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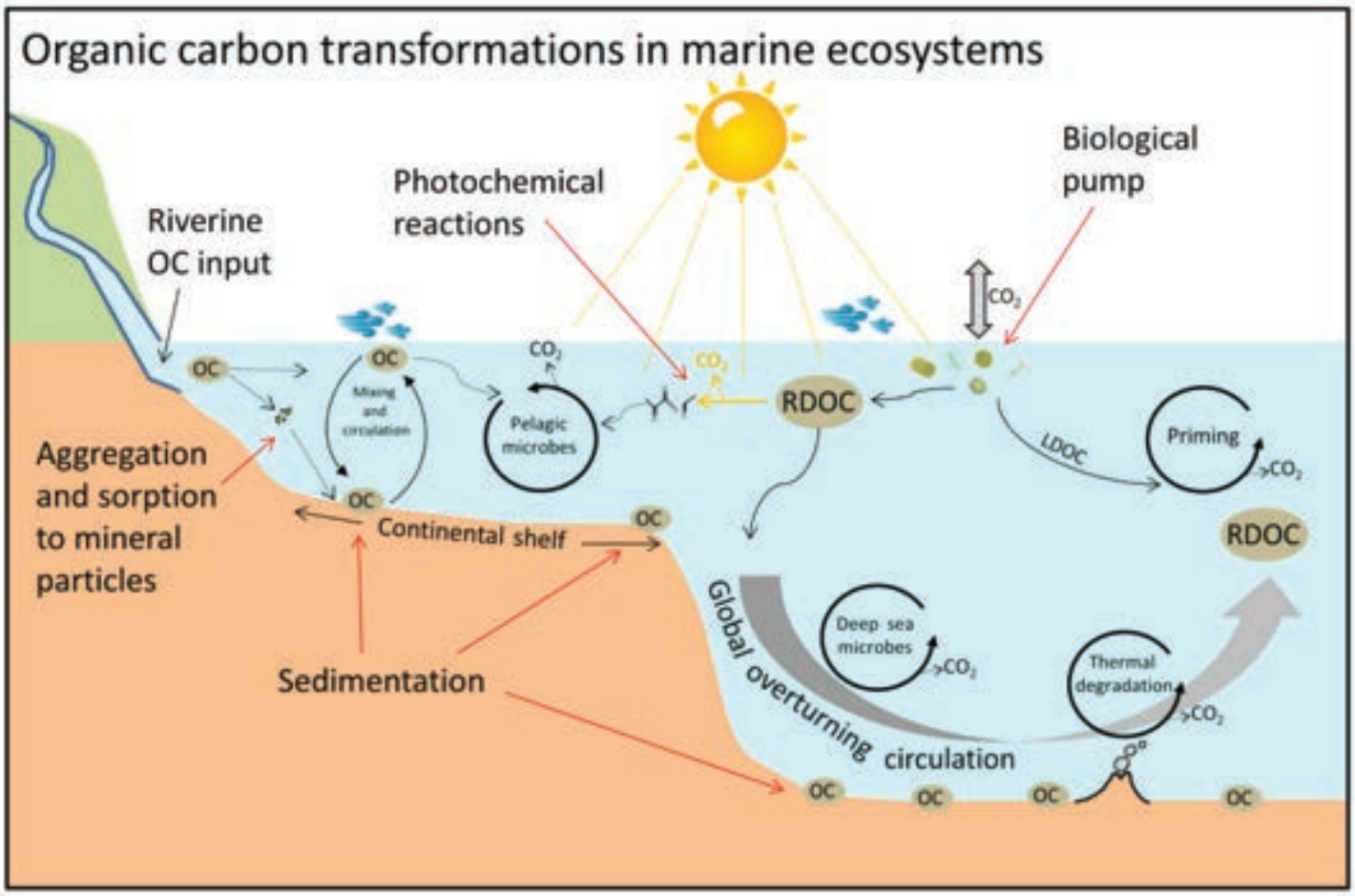
Sources, transformations and fate of particulate and dissolved organic carbon: Implications for the Great Barrier Reef

Ryan M. Burrows, Stephen E. Lewis, Alexandra Garzon-Garcia, Joanne Burton, Jon E. Brodie, Jodie Mehrtens, Jean Erbacher, Kevin Gale and Michele A. Burford



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Sources, transformations and fate of particulate and dissolved organic carbon: Implications for the Great Barrier Reef

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Cover diagram: Ryan M. Burrows designer

This report is available for download from the NESP Tropical Water Quality Hub website:
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ACRONYMS AND ABBREVIATIONS

NESP ..... National Environmental Science Program
RRRC..... Reef and Rainforest Research Centre Limited
TWQ..... Tropical Water Quality
C..... Carbon
CH_4..... Methane
CHL-*a*..... Chlorophyll a
CO_2..... Carbon dioxide
CO_{2aq}..... Aqueous carbon dioxide
CRAMs ..... Carboxyl-rich alicyclic molecules
DIC..... Dissolved inorganic carbon
DIN..... Dissolved inorganic nitrogen
DO..... Dissolved oxygen
DOC ..... Dissolved organic carbon
DoEE..... Department of the Environment and Energy
DOM..... Dissolved organic matter
FT-ICR MS.... Fourier transform ion cyclotron resonance mass spectrometry
GBR ..... Great Barrier Reef
GOC ..... Global overturning circulation
HDOC..... High-molecular weight dissolved organic carbon
HfPOC..... Heavy fraction particulate organic carbon
HPLC ..... High performance liquid chromatography
LDOC..... Low-molecular weight dissolved organic carbon
LfPOC..... Light fraction particulate organic carbon
N..... Nitrogen
OC..... Organic carbon
OET..... Oxygen exposure time
OM ..... Organic matter
P..... Phosphorus
POC ..... Particulate organic carbon
POM..... Particulate organic matter
PON ..... Particulate organic nitrogen
RDOC..... Recalcitrant dissolved organic carbon
TOC..... Total organic carbon
UV ..... Ultra violet

ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

Organic carbon describes a heterogeneous mixture of molecules that originate from a plethora of living and non-living sources on land and in aquatic environments. Almost all organic carbon molecules are originally produced during photosynthesis, except during chemosynthesis which takes place in the absence of light. Organic carbon plays a critical role in global biogeochemical cycles, including in mediating the availability of inorganic nitrogen, and is a key energy source in freshwater and marine food webs. However, organic carbon can also have negative ecological impacts, particularly in coral reef ecosystems. For example, elevated organic carbon concentrations have been reported to cause coral mortality, coral bleaching, reduced rates of photosynthesis in coral zooxanthellae, and can lead to slower coral calcification rates. With this is mind, there has been concern regarding a recent trend of increasing concentrations of dissolved organic carbon and in some locations, particulate organic carbon, at regular monitoring points in coastal waters of the Great Barrier Reef marine ecosystem in north-east Australia. In this review, we summarise the global literature on the sources, transformations, and fate of dissolved organic carbon and particulate organic carbon in coastal marine ecosystems. We then apply the mechanistic understanding gained from this review to identify the key processes relating to organic carbon dynamics in the Great Barrier Reef. Finally, we conduct a preliminary data analysis using existing marine monitoring data to investigate the factors correlating with increases in the concentrations of dissolved organic carbon and particulate organic carbon over time.

Three conceptual scenarios describe the typical biogeochemical and ecological states of the Great Barrier Reef in relation to changes in the source, transformation and fate of dissolved organic carbon and particulate organic carbon:

> **Scenario 1.** “Normal” state where the availability of dissolved organic carbon and particulate organic carbon in the majority of the Great Barrier Reef is controlled by the resuspension and delivery of organic carbon by tides and currents (mainly wind-driven) from benthic sediment, rivers, mangrove, and saltmarshes, as well as from phytoplankton production;
> **Scenario 2.** Extreme-weather event-based increase in terrestrial and marine organic carbon due to elevated freshwater discharge from land and the resuspension of marine sediment during storm events; and,
> **Scenario 3.** Post extreme-weather event scenario whereby the organic carbon that was input and/or resuspended during Scenario 2 promotes the activity of bacterioplankton and phytoplankton.

The mechanistic understanding gained in these three conceptual scenarios highlight numerous potential terrestrial and marine sources of dissolved organic carbon and/or particulate organic carbon in coastal waters of the Great Barrier Reef shelf. The sources, likely current state, the main vector mediating the flux, the natural and anthropogenic driver(s) involved, and the overall flux response are presented in the table below:

Table 1. A summary of the sources, likely current state, main vector mediating any flux, natural and anthropogenic driver(s) involved, and the overall flux response of dissolved and particulate organic carbon in coastal waters of the Great Barrier Reef shelf

Source	Likely current state	Main vector	Driver(s)	Flux response
Seagrass community	Net source of DOC	Exudates released during autotrophic production, DOC and POC released during senesce & decomposition	Ocean acidification, rising water temperature	Potentially greater primary production and increased DOC flux
Seagrass community	Net source of DOC	Exudates released during autotrophic production, DOC and POC released during senesce & decomposition	Greater water column nutrient concentrations	Reduced primary productivity and decreased DOC flux Potentially short-term flux of DOC and POC from seagrass communities and sediment as they die
Macro-algae	Net source of labile DOC to heterotrophic bacteria on tropical reefs	Algae exudates released during autotrophic production	Ocean acidification, rising water temperature, greater water column nutrient concentrations, overfishing	Greater competitive advantage of macro-algae over coral in reef communities Increased DOC flux from macro-algae in reef communities
Benthic cyanobacterial mats	Net source of DOC	Algae exudates released during autotrophic production	Climate change, poor water quality, increased iron input to coastal regions, and the overexploitation of keystone species	Potentially greater primary production and increased DOC flux
Sediment	Major source of POC and DOC	Resuspension by currents, storms and tides	Increased resuspension events due to more frequent extreme weather events	Greater flux of POC and DOC from sediment to the water column
Sediment	Major source of POC and DOC	Resuspension by dredging	Greater spatial and temporal extent of	Greater flux of POC and DOC from sediment to the water column

			dredging	
Sediment	Major source of POC and DOC	Resuspension by currents (mainly wind driven), storms, and tides	Decreased resuspension events due to altered water currents	Reduced flux of POC and DOC from sediment to the water column Increased OM (and OC) storage in benthic sediment
Coral reefs	Source of DOC and POC to reef community, but most is recycled	Release of DOC by coral polyps or flux of POC via sloughing of polyp mucus	Ocean acidification, rising water temperature, greater pelagic nutrient concentrations	Pulse disturbance: coral stress; reduction in DOC flux; no change in POC flux Press disturbance: coral bleaching and death; flux of DOC and POC from decomposition coral organisms; altered macro-algae dynamics (see above)
Land	Major source of POC and DOC to inner shelf of the GBR	Rivers, especially during high-rainfall events	Greater frequency of extreme weather events (i.e. cyclones) due to climate change	Greater flux of terrestrial DOC and POC to inner shelf of GBR
Phytoplankton	Primary source of labile POC, but also some DOC, in pelagic waters	Primary production	Sustained increase in riverine bioavailable-nutrient export from land	Greater phytoplankton-derived POC and DOC concentrations caused by greater primary production associated with increased availability of labile nutrients. Note: greater phytoplankton productivity may not be detected by chlorophyll measures if algal biomass doesn't increase alongside productivity
Phytoplankton	Primary source of labile POC, but also some DOC, in pelagic waters	Primary production	Increase in sea water temperatures	Greater phytoplankton-derived POC and DOC concentrations caused by increased cellular processes and production with greater water temperature
Phytoplankton	Primary source of labile POC in pelagic waters	Primary production	Greater pelagic nutrient concentrations at times of extreme weather events (i.e. cyclones)	Reduced phytoplankton-derived POC concentrations in nearshore environments affected by river plumes, caused by supressed rates of primary production Potentially greater phytoplankton-derived POC concentrations on edge of river plumes, caused by greater

				primary production associated with increased availability of labile nutrients
Mangrove forests and saltmarshes	Source of refractory but large concentrations of POC and DOC to near-shore environments of the GBR	Tides and currents	Reduced mangrove forest extent due to human disturbance and/or extreme weather events (i.e. cyclones)	Reduced nearshore concentrations of DOC and POC Potentially less POC stored in sediment over longer timescales
Coral Sea	Minor source of refractory DOC and POC to outer shelf of the GBR	Tides and currents	Ocean acidification, rising water temperature	Elevated pelagic concentrations of DOC and POC associated with greater rates of ocean primary production, leading to increased flux of DOC and POC to GBR shelf
Coral Sea	Minor source of refractory DOC and POC to outer shelf of the GBR	Primary production	Increased supply of nutrients from the Coral Sea and enhanced phytoplankton production	Elevated pelagic concentrations of DOC and POC
Groundwater	Net source of DOC	Groundwater discharge	Land clearing increases groundwater levels Agricultural practices (i.e. cane production) can enhance DOC and nutrient concentration in groundwater	Greater groundwater discharge of water containing high DOC concentrations to coastal environments of the GBR lagoon Greater groundwater discharge of water containing high DIN and aqueous CO_2 concentrations to coastal environments of the GBR lagoon that may promote DOC production via enhanced phytoplankton productivity

We set out some hypotheses to test potential drivers of elevated dissolved organic carbon and particulate organic carbon concentrations. As there is a plethora of potential sources, vectors and drivers of organic carbon concentrations in coastal waters of the Greater Barrier Reef, this targeted data analysis could help pinpoint the most likely causes for elevated organic carbon concentrations. It must be emphasised that unravelling the precise contribution that particular drivers or vectors may have for explaining the trend of increasing organic carbon concentrations in coastal waters of the Great Barrier Reef is problematic due to a number of factors, including:

- the difficulty in distinguishing organic carbon from terrestrial versus marine sources;

- the relatively unknown spatial and temporal influence of organic carbon delivered to the Great Barrier Reef via groundwater discharge; and,
- the difficulty in separating sustained, long-term (i.e. press disturbances, such as rising sea temperatures) pressures from more periodic, but ecosystem-wide pressures (i.e. tropical cyclones).

The preliminary data analysis revealed that concentrations of dissolved organic carbon were most strongly influenced by those variables known to be directly related to river discharge. Therefore, dissolved organic carbon provides a useful measure of river influences on the Great Barrier Reef. Concentrations of particulate organic carbon were also influenced by these same variables, but there was evidence that sediment resuspension and phytoplankton biomass (i.e. chlorophyll *a* concentrations) may also influence particulate organic carbon concentrations, particularly further from the coast where river discharge has less influence. The correlation between particulate organic carbon and chlorophyll *a* concentrations is not surprising as phytoplankton are typically an important contributor to particulate organic carbon in marine waters. Our analysis also suggests that measuring DOC and POC is beneficial as it provides useful additional information on river discharge effects, and the interplay with coastal processes, such as sediment resuspension. Therefore, overall it appears that the trends in nearshore DOC and POC are driven by river discharge. We stress that this data analysis is preliminary and that further data collection, analysis and modelling are required to confirm any trends identified in this report. Further offshore, other factors come into play, specifically resuspension processes. Phytoplankton become a more important contributor to POC offshore.

We recommend that future research use existing data, in conjunction with other catchment-scale environmental and river-discharge data, to empirically investigate the most likely sources (i.e. terrestrial versus marine), vectors (i.e. river discharge, phytoplankton production, etc.), and drivers (i.e. climate change, land use, land change, etc.) of the variation in the water column dissolved organic carbon and particulate organic carbon concentration in coastal regions of the Great Barrier Reef. A more certain understanding of what is mediating altered organic carbon dynamics in the Great Barrier Reef will help prioritise future research and management actions that aim to minimise (1) future increases in organic carbon concentrations and (2) adverse ecological effects.

1.0 INTRODUCTION

Understanding the sources, transformations and fate of organic carbon (OC) throughout Earth's hydrological cycle has been the subject of increasing research as our planet quickly transitions to a human-dominated and altered landscape (Anthropocene). Despite a plethora of research on OC dynamics along the land-freshwater continuum, there has been comparatively little research on the transformations and fate of OC once it enters coastal marine ecosystems from freshwater systems (Bianchi, 2011; Kandasamy and Nagender Nath, 2016). This research gap has limited our abilities to explain changes in OC concentrations, its ecological and biogeochemical impact, and how OC dynamics interact with climate change and human development in various coastal marine ecosystems. This is highlighted, at the global scale, by the fact that we still cannot explain the discrepancy between the rate of terrestrial OC input to the world's oceans (~0.4 Pg C yr^{-1}) and the quantity deposited in marine sediments (~0.2 Pg C yr^{-1}) (Kandasamy and Nagender Nath, 2016).

