Current management arrangements, as outlined in the most recent GBR Outlook report (5), do not consider the risk of UV filters to the GBR marine ecosystems.

Across the GBR marine ecosystems, chronic contamination of water and sediments from antifouling paint components has been identified as a relatively high risk compared to other emerging contaminants (Figure). With shipping extending out into mid-shelf and offshore waters along shipping lanes and around tourist and fishing areas, chronic exposure is likely to occur continuously throughout the year. This risk is particularly high in the Burnett Mary NRM region due to the high number of ship voyages across all four water bodies (5). This indicates that current management arrangements, which do not consider the risk of routine shipping operations and associated leaching or loss of antifouling paints, may need to be re-assessed.

Our study demonstrates the high risk of marine plastic pollution to the study regions' marine ecosystems relative to the other emerging contaminants (Figure). The risk appears to be particularly high in the Cape York and TS NRM regions due to the documented prevalence of marine debris across all four water bodies of the marine environment (408). This is of concern given the otherwise relatively pristine condition of this area (441), the impacts on marine species including turtles, cetaceans, dugong, and seabirds (423), and potential flow-on effects on culturally significant seafood species and human health risks (5). Most of the marine debris found on islands and cays in the Far Northern Section of the GBR is likely derived from oceanic and local shipping sources (413). Across the study region more broadly, risks related to marine debris have known and potential impacts on matters of national environmental significance and OUV (5, 423). In contrast, the potential flow-on effects on fisheries sustainability and human health, including microplastic ingestion and accumulation of chemical contaminants associated with marine plastics (403-405), are currently unknown.

A large range of marine and land-based sources will contribute to marine plastic debris found in the GBR and TS marine ecosystems, with relative attribution depending on the location. For example, oceanic and local shipping sources contribute to most of the debris found on islands and cays in the Far Northern Section of the GBR (413), while land-based sources can contribute significantly to high concentrations of marine debris in the GBR lagoon (410, 421). Furthermore, the paths of many satellite-tracked global drifters suggest that the South Pacific and Coral Sea are at least a contributing source of marine plastic debris washing up on the GBR and TS coasts and islands (421). Microplastics detected in the GBR and TS regions are mostly ‘secondary microplastics’, with fragments most likely derived from single-use disposable packaging and fishing equipment (411, 414). The persistence of plastics makes marine plastic pollution of the study region a long-term issue, particularly considering the projected exponential increase of plastic production (433).

The qualitative risks of all other emerging contaminants are relatively low with some minor differences between NRM regions (Figure). At a local scale, their impacts on marine ecosystems can still be significant in particular when derived from the same point sources and cumulative effects are likely. Our study showed that both Ports and WWPTs are likely to contribute a wide variety of emerging contaminants to the marine environments, in particular to the GBR due to the higher population density and the location of five larger port facilities. In our study region, ports are main sources of heavy/trace metals and metalloids, petroleum hydrocarbons, and coal particles, while WWTP are main sources of pharmaceuticals and PCPs, and likely contain NMs and microplastics. Release of these contaminants into the GBR marine environment can have localised impacts on water and sediment quality, and marine organisms (for references, see Section 6 of the relevant Chapters).

Compared to the current contaminants of concern, namely sediment, nutrients and pesticides (1, 2), the risks of some PCPs, chronic contamination from antifouling paints, and marine plastic pollution to the GBR and TS marine ecosystems may be equivalent if not higher in at least some NRM regions (Table 14-6). In the Wet Tropics NRM region, the risk of current contaminants of concern to the marine ecosystems is higher than any of the nine emerging contaminants assessed in our project. In contrast, in the TS and Cape York NRM regions, the risk of marine plastic pollution to the marine ecosystems is likely to be higher than that of any of the current contaminants of concern. The relative risk of marine plastic pollution, chronic contamination by antifouling paints, and certain PCPs to marine ecosystems south of Cape York is of concern, and requires further research to improve our understanding of their presence, distribution and ecological impact. Our knowledge of the potential impacts of these priority emerging contaminants on GBR and TS marine ecosystems is much less established than those of the current contaminants of concern. Nevertheless, at a time when the GBR and TS coastal and marine ecosystems are facing multiple threats, the potential that these priority emerging contaminants are adding to the cumulative risks is a concern.