In this review, we will summarise the literature on the sources, transformations, and fate of particulate organic carbon (POC) and dissolved organic carbon (DOC) in coastal marine ecosystems and summarise the scientific understanding of the mechanistic links between catchment inputs, organic carbon measures, and ecosystem responses. Finally, we will apply this understanding to identify the key processes relating to OC dynamics in the Great Barrier Reef (GBR) marine ecosystem in north-east Australia.

Organic carbon describes a variety of simple and highly complex molecules that directly originate from many living and non-living sources, but which are ultimately derived from autotrophic production and senescence (Aitkenhead-Peterson *et al.*, 2003) or from chemosynthesis in the absence of light. OC exists in simple and highly complex molecules, collectively called organic matter (OM), alongside molecules of organic nitrogen and phosphorus (Aitkenhead-Peterson *et al.*, 2003). OM is the largest reservoir of reduced C on Earth and plays a critical role in global biogeochemical cycles and as an energy source for terrestrial and aquatic food webs (Kandasamy and Nagender Nath, 2016). In aquatic ecosystems, OC is typically defined according to its molecular size. POC includes those OC molecules that are retained on a filter with a pore size between 0.1µm and 0.8µm, and DOC refers to all OC molecules that passes through the filter (Benner and Amon, 2015). POC can be further categorised according to its relative weight, similar to what has recently been outlined for particulate organic matter (POM) in Bainbridge et al. (2018): (1) a light fraction (LfPOC), which includes a heterogeneous mixture of plant, animal, and microorganism remains at various stages of decomposition; and (2) a heavy fraction (HfPOC), which includes POC attached to fine mineral particles (including silt and clay) through chemical bonds. DOC can be further separated into high-molecular weight DOC (HDOC) and low-molecular weight DOC (LDOC), with HDOC retained on a pore size of 1nm (Benner and Amon, 2015). While OC size classes are largely arbitrary and dynamic, they generally describe its biogeochemical fate in aquatic ecosystems. For instance, DOC mostly remains suspended in the water column while POC can either remain suspended in the water column or sink to the benthos (Benner and Amon, 2015). It is important to note that these size fractions are spatially and temporally dynamic, with POC continuously synthesised, decomposed and re-mineralised, and DOC is continuously leached from all forms of OC

(Moore *et al.*, 2004). Moreover, DOC can be re-synthesised into larger sized molecules via, for example, aggregation and sorption onto POC and be built up into larger organic complexes (Moore *et al.*, 2004).

Dissolved and particulate OC are an integral component of coastal marine ecosystems. OC is a major form of energy for living organisms and plays a key role in local and global biogeochemical cycles (Wetzel, 2003; Battin *et al.*, 2009; Bianchi, 2011). While it is well understood that autochthonous DOC and POC (i.e. marine-produced OC) is highly bioavailable and tightly cycled in marine food webs (Rochelle-Newall *et al.*, 2008), an increasing number of studies have highlighted the potential energetic importance of allochthonous OC (i.e. terrestrially produced OC) for coastal marine ecosystems (Franklin *et al.*, 2018; Lønborg *et al.*, 2018). For example, recent research in a tropical coastal ecosystem has indicated that allochthonous organic molecules of C, nitrogen (N) and phosphorus (P) can sustain phytoplankton productivity (Lønborg *et al.*, 2018). This growing recognition of the ecological importance of terrestrially produced OC in coastal marine ecosystems is perhaps not surprising given the close proximity of these systems to the main vector of terrestrial OC delivery to coastal oceans, the world's rivers. Despite the beneficial ecological effects of OC in coastal marine ecosystems, organic carbon can also have deleterious ecosystem effects, and this impact is perhaps most evident in coastal tropical ecosystems with coral reefs. For example, elevated DOC concentrations can alter the biotic structure of coral-associated microbial communities by stimulating the activities of heterotrophic microbes (Kline *et al.*, 2006; Haas *et al.*, 2013) and promote the growth of coral pathogens that cause coral bleaching and mortality (Kaczmarsky and Richardson, 2011).

Tropical coastal waters include some of the most diverse and productive ecosystems on Earth, including coral reefs, seagrass beds, and mangrove forests (Nittrouer *et al.*, 1995). High rates of production in these ecosystems are supported by high nutrient availability, water temperature and solar radiation (Nittrouer *et al.*, 1995). The Great Barrier Reef (GBR) is one such tropical coastal ecosystem that is highly diverse and productive (Furnas *et al.*, 2005). The GBR is also the most extensive coral reef ecosystem on Earth and is biogeochemically and ecologically complex (Alongi *et al.*, 2008; Lønborg *et al.*, 2016). Over the past decade (2006-2016), there has been a trend for increasing DOC and POC concentrations in coastal waters of the GBR (Lønborg *et al.*, 2016). Given that OC is an integral component of coastal marine ecosystems (see above), and increases may have possible deleterious effects on the GBR, there is an urgent need to understand the processes responsible for this concentration increase. The GBR, and other tropical coastal ecosystems, are increasingly threatened by a number of individual and cumulative natural and anthropogenic stressors, including climate change as well as terrestrial land use, change and management that often results in highly turbid waters which discharge into the GBR. These stressors have the potential to alter OC dynamics in tropical nearshore ecosystems. There is also a need to unravel and highlight the potential ecosystem effects of changes in OC concentrations, such as how OC links to nutrient cycling, phytoplankton blooms, crown of thorns starfish life cycles, reef building and resilience.

2.0 AIMS AND OBJECTIVES

Our aim in this study is to review the literature on the sources, transformations, and fate of POC and DOC in coastal marine ecosystems and to summarise the mechanistic links between catchment inputs, organic carbon measures, and ecosystem responses. We apply the mechanistic understanding gained from this review to develop conceptual models that identify the key processes relating to organic carbon dynamics in the GBR marine ecosystem. This mechanistic understanding will be used to analyse the water quality monitoring data to gain insights into the trends of increasing DOC and POC in GBR coastal waters. We also identify knowledge gaps requiring further research.

3.0 SOURCES

3.1 Origin of terrestrial OC in aquatic environments

Terrestrially derived OC is all living or non-living organic matter that contains C molecules and which originates on land. Terrestrial OC is a heterogeneous mixture of plant and animal tissue, soil organic matter, fossilised OC from carbonate rock weathering, black carbon (e.g. charcoals and soots), microbial remains, faeces (including sewage), and products secreted, excreted, or exuded from terrestrial and/or subterranean organisms (e.g. extra-cellular polymers, nectar, dissolved organic matter, leachates, and root exudates) (Bianchi, 2011; Kandasamy and Nagender Nath, 2016). While the largest reservoir of terrestrial OC on Earth is in shales and other sedimentary rocks (~15,000,000 Pg C or 90% of Earth's OC) (Bianchi, 2011), the largest contributors of terrestrial OC to upland aquatic ecosystems include soils (~1.9 Pg C yr^{-1}), inland aquatic photosynthetic C fixation (~0.3 Pg C yr^{-1}), and sewage (~0.1 Pg C yr^{-1}) (Kandasamy and Nagender Nath, 2016). Terrestrial soils, in particular, contain equal quantities or more C (1500-2400 Pg C) than is stored within all global marine sediment (1750 Pg C) (Kandasamy and Nagender Nath, 2016). Vascular plants contain ~450-650 Pg C (Kandasamy and Nagender Nath, 2016) but, in comparison to soils, insignificant amounts of plant material are directly input into aquatic ecosystems (i.e. as leaf-litter fall). Rather, OC derived from plant material in aquatic ecosystems is commonly input via the soil reservoir, and is comprised of secondary metabolites and recalcitrant compounds leached from plant material (Bianchi, 2011).

3.2 Biogeochemistry of terrestrial OC

Understanding the biogeochemistry of terrestrial OC is essential because the chemical characteristics of OC influence its biological and physical transformations and its fate in both riverine and marine environments. As outlined above, terrestrial OC originates from a plethora of sources and, in particular, includes molecular compounds from hundreds of thousands of different plant species (Bianchi, 2011). Dissolved organic matter (DOM), in particular, is thought to comprise of millions of different compounds (Aitkenhead-Peterson *et al.*, 2003). OM molecular structural complexity, and the inhibitory substances it contains, influences the relative availability of OC compounds for biotic consumption and its resistance to physical degradation (Alexander, 1965; Benner, 2002). Greater structural complexity of OM molecules generally leads to them being more resistant to biological and physical decay. This is because a high structural complexity is often linked to greater molecular weight, and high molecular weight molecules are usually less bioavailable for microbial consumption (Alexander, 1965; Benner, 2002). A high structural complexity of OC is also generally associated with a high level of physical toughness of organic matter in its particulate form (i.e. leave and bark material), which makes this OC more resistant to physical decay. OC can also be contained within compounds that are inhibitory for biotic degradation, such as high concentrations of metabolites, tannins, and phenolic molecules (Lodge, 1991). For example, many Eucalypt leaves contain inhibitory compounds that can resist biotic degradation (Cooper, 2001), but not in all aquatic environments (Watson and Barmuta, 2011; Burrows *et al.*, 2017).

The age of OC also plays a large role in its potential for biotic degradation in freshwater and marine environments. Older OC is generally more resistant to decay than younger OC

(Raymond and Bauer, 2001). This is because older OC contains more highly complex (high molecular weight and with inhibitory substances) compounds than younger OC, owing to the preferential biotic consumption of less complex C molecules (Raymond and Bauer, 2001; Mayorga *et al.*, 2005). In natural ecosystems, OC that spends more time moving along surface and sub-surface flow paths before being transferred to freshwater environments is often more refractory for aquatic biotic consumption (Raymond and Bauer, 2001). Similarly, aquatic OC compounds with a longer residence time before reaching coastal marine environments are more resistant to biotic decay and are probably more likely to contribute to long-term C storage in marine sediments (Raymond and Bauer, 2001; Blair and Aller, 2012). However, there are instances where the age of OC is not a good proxy for its potential biotic availability. For example, ancient groundwater-derived OC can be highly bioavailable to surface aquatic environments (Fellman *et al.*, 2014) if that ancient OC source remains relatively unprocessed.

3.3 Riverine transformation and flux of terrestrial OC to marine environments

Less than half of the total C delivered to inland waters from terrestrial environments is exported to the world's oceanic coastal shelves and the open ocean (Bianchi, 2011; Kandasamy and Nagender Nath, 2016). This discrepancy indicates that substantial quantities of both inorganic and organic C compounds are transformed, stored, and/or removed along the freshwater to marine continuum (Butman *et al.*, 2007). In upland fluvial environments (i.e. excluding estuaries), approximately 1100 and 100 Tg C yr^{-1} of OC is removed from freshwaters as CO_2 and CH_4, respectively. While much of this outgassing is of allochthonous origin, especially CO_2 produced in soil, a large proportion of this OC can be produced by in-stream biotic processes (i.e. autochthonous OC). For instance, Hotchkiss et al. (2015) used previously published measurements of net ecosystem production from 187 streams and rivers across the contiguous United States to estimate that 28% of CO_2 emissions was due to aquatic metabolism.

The riverine flux of OM represents the largest source of terrestrial DOC and POC to marine ecosystems. Estimates of global riverine DOC and POC flux to marine ecosystems have varied over the past three decades (Dai *et al.*, 2012; Kandasamy and Nagender Nath, 2016). Much of this variation may be due to the various methods used to collect and model data (Dai *et al.*, 2012). Using collated studies since 1990, Kandasamy and Nagender Nath (2016) calculated a mean riverine export of 212 (± 29) Tg C y^{-1} for DOC and 203 (+ 49) Tg C y^{-1} for POC. Li et al. (2017) modelled the DOC and POC flux to oceans from the world's major river basins (Figure 1). Overall, riverine DOC and POC loads have been estimated to be greatest in Asia and lowest in Oceania, with DOC load greatest between latitudes of 0°- 30°S and POC flux greatest between 30°- 60°N (Li *et al.*, 2017). However, the flux of terrestrial DOC and POC to coastal regions is the most uncertain in Oceania, with other studies pointing to large fluxes of riverine POC to oceans in Oceania (Kandasamy and Nagender Nath, 2016). Kandasamy and Negender Nath (2016) recognise the limited data availability of OC flux data from Oceania and the authors recommend more data collection from this region to improve flux estimates.

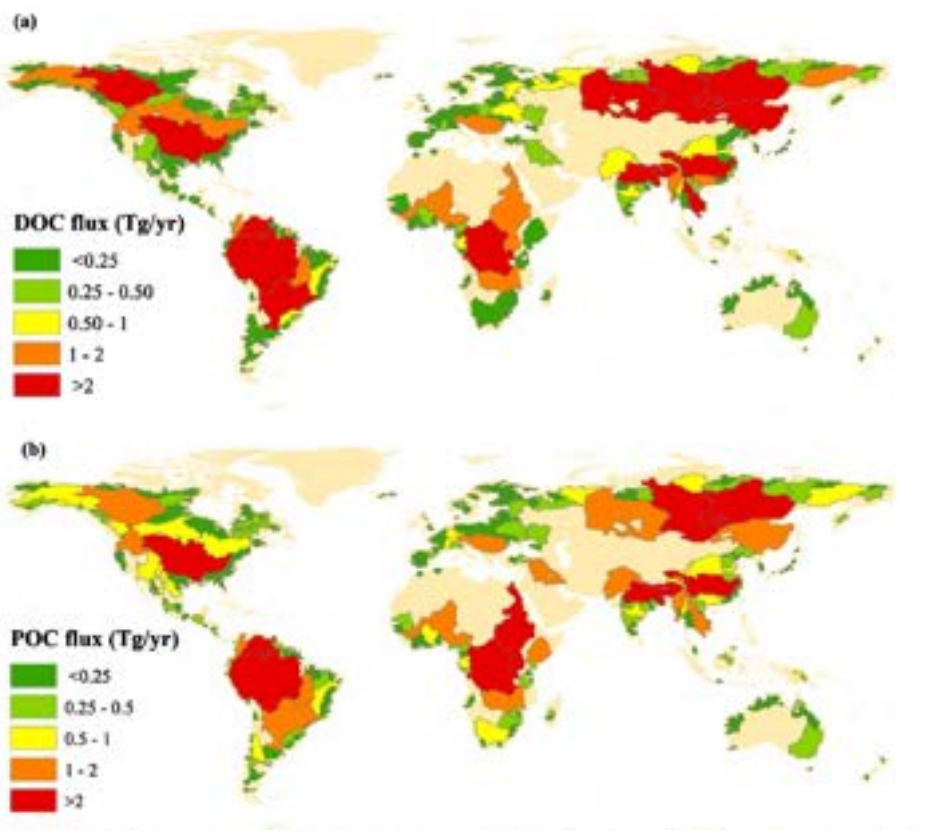

Figure 1. Spatial patterns of simulated (a) DOC and (b) POC flux for global river basins. Source: (Li et al., 2017).

Marsh, mangrove, and wetland ecosystems adjacent to estuaries input an additional 300 Tg C yr^{-1} to aquatic systems (Kandasamy and Nagender Nath, 2016). The DOC and POC from marsh, mangrove, and wetland ecosystems is transferred offshore by tides and currents in what is termed 'outwelling'. The 'outwelling hypothesis' was derived from early ecological studies that determined that the secondary production in coastal waters could only be explained if adjacent marsh-ecosystems exported energy in the form of organic carbon (Odum, 1980). Mangroves, in particular, are an important terrestrial source of DOC and POC for the world's coastal oceans. It has been estimated that mangroves contribute about 11% of the total terrestrial carbon input into the world's oceans, and account for 15% of total C accumulating in modern marine sediments (Jennerjahn and Ittekkot, 2002). This high contribution of mangroves to marine OC is perhaps least surprising in tropical coastal regions where mangroves can comprise nearly 75% of all tidal vegetation (Alongi, 1990).