The qualitative risk assessments conducted as part of this study should be considered relative, and come with a level of uncertainty given the lack of (available) monitoring data for most the emerging contaminants examined. For some emerging contaminants, such as heavy/trace metals and metalloids and marine debris, additional databases were identified but not made available by the respective custodians for our study. This means that not all existing environmental datasets were included in our assessments, with a potential flow-on effect on policy and management not being based on a complete picture of existing relevant information. For other emerging contaminants, such as pharmaceuticals, PCPs and NMs, little to no monitoring data exists for the study region and our assessments relied primarily on information from other Australian or international studies. This highlights the need for local, targeted monitoring campaigns to reduce the uncertainty in future risk assessments.

Finally, we recommend the following three key areas of research to inform management and policy decisions that will maintain and improve the condition of the marine environments in the GBR and Torres Strait regions:

1. To ensure that valuable environmental data are placed into the public domain and made available in integrated databases for building marine baselines for the GBR WHA and TS region (*sensu* (392)). Depending on the emerging contaminant of concern, this would include data from governments and government agencies, universities, research organisations, agricultural industries, port authorities and associated industries, engineers, consultants, NGOs and community groups.
2. To conduct local, targeted monitoring campaigns for emerging contaminants with little or no recent monitoring data for the GBR WHA and TS region, including monitoring of:
   a. microplastics across the region's marine ecosystems;
   b. antifouling paints at GBR anchorage areas off the five major ports (Abbot, Cairns, Gladstone, Hay Point, and Townsville);
   c. UV filters in certain PCPs in WWTPs discharges and *in situ* in tourist hotspots on the reef;
   d. heavy/trace metals and metalloids, petroleum hydrocarbons, and coal particles at high volume GBR ports (Abbot, Cairns, Gladstone, Hay Point, and Townsville), and;
   e. pharmaceuticals, PCPs, NMs and microplastics at WWTPs discharging from the more highly populated areas (Cairns, Townsville, Rockhampton and Gladstone, Bundaberg and the coast surrounding Fraser Island, and Mackay).
3. To examine the ecological impacts of marine plastic pollution, chronic contamination of antifouling paints, and certain PCPs on GBR and TS marine organisms and ecosystems, including cumulative impacts with ocean acidification and sea temperature increase (i.e. the two highest risks to the GBR Region's heritage values (5)).

Figure 8: Comparison of qualitative risks of emerging contaminants to the Great Barrier Reef and Torres Strait Environments, presented for each of the seven NRM regions. The scale boundaries are <10, 10-<20, 20-<30, 30-<40, 40-<50, and 50-<60.

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14.0 APPENDICES

Table 14-1: Contributors to the Australian Marine Debris Initiative, hosted by the Tangaroa Blue Foundation.