3.4 Catchment controls on the sourcing of carbon

Basin geomorphology is a large determinant of the quantity of total OC (and sediment) entering rivers. River basins in more mountainous regions generally deliver more sediment to rivers compared to basins in lowland regions (Milliman and Syvitski, 1992; Wohl *et al.*, 2012). More mountainous basins export more OC in rivers due to the high rates of fossilised OC (OC deposited in sedimentary rocks) erosion in these highly erosive, and often tectonically active, regions (Hilton *et al.*, 2011; Blair and Aller, 2012). As stated in '3.1 Origin of terrestrial OC in aquatic environments', fossilised OC is the largest reservoir of OC on Earth, containing more than 200 times more C than is stored in the atmosphere and oceans (Hilton *et al.*, 2011). The importance of basin morphology in explaining riverine DOC and POC export was recently emphasised in a study modelling and summarising the main

factors driving, DOC and POC flux from the world's main river basins (Li *et al.*, 2017). Basin morphology (maximum basin relief, basin slope length, and gradient) was included as a major factor explaining global variation in riverine POC flux to oceans, and basin slope was included as a factor explaining riverine DOC flux to oceans (Li *et al.*, 2017).

In the study by Li et al. (2017), riverine DOC flux was also affected by soil organic matter content and river discharge, while POC flux was also affected by basin area, meteorological factors, soil properties, and vegetation coverage and composition – emphasising that other natural factors influence the quantity of OC in rivers. Variation in land cover on Earth influences the quantity and quality of DOC and POC in recipient streams and rivers (Schlesinger and Melack, 1981; Wilson and Xenopoulos, 2008). It is thought that approximately 60% of terrestrial OC (DOC and POC) in the world's oceans is delivered from rivers draining forested catchments, especially tropical forests (Schlesinger and Melack, 1981; Li *et al.*, 2017). The high proportion of DOC and POC in rivers draining forested catchments, which cover less than 40% of the Earth's surface, highlights the importance of terrestrial vascular plant productivity, as well as the accumulation and flux of detrital and soil OM (Li *et al.*, 2017), in the global C cycle. Perhaps counterintuitively, it is thought that forests can increase the baseflow contribution of DOC to rivers, rather than interception storage and overland flow (Wilson and Xenopoulos, 2008), because the infiltration capacity of soils is often greater in wooded areas than non-wooded areas (Thompson *et al.*, 2010; Ilstedt *et al.*, 2016). The increased soil infiltration leads to greater water contact with the mineral soil horizon that is a major OC sink in forested catchments (Moore, 2003), and can lead to a greater input of DOC-rich, shallower, groundwater to streams and rivers (Peralta-Tapia *et al.*, 2015). Additionally, vascular plants can contribute DOC directly to aquatic systems via leaf fall and subsequent leaching of organic matter (Neilen *et al.*, 2017). This material has been shown to inhibit growth of some algal species. A recent study emphasised the importance of soil for riverine OC export at the global scale, by reporting positive correlations between riverine DOC flux and total soil OC in the basin as well as between total POC flux and potential soil erosion (Figure 2) (Li *et al.*, 2017).

The proportion of wetlands or peatlands in a drainage basin is also an important factor influencing the quantity, but also quality, of OC in rivers. Rivers draining catchments with higher aerial coverages of wetlands or peatlands are associated with higher DOC (Laudon *et al.*, 2004; Yates *et al.*, 2016) and total OC (TOC) (Mattsson *et al.*, 2005; Mattsson *et al.*, 2015) concentrations. This wetland-derived OC is thought to be more refractory to microbial organisms, compared to forest-derived OC, due to its aromatic nature (Ågren *et al.*, 2008). Spatial variation in groundwater-surface water interactions may also influence the quality of OC, particularly DOC, in recipient streams and rivers. For example, rivers with high groundwater discharge are characterised by DOC that is less humic, and more bioavailable, than rivers with less groundwater discharge (Fellman *et al.*, 2014; Peralta-Tapia *et al.*, 2015; Yates *et al.*, 2016; Holland *et al.*, 2018). Whether substantial quantities of this bioavailable groundwater-derived DOC remains unchanged prior to being exported to coastal marine environments remains unknown.

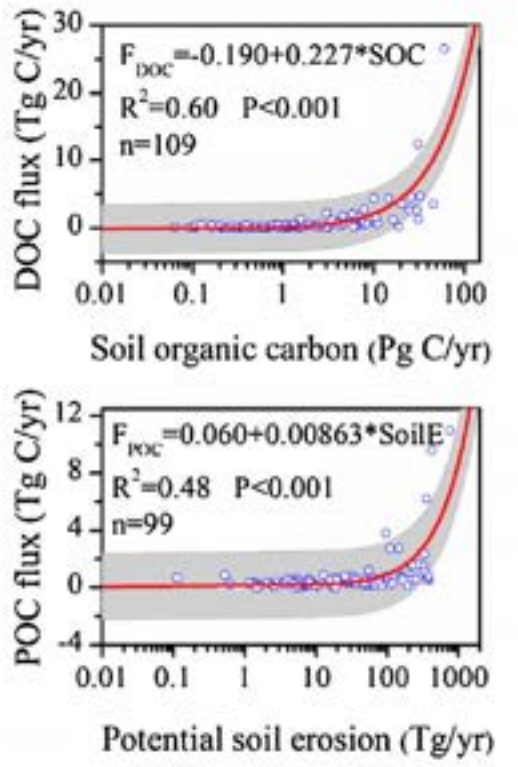

Figure 2. The correlation between dissolved organic carbon (DOC) and soil organic carbon and between particulate organic carbon (POC) and potential soil erosion in global river basins. 95% confidence intervals are represented by grey bands. Source: Li et al. (2017).

The quantity, quality, and terrestrial source of DOC and POC in the water column of recipient streams and rivers can also vary according to episodic, seasonal, and climate-induced changes in surface and sub-surface flow paths. Large periodic and seasonal increases in river flow, due to storm events or the spring snowmelt, can be associated with dramatic changes in DOC (Dalzell *et al.*, 2005; Ågren *et al.*, 2008) and POC (Dalzell *et al.*, 2005) concentration. Greater DOC and POC concentrations during high flow periods is predominately due to an increased activation of surface and sub-surface flow paths which can mobilise DOC-rich molecules in the mineral soil horizon and more 'fresh' OC molecules on land (Moore, 2003; Peralta-Tapia *et al.*, 2015). The majority (up to 70%) of this event-based increase in river OC concentration is thought to occur during large events and during the rising limb of the hydrograph (Raymond and Saiers, 2010). Although OC concentrations tend to increase during large flow events in rivers, the association between discharge and DOC concentrations were less discernible during a high-flow events in coastal north Queensland, Australia (see case study below). An increase in terrestrial OC in river channels is often evidenced by increase in lignin (a macromolecule only present in vascular plants) oxidation products of DOC and TOC during flooding (Dalzell *et al.*, 2005). Changes in DOC and POC character and terrestrial source during high flow events is also predominately due to altered hydrological flow paths on land. For example, Ågren et al. (2008) showed that the activation of surface hydrological flow paths during the spring snowmelt in northern Sweden was associated with more aliphatic DOC that had a lower molecular weight. In contrast, during low-flow periods DOC was characterised by more aromatic molecules which were likely routed to the stream via deep sub-surface flow paths that drained deep wetland soils (Ågren *et al.*, 2008). Finally, changes in POC sources in river water among wet and dry

years, and during a high-flow event, were recorded in an eroding catchment of subtropical Australia (Garzon-Garcia *et al.*, 2017). Although C_3 vegetation litter was the main POC source overall, source-relative contributions to POC export varied (Garzon-Garcia *et al.*, 2017). Subsoil contribution of POC increased during dry years, whilst the surface-soil contribution increased during wet years (Garzon-Garcia *et al.*, 2017). During the sampled high-flow event, the subsoil contribution of POC increased steadily, peaking immediately after peak flow (Garzon-Garcia *et al.*, 2017). These findings indicate the importance of understanding the complexities of POC terrestrial sourcing (quantity and quality) to the aquatic environment, both to inform catchment management programs and to understand impacts downstream, including in the marine environment.

DOC concentrations over river hydrographs and flood plumes – Queensland case study

DOC concentrations over the flood hydrographs from the Burdekin River range from 3.9 to 6.5 mg L^{-1} and do not show strong associations with discharge during elevated flows in 2017 and 2018 (Figure 3). While DOC concentrations from the elevated flows in 2017, predominately from the Bowen-Broken-Bogie River basin, increased with peak flow before declining with the waning flow, the flows from 2018 predominately from the upper Burdekin River tributary showed greater variability over the hydrograph (Figure 3). Further characterisation of the carbon composition over the hydrograph would provide insights on if this variability is related to changes in source material delivered from the different tributaries of the Burdekin. DOC concentrations in the flood plumes from the Burdekin and Tully Rivers from 2017 and 2018 display a general linear conservative mixing trend over the estuarine mixing zone with some outliers (Figure 4).

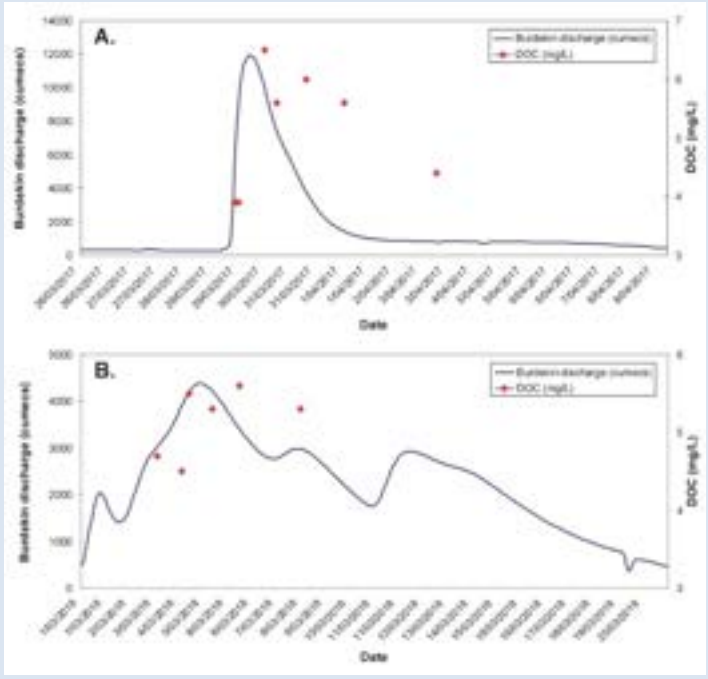

Figure 3. Dissolved organic carbon (DOC) concentrations over the Burdekin flow hydrograph in 2017 (A) and 2018 (B).

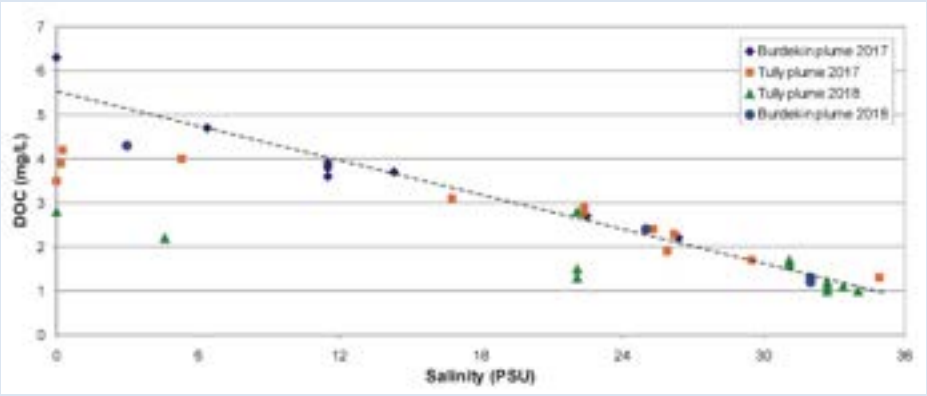

Figure 4. Dissolved organic carbon (DOC) concentrations over the estuarine mixing zone of the Burdekin and Tully Rivers. The dotted line represents a conservative mixing line.

Although precipitation and runoff play secondary roles in comparison to basin topography, for explaining the delivery of total OC to rivers and oceans at the global scale, severe weather systems such as tropical cyclones can be an important control on the delivery of non-fossilised OC to many rivers and oceans, especially in regions where tropical cyclones interact with high tectonic activity (Hilton *et al.*, 2008). Rivers in Oceania are often estimated to deliver more POC to coastal oceans than any other region (Figure 3) (Kandasamy and Nagender Nath, 2016). More data is required from Oceania to confirm this trend (Kandasamy and Nagender Nath, 2016), and recent research contradicts the high riverine POC loads in the Oceania region – although this research doesn't include data from many Pacific islands (Li *et al.*, 2017). It is thought that tropical cyclone activity, specifically in the western Pacific Ocean, is the main reason for the high riverine delivery of POC to coastal oceans (Selvaraj *et al.*, 2015). Hilton et al. (2008) estimated that 77-92% of the total non-fossil POC eroded from a coastal catchment in Taiwan was likely transported during cyclone-induced flooding over a decadal timescale. However, the importance of cyclonic activity for delivering large quantities of OC to rivers and oceans is not limited to mountainous regions with high tectonic activity. Terrestrial sediment accumulation on the inner shelf (0 to ~22m depth) of the GBR, which does not have an active tectonic margin, is thought to largely originate from the delivery of new terrestrial sediment via periodic cyclones (Larcombe and Carter, 2004). Cyclones thus have a large influence on sediment, POC and DOC delivery to coastal areas of the GBR shelf.

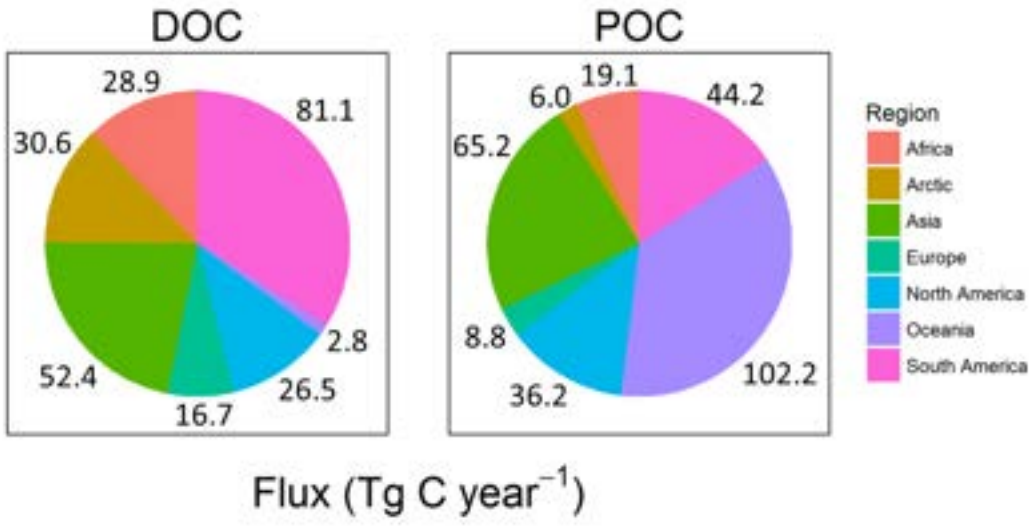

Figure 5. Regional estimates of terrestrial dissolved organic carbon (DOC) and particulate organic carbon (POC) flux (Tg C year^{-1}). Data source: Kandasamy and Nagender Nath (2016).

3.4.1 Groundwater discharge to marine environments

Groundwater discharge is an important yet under-recognised pathway of DOC, and nutrient transport to many marine environments (Burnett *et al.*, 2003; Szymczycha *et al.*, 2014; Kim and Kim, 2017). In fact, groundwater nutrient fluxes rivals river nutrient fluxes in many regions (Slomp and Van Cappellen, 2004); the potential for groundwater discharge to influence OC dynamics in coastal oceans is, thus, very high. Not only will DOC-rich groundwater likely directly increase pelagic DOC concentrations, but groundwater rich in

limiting nutrients and aqueous CO_2 may enhance rates of phytoplankton production (Sorrell *et al.*, 2013) and thus indirectly increase pelagic DOC concentrations (Gagan *et al.*, 2002).

3.5 Anthropogenic influences on the source and flux of terrestrial OC to oceans

Anthropogenic activity is having an increasingly large impact on the source and flux of OC from land to freshwater and marine environments, mainly through changes in riverine sediment flux (Syvitski *et al.*, 2005; Wang *et al.*, 2015). Humans are simultaneously reducing riverine sediment flux to oceans via retention within reservoirs (Syvitski *et al.*, 2005; Wang *et al.*, 2015) and increasing sediment flux through enhanced soil erosion (Syvitski *et al.*, 2005). At the same time, anthropogenic impacts are evidenced by changes to OC input to aquatic ecosystems by sewage (~0.1 Pg C yr^{-1}) (Kandasamy and Nagender Nath, 2016). A recent study by Noacco et al. (2017), using the world's longest record of DOC concentrations (130 years), highlighted the large impact that urbanisation, and associated sewage effluent, can have on OC concentrations in rivers. The authors were able to explain 90% of the long-term rise in Thames River DOC concentrations by increased urbanisation (Noacco *et al.*, 2017). In fact, the authors linked the majority of the DOC rise to increased sewage effluent associated with population growth. Increased riverine DOC concentrations was not associated with rising air temperatures in the Thames River basin, but soil disturbance from land use, especially the conversion of pasture to arable land during the Second World War, explained shorter-term increases in DOC concentrations (Noacco *et al.*, 2017). It is clear that anthropogenic activity can have a large impact on the flux of OC from rivers to the world's oceans, and changes in riverine OC concentrations from human effluent should be considered alongside other potential 'press' (i.e. long-term and consistent changes) disturbances, such as increasing temperatures due to climate change.

Agricultural land use in watersheds can also alter the DOC and POC concentration and the load of recipient rivers and coastal oceans. For example, rivers draining watersheds with a high proportion of agricultural land in central Europe were reported to have much higher discharge-weighted DOC concentrations (6.2-7.1 mc C L^{-1}) compared to predominately forested catchments (1.3-3.8 mg C L^{-1}) (Graeber *et al.*, 2012). However, the proportion of agricultural land use in a catchment can also have negligible (Wilson and Xenopoulos, 2008) or negative (Cronan *et al.*, 1999) associations with stream and river DOC concentrations. Caution must be taken when interpreting the results of catchment-scale predictive models because it can often be difficult to attribute watershed characteristics to changes in river biogeochemistry as many dependent variables co-vary and general patterns can sometimes be masked or overshadowed by catchment-specific environmental conditions or events. For example, Autio et al. (2016) suggested that the lack of association between river DOC concentrations and catchment land use was likely due to the high proportion of wetlands and/or a high soil OM content of boreal watersheds, which masked any land-use effects.
Variation in agricultural practices can also alter the terrestrial source of OC in rivers and its lability once it enters coastal oceans. For example, Manninen et al (2018) assessed the marine biodegradability of DOC, that was collected from surface runoff from different agricultural soils, and found a greater DOC biodegradability when it was collected from watersheds with ploughed soil compared with no-till soil treatments (Manninen *et al.*, 2018). The authors postulated that an increased microbial activity in the surface soil of no-till plots

may lead to the production of more processed, and more aromatic, DOC molecules, leading to less labile DOC for riverine and coastal heterotrophic bacteria (Manninen *et al.*, 2018).
Historical catchment land-use activities can continue to impact river DOC and POC concentrations for many decades. The legacies of catchment land use on river DOC and POC concentrations is highlighted in Australia, where land clearing and livestock introduction associated with European settlement caused a major episode of gully and river channel erosion (Prosser and Slade, 1994; Olley and Wasson, 2003). Gully erosion has been shown to reduce the quantity and bioavailability for mineralisation of C and N stored in upland areas (Garzon-Garcia *et al.*, 2014), and erosion from these gullies and river channels still dominates the sediment sources in many Australian rivers (Caitcheon *et al.*, 2012; Olley *et al.*, 2013; Garzon-Garcia *et al.*, 2017).

3.6 Marine sources of DOC and POC

3.6.1 Biological Pump and the Microbial Carbon Pump

Almost half of all photosynthetic activity on Earth is carried out by phytoplankton in the oceans (Chisholm, 2000). It is the activities of oceanic phytoplankton that produce most of the marine autochthonous OC (Thornton, 2014). In fact, phytoplankton account for 90% of all marine biomass and are the main contributors to the world's 'blue carbon' (Zhang *et al.*, 2017). The mechanism that describes OC production in the oceans is called the 'biological pump' (Figure 4). The biological pump describes the photosynthetic activity of phytoplankton, which captures aqueous carbon dioxide (CO_{2aq}) and converts this inorganic C to living POC (Ducklow *et al.*, 2001). In this way, the biological pump reduces atmospheric CO_2 concentrations by transferring carbon from the euphotic zone in to the deep ocean (DeVries and Weber, 2017). The photosynthetic efficiency of phytoplankton is maximised in waters with sufficient light and nutrient availability (N and P), including iron (Kolber *et al.*, 1994), to meet their cellular stoichiometric requirements (Ducklow *et al.*, 2001). This phytoplankton-derived POC consists mostly of single-celled algae, such as diatoms (Smetacek, 1999). These photosynthetic organisms are then consumed by other organisms in higher trophic levels and can sink through the water column to deposit on marine benthic surfaces (Zhang *et al.*, 2017). However, the majority of this POC is remineralised within the mesopelagic zone (~100-1000m), with less than a few percent reaching oceanic benthic environments through sedimentation (Anderson and Tang, 2010).

Not only does the biological pump increase the quantity of POC but it also increases the production of labile DOC through various metabolic and ecological processes (Figure 4). These processes include both passive (i.e. leakage) and active (i.e. exudation) extra-cellular processes, as well as viral lysis (Anderson and Tang, 2010; Thornton, 2014). It has been estimated that 2-50% of the POC produced by phytoplankton is converted to DOC (Anderson and Tang, 2010; Thornton, 2014). The majority of the DOC produced via the biological pump is highly labile and rapidly assimilated by heterotrophic microorganisms and thus re-enters the food chain via the microbial loop (Azam *et al.*, 1983; Jiao *et al.*, 2010) (Figure 4). However, it is thought that the DOC produced via the biological pump is insufficient to meet all the C requirements of heterotrophic microorganisms (Baines and Pace, 1991; Thornton, 2014). Moreover, a consequence of DOC uptake by heterotrophic

organisms is the respiration of CO_{2aq}, that is then assimilated by autotrophs, re-entering the food chain, or released to the atmosphere (Ducklow *et al.*, 2001).
Only a small fraction (5-7%) of DOC produced by the biological pump exists as recalcitrant DOC (RDOC) (Koch *et al.*, 2014). RDOC is not rapidly mineralised and can persist in the ocean for millennia (Koch *et al.*, 2014). The average age of RDOC is estimated to range from 4000-6000 years (Bauer *et al.*, 1992; McNichol and Aluwihare, 2007). Although produced in relatively small quantities, the long oceanic residence time means that RDOC production is nominally included as marine C sequestration (Zhang *et al.*, 2017). The majority of this oceanic DOC is from marine sources, specifically from the 'microbial carbon pump', with very little DOC in the open ocean from terrestrial sources (Bianchi, 2011).

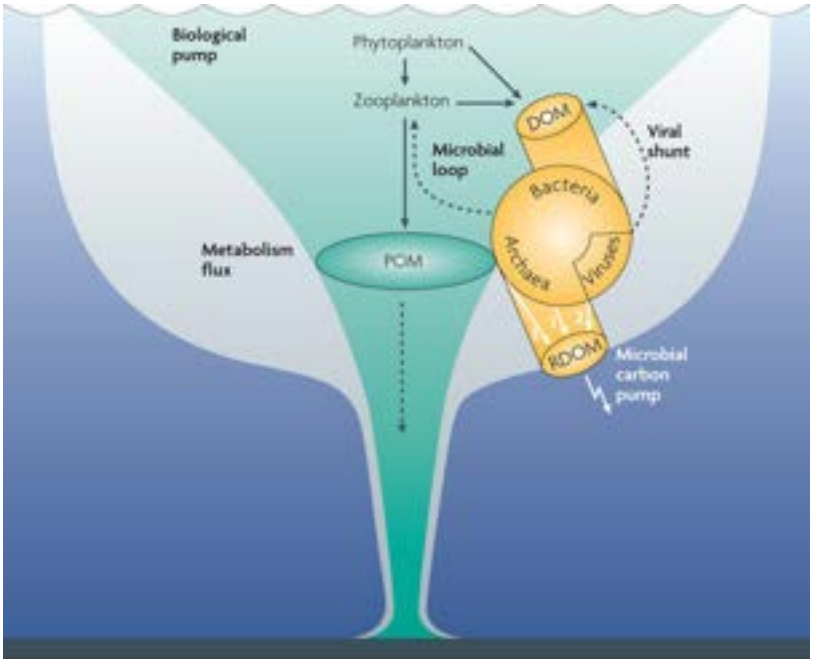

Figure 6. A schematic representation of the relationship between biological pump and the microbial carbon pump. Source: Jiao et al. (2010).

3.6.2 Seagrass meadows, macro-algae beds, and benthic cyanobacterial mats

Marine plants (i.e. seagrasses and macro-algae) cover less than 2% of the ocean surface but play a large role in marine and global C cycles (Duarte *et al.*, 2005; Duarte *et al.*, 2010; Barrón *et al.*, 2014). Research has largely focused on the C storage capacity of marine plants which can accumulate OC in sediment where they grow (Duarte *et al.*, 2010). It has been estimated that seagrasses and macro-algae can store approximately 16 and 0.4% of their net primary production, respectively, in the sediments where they grow (Duarte and Cebrián, 1996). OC accumulation in seagrass sediment is, however, often lower in tropical coastal environments than in more temperate regions (Miyajima *et al.*, 2015; Gullström *et al.*, 2018). Marine plants also trap and accumulate terrestrial and marine POC (i.e. phytoplankton) on the substrate (Hemminga *et al.*, 1991). However, all marine primary producers release part of their C fixed during photosynthesis as DOC into the surrounding water column (Haas *et al.*, 2011), and a recent study of seagrass and macro-algae communities around the world found that nearly all were net sources of DOC to the

surrounding marine environment (Barrón *et al.*, 2014). Hydnes et al. (2014) synthesised research on DOC flux from seagrasses and stated that DOC flux accounts for 2-10% of tropical seagrass daily production. The flux of DOC from marine macrophyte communities is often greater when water temperature is elevated and under eutrophic conditions (Barrón *et al.*, 2014; Hyndes *et al.*, 2014): however, it is still largely unclear whether greater DOC fluxes associated with these environmental conditions is the result of increased organism productivity, senescence and decomposition or a greater DOC flux from benthic sediment.
Cyanobacteria are a natural component of most coastal reef communities where they provide many ecosystem services including nitrogen fixation and primary production (Brocke *et al.*, 2015b; Ford *et al.*, 2018). There has been an increase in their abundance over the past few decades in reefs around the globe leading to the formation of dense benthic cyanobacterial mats (Albert *et al.*, 2005; Brocke *et al.*, 2015a; de Bakker *et al.*, 2017; Ford *et al.*, 2018). Recent research has highlighted that DOC release from benthic cyanobacterial mats can be higher than macro-algae and can represent up to 79% of the DOC release form some reef communities (Brocke *et al.*, 2015b). Consequently, benthic cyanobacterial mats may be a major source of DOC in many coastal marine ecosystems.

3.6.3 Coral reefs

Coral reefs are some of the most diverse (Roberts *et al.*, 2002) and productive (Odum and Odum, 1955) ecosystems on planet Earth. Most reefs have net neutral or positive production rates (Alldredge *et al.*, 2013), with a net C accumulation in inorganic (carbonate coral skeleton) and organic (living biomass) components. However, coral reefs often, and inevitably, experience periods of senescence. Many ecosystem processes mediate the transformation, removal and flux of material from DOC and POC pools in coral reef communities (Figure 5). Removal processes include the consumption of POC by invertebrates and vertebrates (i.e. fish) and sedimentation to benthic surfaces where it can be further decomposed by microbes and detritivores (Alldredge *et al.*, 2013) or remain stored in sediment (Figure 5). Removal processes of DOC include uptake or mineralisation by heterotrophic bacteria or adsorption to mineral or organic surfaces. Production processes for POC include the growth, reproduction, defecation and molting of organisms, including living and non-living organisms produced via photosynthesis, and the resuspension of POC from the benthic surface (Figure 5). The direct excretion, exudation and egestion by microbes and larger organisms can be a source of DOC to reef environments (Figure 5).

Most autochthonous OC (as DOC) in coral reefs is produced by benthic primary producers, including coral-associated symbiotic zooxanthellae, macro-algae, algal turfs and endolithic algae (Silveira *et al.*, 2017). There is usually only a relatively minor contribution (0.3-13%) of OC from phytoplankton in coral reefs (Alldredge *et al.*, 2013). Unlike the open pelagic ocean, the production and nutrient cycling of tropical-reef heterotrophic bacteria is not closely linked with phytoplankton production. Rather, bacterial processes are closely linked to the activity of benthic primary producers, which release labile OC in the form of photosynthates (Torréton *et al.*, 2002; Rochelle-Newall *et al.*, 2008). The high lability and production of DOC from benthic primary producers contributes to bacterial doubling time up to 50 times faster on tropical reefs compared to the open ocean (Silveira *et al.*, 2017).

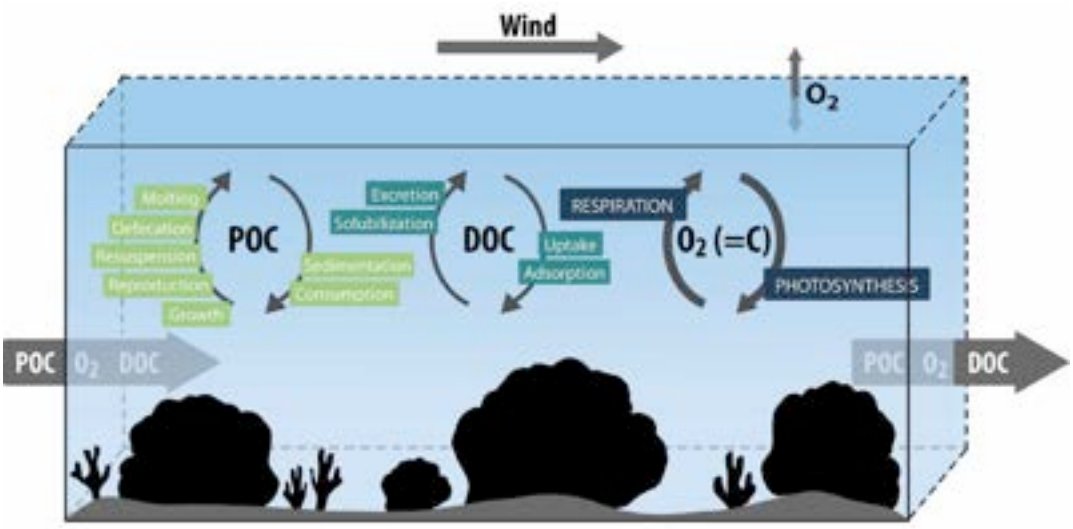

Figure 7. The processes that mediate the transformation, removal and flux of material from coral reef DOC and POC pools. Source: Alldredge et al. (2013).

3.7 Conjecture in the determination of terrestrial versus marine OC

There is currently a lack of analytical methods for determining whether an OC molecule originates from terrestrial or marine sources. Laboratory analysis techniques usually only concentrate on certain facets of OC molecules, such as lignin phenol components, the presence of carboxyl-rich alicyclic molecules (CRAMs), or ultra-violet absorbance and fluorescent spectroscopy for measures of OC aromaticity, relative biotic lability, and molecular size. Multiple analysis techniques are often required to accurately describe changes to, and variation in, the relative contribution of terrestrial and marine OC to marine ecosystem processes. One major issue revolves around the degradation, and thus changes to the chemical structure of OC as it is transported along the land-freshwater-marine continuum. Microbial (Hansell *et al.*, 2009) and photochemical (Mopper *et al.*, 1991) processes degrade OC molecules, and the degree of degradation varies among different compounds within organic molecules (Li *et al.*, 2017). Laboratory analysis techniques may, therefore, wrongly characterise the relative abundance and contribution of terrestrial and marine OC to marine ecosystem processes. For example, Liu et al. (2011) examined water samples, using high performance liquid chromatography (HPLC) coupled with tandem Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), from sites along a river-marine continuum and discovered that a large fraction of resultant chemical forms existed as lignin-like compounds in marine environments. This was generally at odds with most previous research, using lignin-phenol analysis, which identified only trace amounts of lignin-like compounds (often <1% of DOC) in coastal marine environments (Moran *et al.*, 1991; Opsahl and Benner, 1997). Lignin is a compound only produced by vascular plants, and its scarcity in marine DOM samples has generally been accepted as evidence of a minimal terrestrial contribution to marine DOM and DOC. Liu et al. (2011) argued that lignin-derived molecules can be structurally transformed along the land-freshwater-marine continuum so that it can no longer be identified as ‘terrestrial’, using lignin-phenol analysis.