Individual community volunteers
1770 Liquid Adventures
Absolute North Charters
Agnes Water State School
Apudthama Land and Sea Rangers
Australian Institute of Marine Science
Australian Navy
Australian Quarantine Inspection Service (AQIS)
Ayton Butcher
Badu Island Land & Sea Rangers
Barron Catchment Care
Bgwcolman State School
Blackwater State High School
Bloomfield River School
Bluff State School
Boigu Island Land & Sea Rangers
Boot Camp Fitness Crew
Breakthru People Solutions
BT Financial
Bundaberg Regional Council
Burdekin Christian College
Burdekin Shire Council
Burnett Mary Regional Group (BMRG)
Busby Contracting
Cairns & Hinterland Steiner School
Fitzroy River and Coastal Catchments
Friends of Parks, QLD Government
Gidarjil Development Corporation
Gidarjil Land & Sea Rangers
Girringun Aboriginal Rangers
Girringun Aboriginal Rangers - Junior Ranger Program
Gladstone Regional Council
Glenmore State High School
Gordonvale High School
Gordonvale State School
Great Barrier Reef Marine Park Authority (GBRMPA)
Green Cross Australia
Greening Australia
Gudjuda Aboriginal Rangers
Gudjuda Reference Group Aboriginal Corporation
Gumlu State School
Gundoo Indigenous Junior Rangers
Gunggandji Traditional Ower Group
Hambledon State School
Haymanis School
Hikers on Hinchinbrook Island
Holloways Beach Environmental Education Centre
Holy Cross Catholic Primary School
Port Douglas State School
Poruma Island Land & Sea Rangers
Poruma School Campus
Queens Beach Action Group
Queensland Acid Sulfate Soils Investigation Team (QASSIT)
Queensland Boating and Fishing Patrol
Queensland Parks & Wildlife Service (QPWS)
Queensland Trust for Nature
Queensland Turtle Research
Redlynch State College
Reef Check Australia
Reef Connections
Reef Guardian School's Future Leaders Eco Challenge (FLEC)
Responsible Runners QLD
Rockhampton Grammar School
Rockhampton North Side Family Church Youth group
Rockhampton Youth Justice
Rollingstone State School
Sacred Heart School Thursday Island
Sea Turtle Foundation
Smithfield Shopping Centre Corporate Group
South Cape York Catchments (SCYC)
South Tully State School
St Andrews Catholic College
St Anthony's Catholic Primary School

Cairns Local Marine Advisory Committee
Cairns Turtle Rehabilitation Centre
Cairns Youth Justice Service Centre
Cannonvale State School
Cape York marine Advisory Group
Cape York NRM
Capricorn Coast Outriggers
Capricornia Catchments
Cardwell State School
Cassowary Coast Regional Council
Catherines School
Clean Coast Collective
Coast Guard - Port Douglas
Commonwealth Bank
Conservation Volunteers Australia QLD (CVA)
Cook Shire
Cooktown Bakery
Cooktown Chemist
Cooktown Coast Guard
Cooktown Hardware
Cooktown Hospital
Cooktown IGA
Cooktown Landcare
Cooktown Local Marine Advisory Committee (LMAC)
Cooktown Police & Citizens Youth Club
Cooktown Primary School
Cooktown Women's Association
CQ Offroad Club
Home Hill State School
Hopevale Aboriginal Council
Hopevale Congress Rangers
Hopevale State School
Iamalgal Rangers
Ice Works
Ignatins Park College
Isabella State School
Jabalbina Yalanji Aboriginal Corporation
Jabalbina Yalanji Rangers
James Cook University (JCU)
Kawadji Kanidji Land & Sea Rangers
Keppel Bay Sailing Club
Keppel Coast Girl Guides
Keppel Island Conservation Community
Koala Camping
Koiranah Ranger Guides
Kuuku Ya'u Traditional Owners
Lady Elliot Island Eco Resort
Lama Lama Aboriginal Rangers
Lions Yeppoon Tropical Pinefest
Liquid Adventures
Livingstone Shire Council
Lizard Island Resort
Lizard Island Social Club
Lockhart River Aboriginal Council
Lockhart River Land and Sea Rangers
Lockhart River State School
Low Isles Preservation Society
Lower Burdekin Landcare Association
St Augustines School Mossman
St Benedicts Catholic Primary School
St Brendan's College, Yeppoon
St Francis School - Tannum Sands
St Gerard Majella School
St Michaels Catholic College
St Michaels School
State University of New York at Brockport
Study Abroad in Oceana (AUIP)
Sunshine Breeze Guides
Surfrider Foundation Australia QLD
Tagai State College - Badu Island Campus
Tagai State College - Erub Island Campus
Tagai State College - Horn Island Campus
Tagai State College - Mer Island Campus
Tagai State College - Saibai Island Campus
Tagai State College - St Pauls Campus
Tagai State College - Thursday Island Campus
Tangaroa Blue Foundation
Tannum Sands State High School
Tarangba State School
The Bowls Club
Torres Strait Regional Authority - Land & Sea Management Unit (TSRA - LSMU)
Townsville City Council
Transpac and Adams Waste
Trinity Anglican School
Trinity Anglican School Kewarra Beach
Tropical North Queensland TAFE
Virginia Tech