In summary, this study highlights a) that multiple analysis techniques are often required to quantify the relative contribution of terrestrial and marine OC in marine ecosystems, and b) that we still have a very limited understanding of how much terrestrial OC, particularly DOC, is in marine ecosystems and its contribution to marine processes.

4.0 TRANSFORMATIONS

4.1 The tale of the "missing" terrestrial DOC and POC

One of the greatest conundrums of marine biogeochemistry is the fate of the "missing" terrestrial DOC and POC. Although the exact figures are subject to scientific debate, rivers export ~0.2-0.25 Pg of DOC and ~0.15-0.2 Pg of POC from land to the ocean annually (Hedges *et al.*, 1997; Schlünz and Schneider, 2000). However, the global burial rate of OC in marine sediments is estimated to be only 0.1-0.2 Pg C yr^{-1} (Hedges and Keil, 1995; Kandasamy and Nagender Nath, 2016), which accounts for less than half of the total OC input by rivers to the world's oceans (Kandasamy and Nagender Nath, 2016). Further, stable isotope and chemical biomarker data indicate that there is very little terrestrially derived OC in the ocean water column (Bianchi, 2011). This "missing" terrestrial OC may indicate (1) that the ocean's act as a net heterotrophic system, with greater than half of the terrestrial OC delivered from land to oceans being efficiently re-mineralised on an annual basis, or (2) that the processes controlling terrestrial OC burial in marine sediments is poorly understood. From a global perspective, it is probable that a large fraction of terrestrial DOC and POC is transformed in marine ecosystems. However, the degree of, and the potential for, terrestrial OC transformation in marine environments is spatially (i.e. among geological and climatic regions and with distance from the coast) and temporally (i.e. seasonally and due to major weather events) variable, complicating our ability to resolve the conundrum of the "missing" terrestrial DOC and POC.

4.2 OC transformation among active and passive continental margins

On a global scale, variation in the rates of OC transformation (and burial) in coastal marine environments is strongly dependent on the geological and morphological properties of the watershed and the residence time of OC before reaching the deep ocean (Blair and Aller, 2012). Rivers draining watersheds situated in the world's active continental margins, and eroding mountainous regions, generally have more rapid water residence times than rivers draining watersheds in passive continental margins (Blair and Aller, 2012) (Figure 6). The more rapid water residence times associated with active continental margins (i.e. coastal regions of the Eel River in California, Waiapu River in New Zealand, and LiWu River in Taiwan), leads to a reduced opportunity for both riverine physical (particle sorting and selective deposition of OC) and biological (OM mineralisation) processing of more recalcitrant and ancient (fossil C or kerogen) forms of OC (Figure 6). Consequently, there is a greater fidelity of more recalcitrant forms of terrestrial OC (i.e. kerogen) in watersheds draining the world's active continental margins (Figure 6). OC processing in coastal marine environments is generally lowest along active continental margins because of a high proportion of more refractory OC (i.e. kerogen), continental shelves that are often narrow, and fast water residence times (Figure 6). This rapid movement of more refractory OC results in a large proportion of terrestrial OC stored in marine sediments along active margins. The highly erosive steep mountain watersheds of Taiwan are an example of watersheds along an active continental margin that can deliver large quantities of relatively unprocessed terrestrial OC into the coastal marine environments (Hilton *et al.*, 2011). In fact, a recent study revealed that approximately 90% of OC in the deep sea off southern Taiwan was of terrestrial origin (Selvaraj *et al.*, 2015).

In contrast to active margins, passive margins are often associated with a high proportion of more labile OC, wide continental shelves, and slower water residence times (Blair and Aller, 2012). These characteristics of coastal marine environments in passive tectonic margins often lead them to act as “organic matter incinerators” that mineralise a high proportion of the OC input from land, with very little terrestrial OC stored in sediment (i.e. coastal regions of the Amazon River and Mississippi River) (Blair and Aller, 2012). OC mineralisation can be further enhanced in coastal marine environments if passive margins are also characterised by (1) a low water turbidity that allows sufficient light penetration for enhanced benthic and planktonic primary production, and/or (2) high resuspension cycles, caused by strong currents or frequent storm events, which leads to a high oxygen exposure time (OET) (Blair and Aller, 2012). High rates of primary production can enhance OC mineralisation because marine-produced POC and DOC are generally more labile than terrestrial OC, and their presence can promote the cycling of more recalcitrant terrestrial OC via a mechanism termed ‘priming’ (see ‘Priming effect’). Similarly, a greater OET is associated with greater OC mineralisation because low oxygen supply often constrains rates of organic matter mineralisation (Blair and Aller, 2012). The Great Barrier Reef lagoon is an example of a system situated on a passive continental margin with high rates of OC mineralisation (Lønborg *et al.*, 2018).

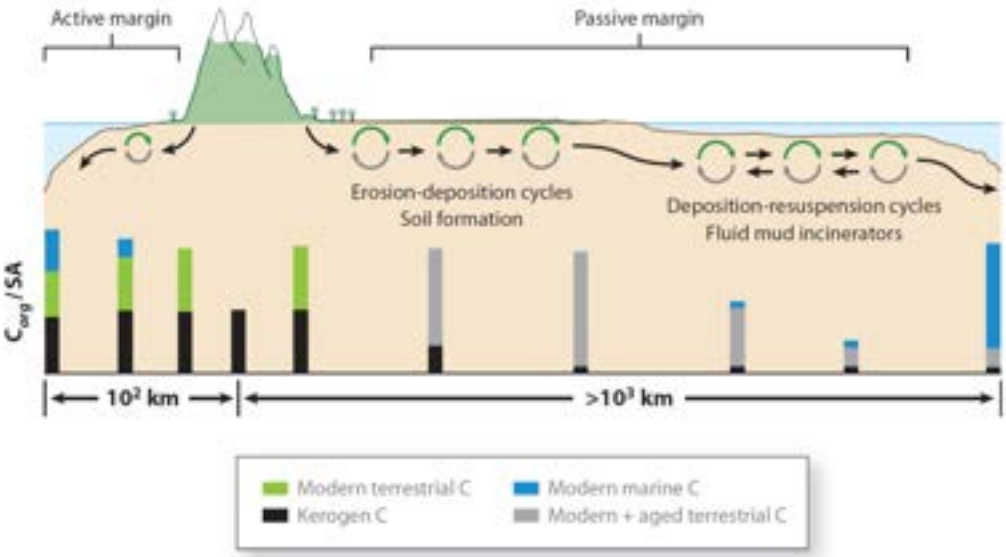

Figure 8. A figure showing the key differences between active- and passive-margin transport-reactive systems. The relative content of different types of organic carbon per surface area (C_{org}/SA) is shown on the bottom of the figure. In general, organic carbon material is subject to less deposition-resuspension cycles on active margins, and is thus transported with greater fidelity compared to on passive margins. Source: Blair and Aller (2012).

4.3 OC transformative processes in marine environments

The transformative processes that describe the removal of DOC and POC from the water column of marine environments are shown in Figure 7. These transformative processes include: biological assimilation in surface pelagic and deep ocean environments (Benner and Amon, 2015; Shen and Benner, 2018), including the priming-related degradation of RDOC in the presence of low-molecular weight DOC (LDOC) (Turnewitsch *et al.*, 2007; van Nugteren

et al., 2009; Bianchi, 2011); photochemical reactions in sunlit waters (Mopper *et al.*, 1991; Bélanger *et al.*, 2006); loss via aggregation and sorption to mineral particles, leading to sedimentation (Hedges *et al.*, 2000); free radical reactions of OM with oxygen that lead to abiotic degradation (Peyton, 1993); and, the thermal degradation of RDOC at hydrothermal vents in the deep ocean (Shen and Benner, 2018).

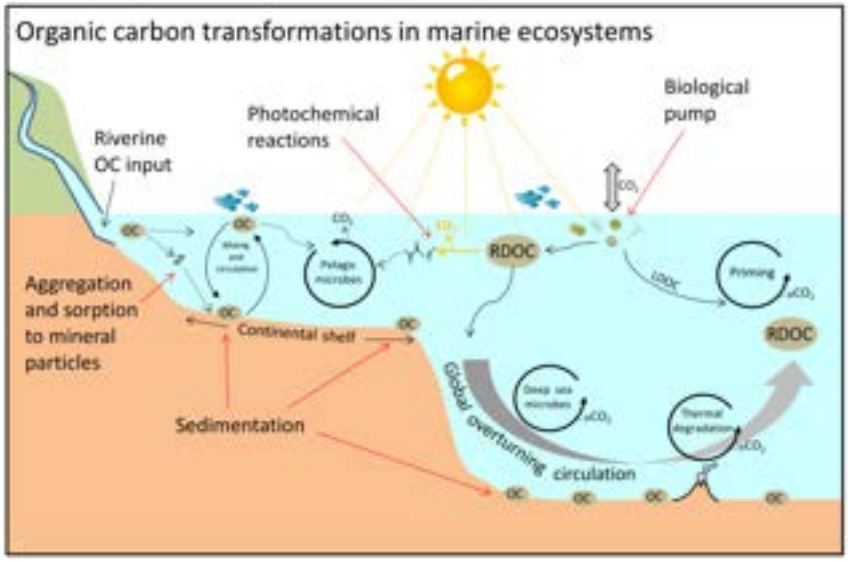

Figure 9. A conceptual diagram showing the main transformative processes in coastal and deeper ocean environments.

4.4 Factors influencing transformations of DOC and POC

While the geomorphic properties of a watershed, including its water residence time and OET, has a large and overarching influence on OC transformative processes in rivers and continental ocean shelves, there are numerous other intrinsic (i.e. molecular structure of OC) and environmental characteristics that influence OC transformation in space and time. Below we review the many intrinsic and environmental factors that influence both terrestrial and marine-produced OC transformations in marine environments and outline how spatial and temporal variation in these factors can lead to large differences in the proportion of terrestrial OC that is transformed in various near-shore marine environments.

4.4.1 Molecular and size-fraction effects on OC transformation

The transformations of most POC and DOC in the world's oceans are tightly coupled with the biogeochemical cycles of other major essential elements, particularly nitrogen (N) and phosphorus (P). This is because OC exists in heterogeneous molecules containing various quantities of organic C, N and P. The processing of organic nutrients is increasingly viewed as vital for ocean productivity (Torres-Valdés *et al.*, 2009). The molar ratios of nutrient elements in POM and DOM describe its stoichiometry, and a compound's stoichiometry influences its biological degradation (Sterner and Elser, 2002). Given that the low availability (i.e. concentration and/or supply rate) of N and P, as well as C, are common resource constraints to aquatic microbial activity, the stoichiometry of POM and DOM directly impacts its potential transformability, and ultimately its fate.

The biological reactivity of OC is directly related to its molecular size, as described by the size-reactivity continuum model (Figure 8) (Amon and Ronald., 1996; Benner and Amon, 2015). In this model, larger OM compounds are more biologically reactive because they are generally more 'fresh' (recently synthesised or produced) and contain more labile, nutrient-rich compounds (Benner and Amon, 2015). Over time, OM compounds are decomposed into smaller compounds and biological processes selectively remove the more labile, nutrient-rich compounds (Figure 8). In accordance with this prediction, OC biological reactivity decreases along a continuum from POC to DOC (Lønborg *et al.*, 2018) and from HDOC to LDOC (Figure 9) (Hama *et al.*, 2004; Benner and Amon, 2015).

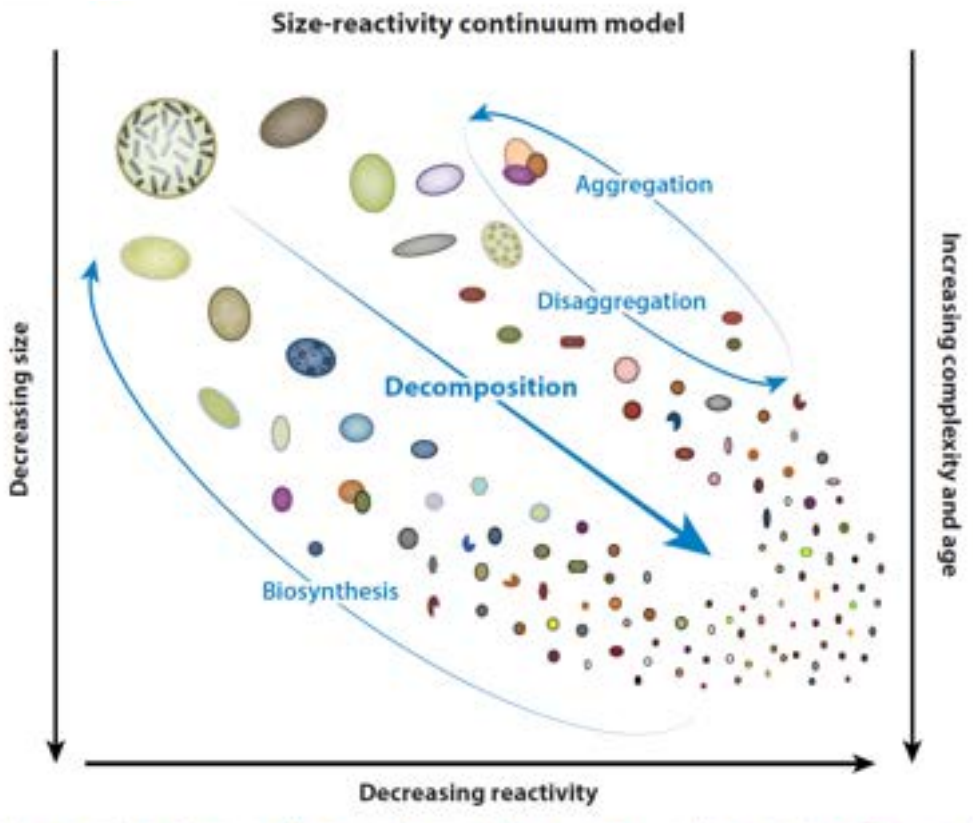

Figure 10. A conceptual diagram of the size-reactivity continuum model. Source: Benner and Amon (2015).

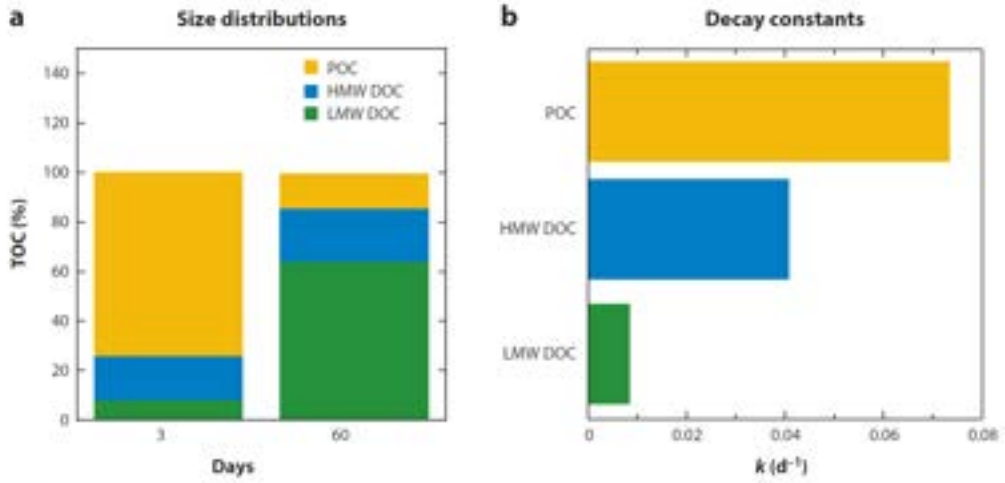

Figure 11. (a) Size distributions of total organic carbon (TOC) as particulate organic carbon (POC), high-molecular weight dissolved organic carbon (HMW DOC), and low molecular weight DOC (LMW DOC) after three and sixty days of an incubation study. (b) Exponential decay constants for the TOC size fractions. Source: figure is from Benner and Amon (2015), and the data is from Hama et al. (2004).

The vast majority of DOC in the world's oceans exists as semi-labile to refractory organic molecules which resist degradation for millennia (5000 years, on average) (Shen and Benner, 2018). Despite its relative refractory nature and long transformation times, DOM is still the most important reservoir of oceanic reduced C. In fact, DOM contains more than 200 times more C (662 Pg C) than is contained in marine organisms (Hansell *et al.*, 2009). It is worth noting that while DOC concentrations can be high in coastal marine environments (i.e. near river estuaries), the majority of oceanic DOC exists at very low concentrations in the world's open oceans (Hansell *et al.*, 2009).

The nature of colloids and coarse dispersions in river and ocean water can affect the physical availability of some forms of DOC to degradation. Bioavailable forms of DOC, such as labile proteins and peptides, can be physically 'shielded' from degradation inside folded large molecules and aggregation of smaller molecules (Hedges *et al.*, 2000). This is particularly the case if the internal micro-environments of these molecules are hydrophobic, because water is required for enzymatic reactions to occur (Hedges *et al.*, 2000). This notion is consistent with the presence of bioavailable DOC in ancient sediments (Hedges *et al.*, 2000).

4.4.2 Water-column physico-chemical characteristics

The turbidity of river plume water, and subsequent changes in light availability, influence the transformation of OC in marine environments. The influences of these two factors are intertwined and collectively impact the autotrophic productivity of, and autotrophic-derived OC in, river water that discharges into the world's oceans. Highly turbid rivers generally have relatively low rates of primary production, compared to less turbid rivers, because low levels of light penetration constrain photosynthetic activity (Hall *et al.*, 2015). The Amazon River is one extreme case, where highly turbid waters constrain light availability and thus photosynthetic activity (Medeiros *et al.*, 2015). As a result, the Amazon River exports very minimal quantities of OC originating from photosynthetic activity and a high proportion of

mostly refractory, terrestrial-derived OC compounds (Medeiros *et al.*, 2015). This terrestrial-derived OC remains relatively stable (i.e. minimal transformation) in the coastal ocean compared to other regions (Medeiros *et al.*, 2015) (see case study below). The low levels of light penetration in highly turbid freshwater and marine environments also restrict the degree of OC photodegradation, which can be an important physical process mineralising OC (Shen and Benner, 2018; see Figure 7). However, OC photodegradation can be a relatively slow processes, with Mopper et al. (1991) finding that 12-48% of photochemically reactive DOC may be degraded by sunlight for an ocean mixing cycle of 500 years.

Amazon River basin case study

The Amazon River is a highly heterotrophic system, owing to high inputs of terrestrial OC and constrained primary production due to turbid waters that limit light penetration. Minimal inputs of autotrophic-derived OC in the Amazon River, combined with high rates of heterotrophic microbial degradation in fluvial waters (Wissmar *et al.*, 1981), results in the export of largely refractory OC compounds to the Atlantic Ocean (Medeiros *et al.*, 2015). The refractory nature of Amazon River OC is thought to be one of the main factors leading to minimal transformations of terrestrial OC across the Atlantic Ocean congenital margin. Additionally, the high turbidity in the Amazon River plume, which extends several hundred kilometres from the river mouth (Molleri *et al.*, 2010), likely decreases light availability, and the photomineralisation of terrestrial OC as it moves across coastal regions. In fact, it has been estimated that 50-76% of Amazon River DOM remains untransformed in the coastal ocean of the Atlantic (Medeiros *et al.*, 2015).

4.4.3 Hydrology, shelf morphology, and ocean currents

The morphology and hydrological characteristics of coastal shelves can influence the transformation of terrestrial- and marine-produced OC. In more narrow coastal shelves, a higher proportion of OC is exported relatively unchanged to the open ocean compared to more broad coastal shelf systems. These broader coastal shelves are associated with a higher water residency time in shallower, more productive seas (Blair and Aller, 2012), leading to increased opportunities for microbial and physical degradation of OC molecules (Lønborg *et al.*, 2018). A key example of how shelf width can influence OC transformation is by comparing the two tropical coastal shelves of the Bismarck Sea and the GBR lagoon. The Bismarck Sea, off the coast of north-east Papua New Guinea, has a narrow coastal shelf and research suggests that much of the OC delivered from land, and produced near-shore, is transformed minimally before reaching deeper waters of the Pacific Ocean (Burns *et al.*, 2008).

In contrast, the GBR lagoon is a broad coastal shelf and almost all OC is degraded before leaving the shelf (Lønborg *et al.*, 2018). The high transformation rates of terrestrial OC in the GBR lagoon has been linked to the relatively insignificant quantities of OC and N accumulation in shelf sediments (Alongi *et al.*, 2011). It is clear that variation in water residence time across coastal marine-shelf systems can be a key factor influencing differences in OC transformation between coastal marine systems. However, water residence time itself can have large impacts on OC transformations, regardless of shelf width. For instance, plume waters from the Amazon River are exported from the continental shelf relatively quickly (<30-60 days) compared to the plume waters from the Mississippi

River (> several months) (Fichot and Benner, 2014; Medeiros *et al.*, 2015). This relatively short water residence time of the Amazon River plume is associated with the export of relatively unchanged (50-76%) OC reaching the Atlantic Ocean (Medeiros *et al.*, 2015). In comparison, less than 50% of OC in the Mississippi River plume remains unchanged inshore of the 200 m isobath (Fichot and Benner, 2014).

Seasonal variation in river discharge can also play a large role in regulating the transformations of terrestrial- and marine-produced OC in coastal marine environments via changes in water residence times. For example, Medeiros et al. (2015) estimated that at periods of high Amazon River discharge, approximately 26% more terrestrial DOM, which includes OC molecules, is exported unchanged beyond the continental shelf compared to periods of low discharge. While decreased water residence time, and thus reduced biological and physical processing, was postulated to contribute to the increased proportion of untransformed DOM, increased DOC concentrations can occur during high-flow periods in the Amazon River (Ward *et al.*, 2013) and may influence the proportion of untransformed DOM during this time (Medeiros *et al.*, 2015).

The mixing and circulation of water in coastal and open oceans have a large influence on the rates of OC transformation, particularly for DOC (Blair and Aller, 2012). One well studied example is the impact that strong currents and infrequent cyclonic events have on OC cycling in the GBR lagoon. These currents and seasonal weather events constantly mix pelagic and benthic DOC and POC into oxygen-rich water (Alongi and McKinnon, 2005; Alongi *et al.*, 2011). In these oxygen-rich systems, more refractory OC compounds are constantly being exposed to (1) oxygenated conditions (i.e. greater oxygen exposure time), (2) more fresh and labile OC compounds, and (3) high UV light conditions at the surface, that leads to eventual microbial (direct and due to priming) and photochemical degradation (Blair and Aller, 2012). This constant mixing and degradation is thought to be largely responsible for the very low concentrations of POC stored in sediment in the GBR (Alongi *et al.*, 2011). In the open ocean, the turnover of the oceanic water column, termed the global overturning circulation (GOC), is responsible for much of the degradation of more refractory DOC compounds (Shen and Benner, 2018). As DOC concentrations are relatively low in the open ocean, the GOC plays a critical role in transporting more refractory DOC compounds to microbes and physicochemical conditions (i.e. sunlit waters and hydrothermal vents) that degrade them (see ‘Molecular and size-fraction effects on OC transformation’). In fact, the lifetime of DOC compounds is thought to be directly related to the rate of GOC (Shen and Benner, 2018). The main physicochemical conditions and processes that the GOC mediates in the deep ocean include the thermal degradation of DOC at hydrothermal vents, microbial degradation of DOC in the presence of more labile OM additions (i.e. priming effect), and the mixing of subsurface waters to sunlit waters. This exposes refractory DOC to warmer temperatures and photochemical processes and can mineralise and transform them into simpler, more biologically labile compounds (Shen and Benner, 2018).

4.4.4 Priming effect

Priming is the process whereby the addition of a labile compound enhances the microbial degradation of less labile compounds (Bianchi, 2011), and there are many priming substrates that exist in terrestrial, freshwater and marine environments (Figure 12). The

'priming effect' was first described in soils (Bingeman *et al.*, 1953), and has only recently been incorporated into research on aquatic OM dynamics. Bianchi (2011) indicated that priming of more refractory terrestrially derived OC in the oceans, by more labile sources, may help resolve the discrepancy between the quantity of OC input from rivers (~0.2-0.25 Pg yr^{-1} of DOC and ~0.15-0.2 Pg yr^{-1}) and the global burial rate of OC in marine sediments (0.1-0.2 Pg yr^{-1}) (Hedges *et al.*, 1997). Several studies in marine environments have shown that OC additions from algae can increase background mineralisation rates of OC in sediment (Turnewitsch *et al.*, 2007; van Nugteren *et al.*, 2009). In fact, van Nugteren et al. (2009) reported that algal OC additions increased background rates of sediment remineralisation by up to 31%. However, Lønborg et al. (2018) found no evidence for priming when more bioavailable POC was added to less bioavailable DOC in water collected from coastal waters of the Great Barrier Reef.

Priming is thought to be one of the processes contributing to the eventual decomposition of RDOC in the deep ocean (Figure 9). As RDOC is moved to the oceanic surface via global overturning circulation it mixes with more labile OM originating from phytoplankton processes. The more labile phytoplankton-derived OM, alongside the abiotic processes of photolysis by ultraviolet irradiation and interactions with suspended particles (Hansell *et al.*, 2009), may contribute to the eventual decomposition by heterotrophic microbes of RDOC. These compounds have remained unchanged for millennia. In this way, autotrophic processes can be strongly coupled with heterotrophic processes in marine environments.

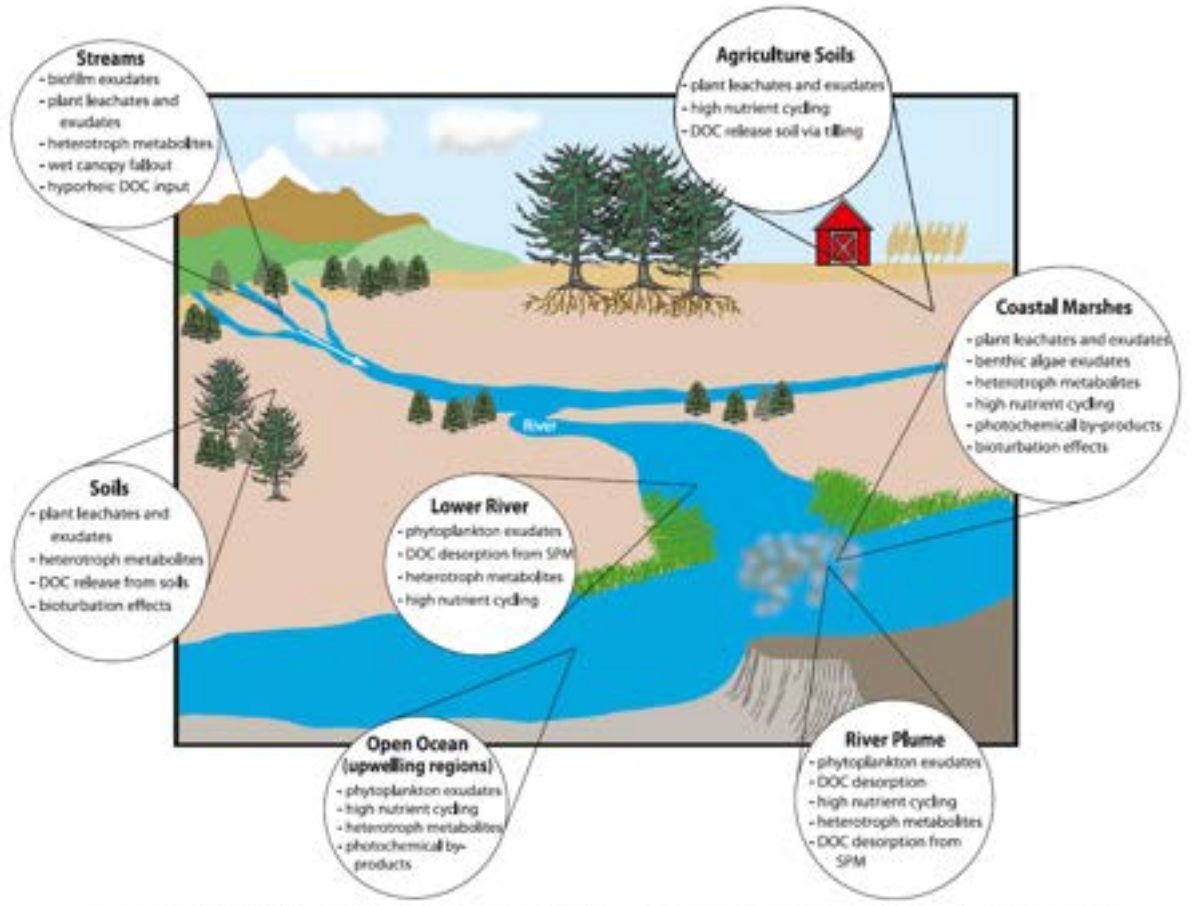

Figure 12: Potential sources of priming substrates in terrestrial, freshwater, and marine environments (Source: Bianchi, 2011).

5.0 FATE

There are three ultimate fates of OC in marine ecosystems (Blair and Aller, 2012): (1) near permanent burial and/or water column sequestration as refractory OC (mainly DOC, at geological timescales); (2) biological assimilation; and, (3) evasion to the atmosphere as CO_2. We illustrate the complexities of the factors that can influence the fate of OC in Figure 13.

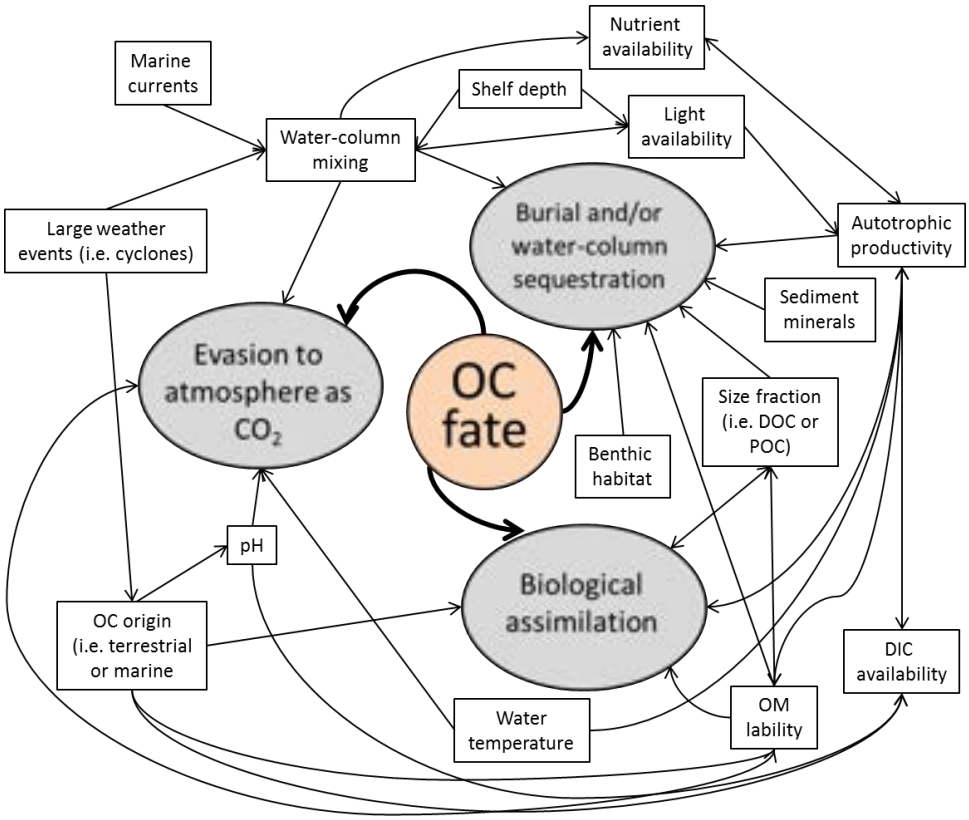

Figure 13. The direction of influence and connectedness (arrows) of the factors mediating the fate of organic carbon (OC) in coastal marine ecosystems.