CQUniversity, Indigenous Land and Sea Program
Daintree State School
Darumbal Traditional Owners and Elders
Department of Environment and Heritage Protection (QLD)
Department Of Justice and Attorney-General QLD
Department of National Parks, Recreation, Sport and Racing - Marine Parks
Dharumbal Traditional Owners
Dingo State School
Discovery Coast Environment Group
Djunbunji Junior Rangers
Djunbunji Ltd Land and Sea Program
Douglas Shire Council
Earth Smart Science Program
Eastern Kuku Yalanji Community
Eco Barge Clean Seas Inc
Edge Hill State School
Emerald Marist College
Evoke Eco Yoga
Farnborough State School
Feluga State School
Fitzroy Basin Association
Fitzroy Basin Elders Committee Inc
Mabuiag Island land & Sea Rangers
Mackay Regional Council
Magnetic Island State School
Maidvale State School
Marlborough State School
Masig Land & Sea Rangers
Mercy College Mackay
Miallo State School
Mission Beach State School
Moa Island Land & Sea Rangers
Mossman Elders Justice Group
Mossman Senior High School
Mossman State School
My Pathway
NAILSMA
Network for Sustainable Fishing Douglas Region
North Keppel Island Environmental Education Centre
North Mackay State High School
North Queensland Bulk Ports Corporation
NQ Dry Tropics
NQ Dry Tropics NRM
Oceanwatch Australia Ltd QLD
Parley for the Oceans
Wangetti Recovery Group
Warraber Island Land & Sea Rangers
Warraber Ngurpay Lag
Weary Bay Community
Wet Tropics NRM
Wild Mob
Wildlands Studies Australia
Wildlands Studies Program - USA
Wonga Beach State School
Woree State School
Worimi Local Aboriginal Land Council
Wujal Wujal Aboriginal Community & Traditional Owners
Wunjunga Progress Association
Yarrabah Aboriginal Shire Council
Yarrabah Police-Citizens Youth Club
Yarrabah State School
Yeppoon State School
Yintjingga Aboriginal Corporation
Yirrganydji Traditional Owners
Yongala Dive
Yorkeys Knob State School
Yuku-Baja-Muliku Rangers

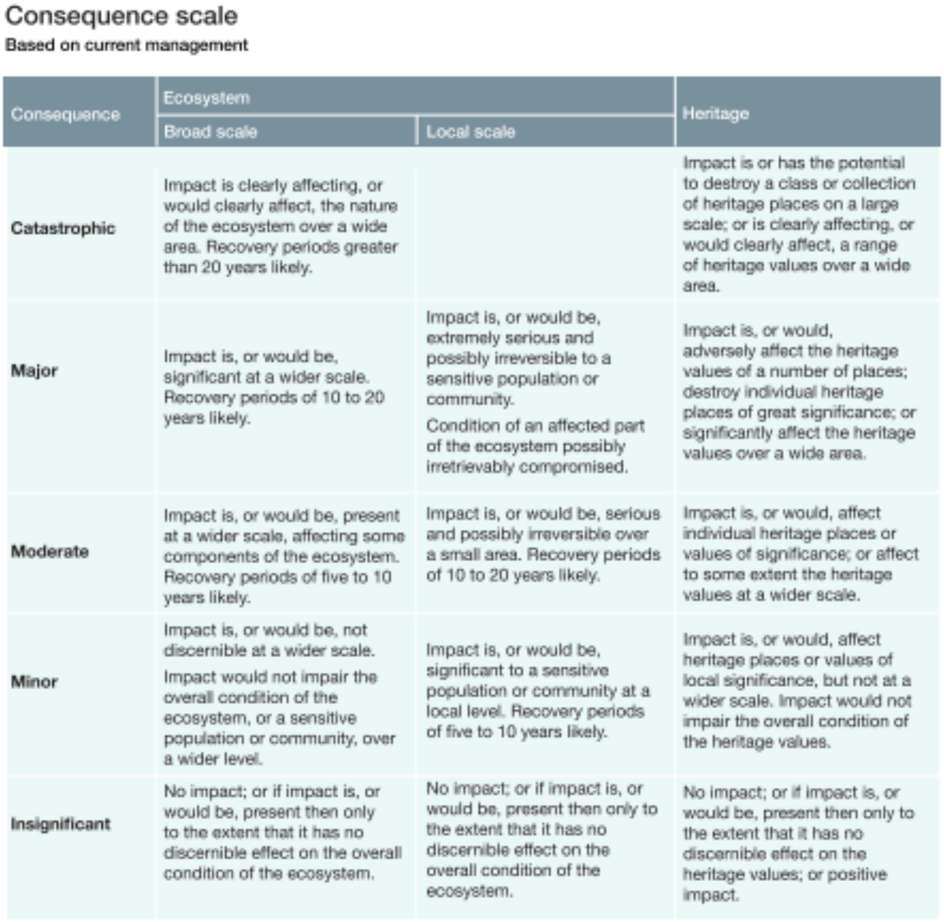
Table 14-2: Risk assessment framework used in this project, modified from the Australian Standard for Risk Assessment, combining *Likelihood* and *Consequence* (5), as well as *Area* to include the number of water bodies the risk may occur.