5.1 Burial and/or water-column sequestration

On a global scale, river-influenced coastal margins are the primary locations of terrestrial- and marine-produced OC storage in benthic sediment (Hedges and Keil, 1995). This is because rivers play a major role in transporting sediment (Kandasamy and Nagender Nath, 2016). In fact, the total organic matter burial rate in deltaic sediments (47 ± 17 Tg C y^{-1}) is more than four times that of non-deltaic continental margin sediments (11 ± 3 Tg C y^{-1}) (Burdige, 2005). In general, the quantity of OC stored in marine sediment, mainly as POC, is a function of the sediment accumulation rate of a particular location, the biogeochemical reactivity of the OC substrate, and/or the oxidative state of the water column (Blair and Aller, 2012). The dissolved oxygen (DO) conditions of the water column is particularly important, because a greater OET increases the likelihood of efficient mineralisation of OC molecules, even of more refractory compounds (Blair and Aller, 2012). Therefore, OC burial in marine sediments is greatest in coastal regions that experience large inputs of OC in sediment but where OC particles are subject to low OETs (Blair and Aller, 2012). The importance of DO conditions of the water column for mediating OC burial in sediment is demonstrated by the

high OC burial efficiencies in the coastal regions of the Eel and Waiapu River. Even though these river systems export moderate quantities of OC, by global standards, they have the highest recorded OC burial rates yet identified due to the rapid delivery, and thus reduced OETs, of OC from land to the deep ocean (Blair and Aller, 2012). In contrast, OC burial rates are lowest in oxygenated coastal marine environments with long residence times, and thus an extended period for OC mineralisation (Blair and Aller, 2012). The GBR marine shelf is an example of a region with low OC burial rates, and the case study below describes OC burial dynamics in the GBR shelf. Although accumulation of POC in sediment is a major component of the OC cycle in coastal regions, the majority of OC is stored as DOC in the global oceans (Zhang *et al.*, 2017). In fact, about 97% of all ocean OM is in the DOM fraction (Hedges, 2002).

The incorporation of OC into the marine biological biomass in coastal marine environments is largely dependent on its molecular size. Conventional wisdom dictates that POC fixed by riverine and oceanic autotrophic processes (i.e. as phytoplankton) is transferred to grazers, and then to higher trophic-level organisms such as fish, whereas DOC, from terrestrial or marine sources, is largely contained within the microbial loop (Azam *et al.*, 1983; Ducklow, 1983). However, the mechanisms describing the biological assimilation of DOC and POC are highly complex and remain largely understudied. This complexity is driven mainly by the difficulty in separating the biotic effects caused by OC from that of organic nutrients in DOM and POM. Further, the influence of DOM on algal and bacterial production is often coupled (Amon and Benner, 1998; Croft *et al.*, 2005; Prieto *et al.*, 2016) and can be interactive over very short temporal (i.e. seconds to minutes) and spatial (across extracellular matrices) scales. The complexity in interactions between the algal and bacterial use of DOC is conceptualised in Figure 14. In this conceptual model, the influence of DOC availability, of both terrestrial and marine origin, on algal growth can be mediated via the activities of bacteria. Bacteria utilise DOC as an energy source during the cellular process of metabolism and release CO_2 as a by-product. Labile organic nutrients (i.e. amino acids) are also released via passive (i.e. leakage) and active (i.e. exudation) extra-cellular processes, as well as via viral lysis. The CO_2 and inorganic and organic nutrients released, as well as CO_2 and nutrients in the water column from other sources, can be assimilated directly by autotrophic organisms during photosynthesis. It has been shown that some aquatic phytoplankton can uptake LDOC directly from the water column, but this usually occurs at very insignificant levels (Znachor and Nedoma, 2010). They can also use simple forms of organic N and P (Bronk *et al.*, 2007; Dyhrman *et al.*, 2007). Increased rates of primary productivity may also increase concentrations of oxygen, DOC (LDOC and RDOC), and POC in marine waters. It is worth noting that elevated rates of primary productivity, and subsequent bacterial activity, can actually lead to reduced dissolved oxygen conditions, especially under eutrophic conditions (Chislock *et al.*, 2013). This algal-derived DOC (mainly as LDOC) and oxygen is rapidly recycled through the microbial loop. A small fraction (5-7%) of the DOC produced during algal and bacterial processes (i.e. the biological pump) exists as recalcitrant DOC (RDOC) and can persist in the ocean for millennia (see section 3.6.1).

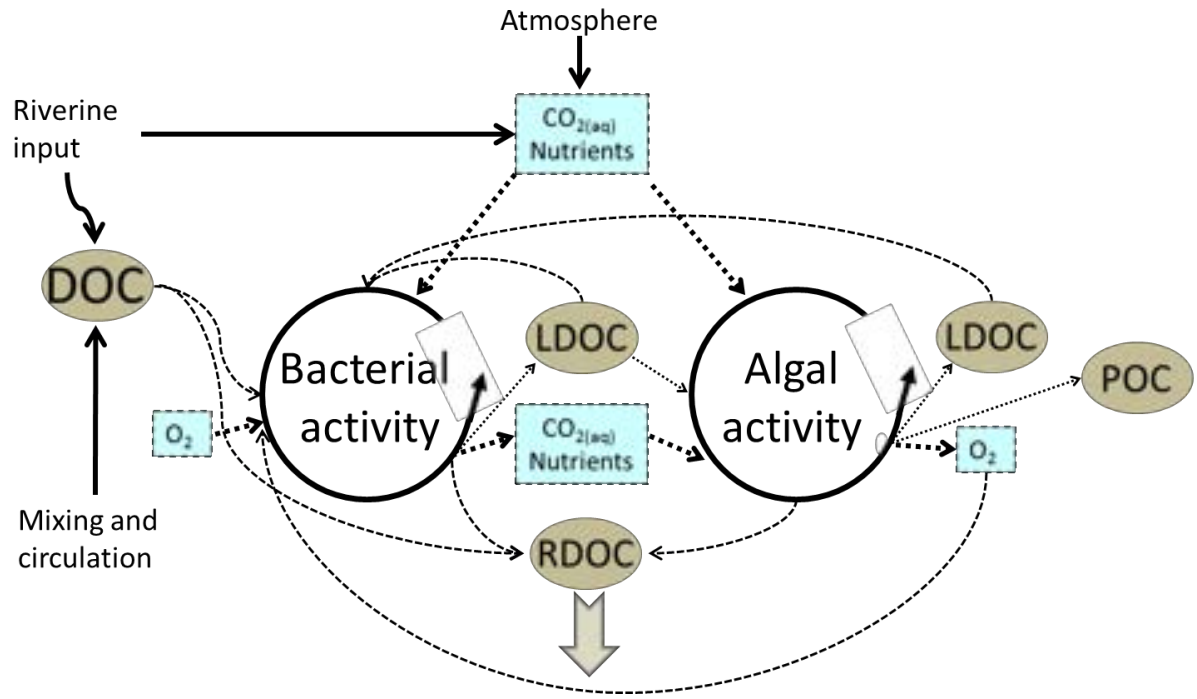

Figure 14. The processes and fluxes potentially linking DOC availability with the activities of heterotrophic bacteria and algae in coastal marine environments.

5.1.1 Fate of mangrove-derived OC

Mangroves have the potential to be major sources of OC to coastal marine environments, however they are generally thought to contribute minimally to coastal primary and secondary production (Alongi, 1990). Mangrove leaf litter is generally considered a poor-quality C source for marine food webs (Loneragan *et al.*, 1997; Chong *et al.*, 2001), due to the refractory nature of mangrove leaves and leached organic compounds (Alongi *et al.*, 1989), but there are exceptions for some coastal species (Kristensen *et al.*, 2017; Peng *et al.*, 2017). Further, the biological influence of mangroves has a limited geographical extent. Several studies have concluded that the contribution of mangrove OC to marine primary and secondary production extends only a few kilometres from mangrove forests (Rodelli *et al.*, 1984; Alongi, 1990; Chong *et al.*, 2001). Although mangrove litter is generally considered refractory, productive sedimentary bacterial communities do occur in close vicinity to mangrove forests (Alongi *et al.*, 1989) and are presumably capable of mineralising this refractory C source (Alongi, 1990). Indeed, most mangrove-derived OC is retained and recycled through the sedimentary microbial food web (Hyndes *et al.*, 2014).

5.1.2 Relative importance of terrestrial OC

Variation in the biological fate of terrestrial OC in marine ecosystems can often be a function of the relative biological availability of terrestrial versus marine OC sources. Terrestrially derived OC is generally considered more refractory for marine heterotrophic organisms because it has been subject to more transformative processes in rivers before entering coastal environments. This notion is supported by studies which have found that terrestrial (riverine and mangrove origin) OC is selectively preserved along fluvial networks (Prahl *et al.*, 2003), or a much poorer C substrate for heterotrophic microbial processes(Alongi *et al.*,

2008), than marine-produced OC. However, when primary production is constrained, terrestrial-derived OC is thought to be more important in marine ecosystems. For example, it has been postulated that terrestrial OC sources may have a stabilising and relatively large biological influence for glacial-influenced coastal-marine ecosystems due to the low in situ primary production that often characterises these systems (Piwosz *et al.*, 2009). The physical conditions in these coastal marine ecosystems are often characterised by low water temperatures, variable water salinity, and a high turbidity caused by mineral particles in glacial silt (Svendsen *et al.*, 2002). High turbidity, in particular, restricts light penetration and reduces the euphotic zone, the layer in which photosynthesis can occur (Svendsen *et al.*, 2002). However, a recent food web study in coastal waters in the Gulf of Alaska estimated that the source contribution of allochthonous OM to higher trophic levels, such as fish and sea birds, was relatively low, ranging from 12% to 44% (Arimitsu *et al.*, 2018). This was despite the high microbial lability of the bulk glacier-derived OM pool in rivers (Hood *et al.*, 2009). Research is yet to investigate the transformations of the glacier-derived OM pool as it moves from rivers to coastal ecosystems, and it is possible that the labile pool of bulk OM is rapidly diminished before entering coastal marine ecosystems.

5.2 Evasion of inorganic C originating from OC

The evasion of inorganic C (as CO_2) to the atmosphere represents one of the fates of OC in marine environments (Kandasamy and Nagender Nath, 2016). Heterotrophic microbes assimilate DOC from both terrestrial and marine sources and, during respiration, respire CO_2 (Cole, 2013). This CO_2 reacts with water and forms a balance between several sources of dissolved inorganic carbon (DIC): aqueous $CO_{2(aq)}$, carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (Raven and Falkowski, 1999; Cole, 2013). In the form of $CO_{2(aq)}$, DIC can be emitted to the atmosphere through the processes of molecular diffusion at the ocean surface (Cole, 2013). Differences in gas partial pressure between the ocean and atmosphere control rates of molecular diffusion (Liss, 1973). Before the industrial revolution, a lower partial pressure in the atmosphere, compared to the oceans, led to a net positive flux of CO_2 from the oceans to the atmosphere (Raven and Falkowski, 1999). Since the industrial revolution, however, a higher partial pressure in the atmosphere has led to a net positive flux of CO_2 from the atmosphere to the world's oceans (Raven and Falkowski, 1999). Despite the net positive flux of CO_2 from the atmosphere to the world's oceans, there are 'hotspots' of oceanic CO_2 evasion in areas that receive large inputs of OC, such as estuaries and coastal regions (Cai, 2011).

5.3 Effects for marine corals

In tropical oceans, calcifying organisms play a major role in building coral reefs (Hutchings *et al.*, 2008). These coral reefs are some of the greatest hotspots of biodiversity in the world (Hutchings *et al.*, 2008). However, the activities of calcifying organisms are influenced by a plethora of global and local stressors, such as increased water temperatures, biological invasions, elevated bicarbonate concentration, lowered ocean pH, and increased riverine input of dissolved and particulate inorganic and organic solutes (i.e. nutrients, carbon, metals) (Hutchings *et al.*, 2008). Until recently, the role of OC in shaping the activities of corals has been largely unknown (Kline *et al.*, 2006). Nonetheless, research is now illuminating the various direct and indirect pathways that elevated OC concentrations can

have on coral mortality and bleaching, as well as coral-associated algae photosynthetic performance and calcification rates.

Increasing OC concentrations (DOC and POC), above that experienced naturally, has an overwhelmingly negative impact on coral functioning in tropical environments (see Table 2). Greater coral mortality (Kline *et al.*, 2006; Bessell-Browne *et al.*, 2017) and bleaching (Kline *et al.*, 2006; Haas *et al.*, 2009), reduced net and/or gross photosynthesis (Meyer *et al.*, 2015; Meyer *et al.*, 2016) and chlorophyll *a* tissue concentrations in zooxanthellae (Haas *et al.*, 2009), as well as slower calcification rates (Meyer *et al.*, 2015) have all been reported under elevated OC conditions. In contrast, Meyer et al. (2016) reported enhanced coral growth by 42% with DOC amendment compared to unamended experimental controls. The authors reported that this was due to increased heterotrophic activity to compensate for losses in labile assimilates due to reduced photosynthesis. While greater OC concentrations had an overwhelming negative impact on coral functioning, the variation in parameter effects among and within studies (i.e. not all coral processes within a study were negatively affected), and evidence of a positive functional effect, indicate that species-specific impacts are very likely. Indeed, several authors highlight the complexity of responses to elevated OC among different coral species from similar locations (Kuntz *et al.*, 2005; Meyer *et al.*, 2015). The species-specific responses revealed in these studies indicate that, on an individual species level, the impact of elevated DOC concentrations in tropical marine environments may be difficult to predict.

In many cases, authors reported additive or synergistic effects of elevated DOC concentrations on coral functioning when seawater DIC was simultaneously elevated. For instance, two controlled laboratory experiments of coral functioning in the Great Barrier Reef reported that while additions of DOC alone did not affect coral calcification, when added in combination with DIC, there was a significant reduction in dark coral calcification (Meyer *et al.*, 2015; Meyer *et al.*, 2016). Meyer *et al.* (2016) postulated that greater bacterial respiration under high DOC concentrations increased local concentrations of DIC, above that of the DIC treatment alone, with the combined effect being greater carbonate dissolution at night. DOC and DIC concentrations often increase simultaneously in response to high riverine discharge (Prokushkin *et al.*, 2011; Giesler *et al.*, 2014), and there would rarely be occasions when these C sources would individually be substantially elevated in coastal marine environments. The potential for additive or synergistic responses of coral functioning to simultaneous increases in DOC and DIC concentrations suggests that the occurrence of multiple stressors may be more harmful than individual stressors. This highlights two main points: (1) DOC biogeochemical reactions, and its potential functional impact to coral, do not occur in isolation and studies should incorporate DOC cycling in conjunction with DIC and nutrients; and, (2) multiple stressors will likely cause greater detrimental impacts to coral than single stressors. Indeed, Kuntz *et al.* (2005) found that coral mortality increased significantly over time with continual exposure of multiple stressors. Chronic multiple stressors will be more harmful to corals than acute multiple stressors.

The impact of elevated marine OC concentrations on coral is thought to be largely manifested by changes in the balance between coral photosynthetic organisms and its associated heterotrophic microbiota (Kuntz *et al.*, 2005; Kline *et al.*, 2006). Marine bacterial activity will increase under increased labile DOC concentrations, assuming other stoichiometric requirements are satisfied, because DOC is an essential substrate for

heterotrophic microbial growth. Further, greater bacterial activity can suppress the photosynthetic ability of aquatic photosynthetic organisms via proteolysis (breakdown of proteins) associated with bacteria-enzymes, the competition for space and resources (dissolved and organic nutrients), as well as by reducing the nutrient and gas exchange over algae tissue (Cole, 1982). All-in-all, changes to coral functioning on tropical reefs will likely depend on the types and duration of stressors, as well as the species of coral inhabiting a particular reef.

Table 2. Summary of the impacts of elevated organic carbon (OC) concentrations on coral functioning.