Likelihood scale (1-5, with 1 being rare and 5 being almost certain, etc.)

Likelihood scale

Likelihood	Expected frequency of a given threat
Almost certain	Expected to occur more or less continuously throughout a year
Likely	Not expected to be continuous but expected to occur one or more times in a year
Possible	Not expected to occur annually but expected to occur within a 10-year period
Unlikely	Not expected to occur in a 10-year period but expected to occur in a 100-year period
Rare	Not expected to occur within the next 100 years

Consequence scale (1-5, with 1 being insignificant and 5 being catastrophic, etc.)



Consequence scale

Based on current management

Consequence	Ecosystem		Heritage
	Broad scale	Local scale	
Catastrophic	Impact is clearly affecting, or would clearly affect, the nature of the ecosystem over a wide area. Recovery periods greater than 20 years likely.		Impact is or has the potential to destroy a class or collection of heritage places on a large scale; or is clearly affecting, or would clearly affect, a range of heritage values over a wide area.
Major	Impact is, or would be, significant at a wider scale. Recovery periods of 10 to 20 years likely.	Impact is, or would be, extremely serious and possibly irreversible to a sensitive population or community. Condition of an affected part of the ecosystem possibly irretrievably compromised.	Impact is, or would, adversely affect the heritage values of a number of places; destroy individual heritage places of great significance; or significantly affect the heritage values over a wide area.
Moderate	Impact is, or would be, present at a wider scale, affecting some components of the ecosystem. Recovery periods of five to 10 years likely.	Impact is, or would be, serious and possibly irreversible over a small area. Recovery periods of 10 to 20 years likely.	Impact is, or would, affect individual heritage places or values of significance; or affect to some extent the heritage values at a wider scale.
Minor	Impact is, or would be, not discernible at a wider scale. Impact would not impair the overall condition of the ecosystem, or a sensitive population or community, over a wider level.	Impact is, or would be, significant to a sensitive population or community at a local level. Recovery periods of five to 10 years likely.	Impact is, or would, affect heritage places or values of local significance, but not at a wider scale. Impact would not impair the overall condition of the heritage values.
Insignificant	No impact; or if impact is, or would be, present then only to the extent that it has no discernible effect on the overall condition of the ecosystem.	No impact; or if impact is, or would be, present then only to the extent that it has no discernible effect on the overall condition of the ecosystem.	No impact; or if impact is, or would be, present then only to the extent that it has no discernible effect on the heritage values; or positive impact.

Area Scale (1-4, with 1 covering one water body; 4 covering all four water bodies, etc.)

Area	
Extreme (4)	All four water bodies (enclosed coastal, open coastal, mid-shelf and offshore marine)
Large (3)	Any three water bodies (enclosed coastal, open coastal, mid-shelf and/or offshore marine)
Medium (2)	Any two water bodies (enclosed coastal, open coastal, mid-shelf and/or offshore marine)
Small (1)	Any one water body (enclosed coastal, open coastal, mid-shelf or offshore marine)

Table 14-3: Likelihood of contribution sources to contamination by petroleum hydrocarbons in different GBR and TS locations. Scale 1-5 with 0 being not possible, 1 being low and 5 almost certain.

Contributing sources	**Locations**			
	Large ports with low urban and agricultural populations	Large ports with large urban populations and/or agricultural catchments	Urban and agricultural catchments without large ports	Coastal and reef locations distant from large port and urban influences
Agriculture: including runoff of minor spills and leaks	1	2	2	1
Urban inputs: including the runoff of minor spills and leaks	1	2	2	1
Port industrial activities: including spills and leaks from refuelling and loading facilities, including coal	4	5	3	1
Small boat discharge from engines into the water and spills	2	3	2	1
Ship discharge from engines into the water and spills	2	2	1	1
Shipping accidents: including groundings and collisions	2	2	1	2
Atmospheric deposition: including burnt fuel and coal dust	2	2	1	1
Oil extraction	0	0	0	0

Table 14-4: Studies conducted on the impacts of coal particles to aquatic flora and fauna.

Study organism	**Coal treatment**	**Observed effect**	**Conclusions and comments**	**Source**
Aquatic moss (*Eurhynchium riparioides*)	3 wk exposure to range of coal concentrations.	Abrasive damage and reductions in chl *a* production	Effects at high concentrations 5000 mg l^{-1}	(239)
Macroalgae, (*Ulva lactuca)*	< 500 µm, 500-2000 µm, and 0-2000 µm under turbulent (shaken) and still conditions for 8 days.	*U. lactuca* lost weight in the presence of colliery waste but only under turbulent conditions	Large grain sizes of colliery waste caused physical abrasion to macroalgae in turbulent conditions, which could result in the lowering of species richness in proximity to colliery waste inputs; In still conditions, colliery waste promoted the growth of *U. lactuca*, suggesting that waste could be beneficial to rock pool flora.	(240)
Mangroves (*Avicennia marina*)	Coal dust was found to accumulate on leaf surfaces, branches, trunks near a South African coal port	Dust reduced carbon dioxide exchange and chlorophyll fluorescence by 17-39%, decreasing photosynthetic performance.	Chronic contamination may reduce mangrove productivity	(241)
Coho salmon (*Oncorhynchus kisutch*)	Exposed to suspended coal particles at 13,500, 8,000, 3,500 and 3,000 mg l^{-1}.	96 hour LC_{50} of 7,000 mg l^{-1}; mortalities occurred at concentrations > 3,000 mg l^{-1}.	Few fish were found to feed during the experiment however those that did feed contained coal particles in the alimentary tract; The authors did not attribute the Coho mortalities to a specific cause and only conducted histological examinations on the fish that did not die during exposure.	(242)
Dungeness crabs (*Metacarcinus magister*)	Coal was mixed with sand for 21 day exposure experiment to examine effect on oxygen consumption and gill ventilation.	No mortalities in crabs. Deposition of coal the lamellae of the crabs, but oxygen consumption and gill ventilation were not impacted.	The coal was mixed within the sediment and was not in suspension, suggesting that the response of the crabs to coal in suspension was not measured.	(242, 243)
Coral (*Acropora tenuis*), fish (*Acanthochromis polyacanthus*), seagrass (Halodule uninervis)	Exposures to fine (<63 µm) coal particles in a flow-through experimental system for up to 28 d	Mortality in coral at 38 mg l^{-1}. Reduced growth in fish and seagrass at 38 and 73 mg l^{-1} respectively	This represents the only experimental data on the effects of suspended coal particles on tropical marine taxa. The effects on corals and seagrass were likely due to light attenuation and surface attachment/smothering, while the effects on fish were likely due to blocked feeding and digestion.	(442)

Table 14-5: Studies conducted on the leaching of metals and PAHs from coal into seawater and/or the effects on marine and freshwater organisms.

Study organism	**Coal treatment**	**Observed effect**	**Conclusions / comments**	**Source**
N/A	Investigated leaching with a number of variables such as temperature, pH, particle size, O_2 saturation, contact time, flow.	Increases in temperature and decreases in pH generally resulted in increased leachate concentrations of most metals analysed; Sulphur rich coal had a lower leachate pH and generally leached higher concentrations of metals such as Cd, Co, Cu, Mn, Ni and Zn.	High coal sulphur content and low leachate pH are linked with elevated metal concentrations in coal leachates.	(443)
N/A	Coal of a wide particle size distribution from the Bowen Basin, QLD shaken in seawater for 2 hours and left to leach for 24 h.	Leaching of Cd, Cu, Pb, Mn, Mo, Ni and Zn was detected	Cu and Mn in leachate exceeded ANZECC 2000 water quality guidelines.	(60)
N/A	Environmental monitoring of metals in colliery waste washed up on beaches in comparison to that measured in coal and waste prior to dumping.	Detected lower metal concentrations (many below guidelines levels) in colliery waste washed up on a beach compared to that measured in coal and waste prior to dumping.	The lower metal levels on the beach suggested that metal content was leached out while on the seabed and could have been bioavailable to aquatic organisms.	(444)
Marine bivalves *Mytilus edulis* and *Macoma balthica*	Environmental sampling from petroleum and coal contaminated marine waters	Both species contained hydrocarbons of non-algal and planktonic origin, indicating ingestion or passive uptake by contact	Multiple sources of hydrocarbon contamination limit conclusive evidence of the contribution by coal	(445)
Marine gastropod *Hexaplex trunculus*	Gastropods were exposed to coal particles in the substrate.	Bioaccumulation of Cd from coal was detected in the hepatopancreas.	Damaged external epithelia and significantly more metallothioneins (which play an important role in metal detoxification) were detected in exposed organisms.	(446)
Marine fish (*Fundulus heteroclitus*)	Fish were dosed in static exposure tanks with water extracts of coal (leachates).	A significant reduction in sperm production by fish exposed to some, but not all coal leachates. Sperm production during the breeding season by six field populations of Fundulus, either adjacent to, or 2 miles upstream from coal-fired power plants were not significantly different from one another.	Possible effects of coal leachate on reproductive success of some fish.	(447, 448)
Marine oysters (*Crassostrea virginica*)	Exposure to coal dust plus leachate (10 mg L^{-1}) for 15 days, and 1 mg L^{-1} coal dust for 28 days in a flow through system.	After 7, 14, and 28 days exposure, PAH body burden had not increased, provided coal particles were first purged from their guts. Additionally, high coal exposure did not exhibit any effect on shell growth.	PAHs were not bioavailable to the oysters.	(449)
Freshwater Zebra fish (*Danio rerio*) embryos	Fish embryos were exposed to solvent-extracted polyaromatic compounds from coal including PAHS (PACs)	Effects of PACs on fish embryo mortality were highly dependent on the coal type.	While toxicity was observed, the method of extraction of PACs (with solvents) is likely to overestimate the potential harm to organisms in the environment.	(450)

Table 14-6: Details of qualitative risk assessments, using an established risk assessment framework considering '*Likelihood*' and '*Consequence*' (5), as well as '*Area*' (see Table 14-2), for nine main classes of emerging contaminants.

Main classes of emerging contaminant	**NRM regions**						
	Torres Strait	**Cape York**	**Wet Tropics**	**Burdekin**	**Mackay Whitsunday**	**Fitzroy**	**Burnett Mary**
Heavy and trace metals/metalloids	24	24	20	20	20	20	16
	(4x3x2)	(4x3x2)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(4x2x2)
Alternate pesticides							
Metolachlor, metribuzin and imidacloprid	2	2	16	16	16	16	6
	(2x1x1)	(2x1x1)	(4x2x2)	(4x2x2)	(4x2x2)	(4x2x2)	(3x2x1)
Petroleum hydrocarbons							
Chronic contamination of water and sediments	4	8	20	20	20	20	8
	(1x2x2)	(1x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(2x2x2)
Ship collisions and groundings	16	16	16	16	16	16	16
	(2x4x2)	(2x4x2)	(2x4x2)	(2x4x2)	(2x4x2)	(2x4x2)	(2x4x2)
Coal							
Dust - colliery waste from rivers, storage, loading and transport activities	2	2	2	20	20	20	2
	(1x2x1)	(1x2x1)	(1x2x1)	(5x2x2)	(5x2x2)	(5x2x2)	(1x2x1)
Particles - ship collisions and groundings	9	9	9	9	9	9	9
	(3x3x1)	(3x3x1)	(3x3x1)	(3x3x1)	(3x3x1)	(3x3x1)	(3x3x1)
Pharmaceuticals							
Gemfibrozil, Venlafaxine, Tramadol	4	4	20	20	20	20	20
	(2x2x1)	(2x2x1)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)
Personal care products							
Benzophenone 3	12	12	30	30	30	30	30
	(2x3x2)	(2x3x2)	(5x3x2)	(5x3x2)	(5x3x2)	(5x3x2)	(5x3x2)
DEHP	8	8	20	20	20	20	20
	(2x2x2)	(2x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)	(5x2x2)
Galaxolide, Triclosan	4	4	16	16	16	16	16

	(1x2x2)	(1x2x2)	(4x2x2)	(4x2x2)	(4x2x2)	(4x2x2)	(4x2x2)
Benzalkonium Cl	3	3	12	12	12	12	12
	(1x3x1)	(1x3x1)	(4x3x1)	(4x3x1)	(4x3x1)	(4x3x1)	(4x3x1)
Bisphenol A	4	4	10	10	10	10	10
	(2x2x1)	(2x2x1)	(5x2x1)	(5x2x1)	(5x2x1)	(5x2x1)	(5x2x1)
Nanomaterials							
Ag, TiO_2, ZnO	2	2	8	8	8	8	8
	(1x2x1)	(1x2x1)	(2x2x2)	(2x2x2)	(2x2x2)	(2x2x2)	(2x2x2)
CeO_2, Carbon (e.g. fullerenes)	2	2	4	4	4	4	4
	(1x2x1)	(1x2x1)	(2x2x1)	(2x2x1)	(2x2x1)	(2x2x1)	(2x2x1)
Antifouling paints							
Chronic contamination of water and sediments	16	16	30	30	30	30	40
	(4x2x2)	(4x2x2)	(5x2x3)	(5x2x3)	(5x2x3)	(5x2x3)	(5x2x4)
Ship collisions and groundings	18	18	18	18	18	18	18
	(3x3x2)	(3x3x2)	(3x3x2)	(3x3x2)	(3x3x2)	(3x3x2)	(3x3x2)
Marine debris and microplastics							
Macroplastic	60	60	45	45	45	45	30
	(5x3x4)	(5x3x4)	(5x3x3)	(5x3x3)	(5x3x3)	(5x3x3)	(5x3x2)
Other marine debris (glass, metal, cloth)	24	24	18	18	18	18	12
	(3x2x4)	(3x2x4)	(3x2x3)	(3x2x3)	(3x2x3)	(3x2x3)	(3x2x2)
Microplastic	60	60	45	45	45	45	30
	(5x3x4)	(5x3x4)	(5x3x3)	(5x3x3)	(5x3x3)	(5x3x3)	(5x3x2)
Current pollutants of concern (1, 2)							
Sediment	3	36	80	40	40	40	40
	(1x3x1)	(3x3x4)	(5x4x4)	(5x4x2)	(5x4x2)	(5x4x2)	(5x4x2)
Dissolved inorganic nitrogen	2	24	80	40	40	40	40
	(1x2x1)	(2x3x4)	(5x4x4)	(5x4x2)	(5x4x2)	(5x4x2)	(5x4x2)
PSII herbicides	2	16	60	30	30	30	30
	(1x2x1)	(2x2x4)	(5x3x4)	(5x3x2)	(5x3x2)	(5x3x2)	(5x3x2)

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