Effect of OC addition	OC type	Coral location	Mechanisms	Reference
Increased coral mortality	Glucose, lactose, galactose, starch, and arabinose	Bocas del Toro, Republic of Panama	Disruption of the balance between the coral and its associated microbiota	Kline et al., 2006
Coral bleaching	Seawater POC	Bocas del Toro, Republic of Panama	Disruption of the balance between the coral and its associated microbiota	Kline et al., 2006
Reduced chlorophyll *a* tissue concentrations of coral and visible bleaching	Glucose	Northern Gulf of Aqaba, Jordan	Low dissolved oxygen concentrations; stimulated bacteria growth and production of coral-damaging secondary metabolites	Haas et al., 2009
Reduced net and/or gross photosynthesis of calcifying green algae. Species-specific responses.	Glucose	Great Barrier Reef, Australia	Favour of non-beneficial and/or harmful bacterial growth	Meyer et al., 2015
Reduced dark calcification of calcifying green algae.	Glucose	Great Barrier Reef, Australia	Reduction in photosynthesis and favour of non-beneficial and/or harmful bacterial growth	Meyer et al., 2015
Increased coral mortality and bleaching. Species-specific responses.	Starch, lactose, arabinose and mannose	Bocas del Toro, Republic of Panama	Coral mortality by over-stimulating the growth of coral mucus-associated microbes	Kuntz et al., 2005
Increased coral growth	Glucose	Great Barrier Reef, Australia	Heterotrophic compensation of losses in labile assimilates due to reduced photosynthesis	Meyer et al., 2016

Reduced net and/or gross photosynthesis	Glucose	Great Barrier Reef, Australia	Reduced pH on coral surface caused by increased microbial respiration	Meyer et al., 2016
Coral mortality, but only in low-light conditions	Suspended sediment (DOC and POC)	Great Barrier Reef, Australia	Reduced photosynthesis of coral-associated algae due to light reduction associated with turbidity	Bessell-Browne et al., 2017

6.0 ORGANIC CARBON DYNAMICS ON THE GBR SHELF

6.1 The GBR shelf system

The GBR shelf is the most extensive modern tropical mixed carbonate-siliciclastic shelf system on Earth (Larcombe and Carter, 2004). The GBR shelf contains tropical reefs that extend over 14 degrees of latitude (Hopley, 2008) and was once one of the world's most intact coral reefs (Bellwood *et al.*, 2004). The outer extent of the reef varies according to latitude, approaching 23 km offshore at 14°S and up to 260 km offshore at 21°S (Hopley, 2008). The modern GBR shelf developed 19,000 to 26,500 years ago as the continental shelf was flooded following the last glacial maximum (Hopley, 2008). Although subject to variation, much of the central GBR shelf can be characterised according to three distinct parallel sedimentary zones (Larcombe and Carter, 2004):

1. **The inner shelf.** Between 0-22m water depth and comprising sediment of largely terrestrial origin that is commonly 5-10m thick.
2. **The middle shelf.** Between 22-40m water depth, mostly starved of terrestrial sediment, and is generally devoid of coral reefs.
3. **The outer shelf.** Between 40-80m water depth, also starved of terrestrial sediment, and comprises scattered accumulations of modern coral reefs.

6.2 Source and transformations of DOC and POC

It has been suggested that one of the most consistent ecological features of the GBR shelf is the high rates of both sediment and pelagic microbial respiration (Alongi and McKinnon, 2005; Alongi *et al.*, 2011). Microbial organisms are thought to mineralise most of the organic material deposited on the GBR shelf (Alongi and McKinnon, 2005; Alongi *et al.*, 2008; Lønborg *et al.*, 2018), and this has been linked to the relatively insignificant quantities of OC and organic matter accumulation in shelf sediments (Alongi *et al.*, 2011). In fact, Alongi et al. (2011) describes the biogeochemical functioning of the GBR shelf as an efficient OC 'incinerator'. A study investigating the bioavailability of predominately marine-origin DOM and POM in coastal waters of the GBR reported that more than 83% of bioavailable DOM and greater than 96% of bioavailable POM was degraded before reaching the outer shelf of the GBR (Lønborg *et al.*, 2018). Further, Alongi and Pfitzner (2008) recorded average benthic mineralisation efficiencies of OC of 92% in the inner shelf, with total benthic C mineralisation significantly decreasing with distance from the coast. These studies highlight the high transformation rates of OM, including DOC and POC, in the GBR. The factors driving the high rates of OC mineralisation in the reef include year-round high water temperature, an oxic water column (Alongi *et al.*, 2011), and the input of high-quality OM from macroalgae, phytoplankton and reef-derived OM (Alongi *et al.*, 2008). However, the input of terrestrial OM is likely a major factor, especially considering the significant relationship observed by Alongi and Pfitzner (2008) of decreasing OC mineralisation with distance from the coast.

Terrestrially-derived OM is thought to play a major role in coastal ecosystem processes, with chlorophyll *a* biomass (Brodie *et al.*, 2007) and the associated production (Furnas and Mitchell, 1988) also decreasing with distance from the coast. It is clear that both heterotrophic and autotrophic processes are stimulated in the inner shelf of the GBR, and

recent research is beginning to highlight the important role that terrestrial OM may play in coastal waters of the GBR (Franklin *et al.*, 2018; Garzon-Garcia *et al.*, 2018). Franklin et al. (2018) investigated the response of freshwater and marine phytoplankton to terrestrial sediment collected from two catchments that drain into the GBR. Using laboratory incubations, the authors identified a subset of sediment types (~40%) that enhanced marine phytoplankton activity (Franklin *et al.*, 2018). Further investigation revealed that measures of soluble OC, POC and PON in terrestrial sediment were included as parameters in the best fitting models predicting phytoplankton response (Garzon-Garcia *et al.*, 2018). It was postulated that (1) organic nutrients may directly promote phytoplankton activity, once they are in soluble form, and that (2) POC may indirectly promote marine phytoplankton growth because more labile inorganic and organic compounds are produced from the mineralisation of POC (and leached DOC) by heterotrophic bacteria (Franklin *et al.*, 2018; Garzon-Garcia *et al.*, 2018). However, phytoplankton activity was also enhanced in freshwater when exposed to terrestrial sediment (Garzon-Garcia *et al.*, 2018), indicating that processing of this terrestrial-derived OM, including of POC and DOC, may occur before reaching the GBR. Supporting this was a trend for reduced marine phytoplankton activity when exposed to riverine sediment (Franklin *et al.*, 2018), presumably because river sediment has been subject to more biological and physical processes that have diminished the most available organic compounds. Periods of high flow in rivers, such as deluges associated with tropical cyclones, play a key role for sediment and OC delivery from land to coastal environments (Larcombe and Carter, 2004). High flow will reduce riverine biological degradation at these times.

6.3 Fate of DOC and POC

6.3.1 Burial

In general, relatively small quantities of POC accumulate in sediments of the GBR shelf (Alongi *et al.*, 2011), with very little or no OC found in sediments of the mid- and outer-shelf (Alongi and McKinnon, 2005; Alongi *et al.*, 2011). This coastal reservoir of OC storage coincides with where terrestrial sediment accumulates – terrestrial sediment is mostly contained within ~11km of the coastline (Belperio, 1983; Currie and Johns, 1989; Johns *et al.*, 1994; Orpin *et al.*, 2004). Research quantifying the input, distribution and burial rate of organic and inorganic C in the Herbert River estuary and continental shelf region of the GBR found that the total OC burial mass (8.9 $x10^9$ mol C yr^{-1}) was an order of magnitude lower than the total annual OC production (310 $x10^9$ mol C yr^{-1}; this OC quantity includes that due to river input, mangrove input, and autochthonous production) (Brunskill *et al.*, 2002). The authors conclude that nearly all OC input to the GBR shelf is respired, emphasising the highly oxidative nature of the GBR heterotrophic microbial community. Although total OC burial rates in sediment were low in the Herbert River estuary and continental shelf region, the greatest sediment accumulation occurred in small areas of wind-protected mangrove-lined channels - in fact, the burial rate of OC decreased, almost exponentially, from intertidal mangrove mudbanks to the continental slope at 1000m depth (Brunskill *et al.*, 2002). In this study, approximately 89% of the total shelf OC burial was contained within nearshore sediments at depths of 0-20m (Brunskill *et al.*, 2002). Radke et al. (2010) also recorded greater sediment OC (as TOC) concentrations in near-shore environments compared to

further offshore. Finally, both Currie and Johns (1989) and Johns et al. (1994) reported that terrestrial silt and sediment deposition is confined to within 11 km of the northern GBR coast. The striking reduction in OC sediment burial rates from the coast to the outer reef alludes to the effect that OC origin has upon its fate in the GBR shelf. Refractory OC molecules are more likely to accumulate on marine sediments than more bioavailable OC molecules (Watanabe and Kuwae, 2015). Therefore, the greater burial of OC in nearshore environments of the GBR shelf is likely, at least partially, due to high rates of terrestrial OC sedimentation. All-in-all, there is strong evidence that terrestrial OC is a less preferred substrate for heterotrophic microbial processes and that the burial of this refractory terrestrial OC may explain the pattern of decreasing POC in sediment along a gradient from west to east on the GBR shelf.

6.3.2 Biological assimilation

The degree of DOC and POC incorporation into the marine biological biomass on the GBR varies according to OM lability which is, in turn, related to its source. Terrestrially derived OC is generally considered more refractory for marine heterotrophic organisms because it has been subject to more transformative processes in rivers before entering coastal environments. In particular, POC and DOC of mangrove origin are a much poorer C substrate for heterotrophic microbial processes than other terrestrial- or marine-produced OC (Alongi *et al.*, 1989). Although mangrove litter is generally considered refractory, productive sedimentary bacterial communities do occur in close vicinity to mangrove forests (Alongi *et al.*, 1989) and are presumably capable of mineralising this refractory C source (Alongi, 1990). The refractory nature of mangroves leaves (i.e. POC), however, means that they contribute minimally to the overall coastal primary and secondary production (Alongi, 1990), as well as a C source for marine food webs (Loneragan *et al.*, 1997; Chong *et al.*, 2001). However, certain species do rely on mangrove forests as both a food source and refuge space (Kristensen *et al.*, 2017; Peng *et al.*, 2017).

Despite the general refractory nature of terrestrial OC, compared to marine OC, the high water temperatures (Alongi *et al.*, 2008) and an oxic water column (Alongi *et al.*, 2011) of the GBR lead to high rates of OC mineralisation in coastal waters (Alongi *et al.*, 2008). Labile DOC and POC associated with elevated chlorophyll *a* biomass (Brodie *et al.*, 2007) and phytoplankton production (Furnas and Mitchell, 1988) in coastal waters of the GBR have also been postulated to be responsible for high rates of OC mineralisation in coastal waters. There is a link between sediment delivery from land and elevated phytoplankton activity in the GBR (Bainbridge *et al.*, 2012; Franklin *et al.*, 2018; Garzon-Garcia *et al.*, 2018), and it is possible that coupled bacterial-algal processes may enhance the biological assimilation of OC delivered from terrestrial sources.

6.4 Organic carbon dynamics in coastal waters of the GBR shelf

A recent report for the Great Barrier Reef (GBR) Marine Park Authority identified a trend for increasing DOC at many sites, and POC concentrations at some sites, over the past 10 years in inshore waters in a variety of monitoring locations spanning the length of the GBR (Lønborg *et al.*, 2016) (Figure 15). In particular, there is evidence for a sustained increase in DOC concentrations since approximately 2009, with a peak in concentrations in 2012-2013

(Figure 15). Further, POC concentrations have increased steadily since approximately 2012 (Figure 15). While the broader ecological impacts of elevated OC concentrations in the GBR ecosystem are not well understood, increases in OC concentrations have been shown in both laboratory and field-based investigations to promote the productivity of heterotrophic microbes and some coral diseases in the GBR (Meyer *et al.*, 2016; Bessell-Browne *et al.*, 2017) and in other tropical coastal ecosystems (see section 0). There is, therefore, concern that elevated OC concentrations may have deleterious impacts on the structure and functioning of the GBR marine ecosystem.

In order to fully contextualise potential ecological impacts, we first need a better mechanistic understanding of the reasons for increasing DOC and POC concentrations in inshore waters of the GBR. Several mechanisms have been hypothesised to help explain elevated DOC and POC concentrations in inshore waters of the GBR (Lønborg *et al.*, 2016; Waterhouse *et al.*, 2018). These hypothesised mechanisms include (1) an increase in coral and planktonic primary production, (2) autotrophs are allocating more of their production towards DOC release; and (3) an increased export of terrestrial OC. However, there are likely other, potentially interactive, mechanisms controlling variation in DOC and POC concentrations. Coastal waters of the GBR are ecologically and biogeochemically complex, and an understanding of how the source, transformations, and fate of OC changes through space and time is required in order to contextualise the potential mechanisms that help explain elevated DOC and POC concentrations in inshore waters of the GBR.

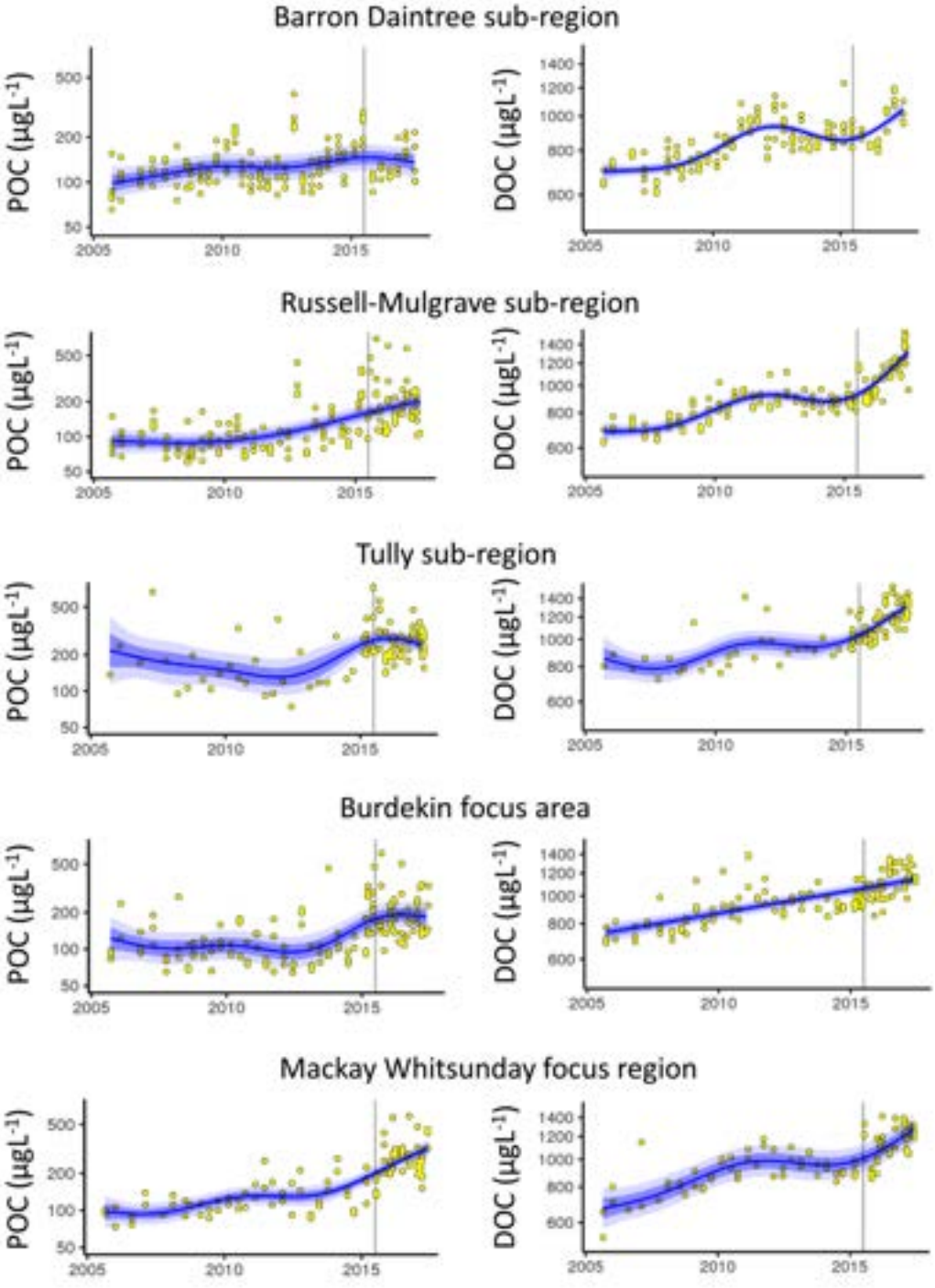

Figure 15. The temporal trends in particulate organic carbon (POC) and dissolved organic carbon (DOC) in five sub-regions and focus regions of the Marine Monitoring Program at the Great Barrier Reef Marine Park Authority. Source:(Waterhouse *et al.*, 2018). Vertical dashed lines indicate when the sampling design was changed (February 2015).

Below we describe the typical biogeochemical and ecological state of near-shore environments of the GBR shelf in relation to changes in the source, transformation and fate of DOC and POC. Mechanisms that may increase DOC and POC concentrations in coastal waters are highlighted in each scenario within a conceptual figure. The mechanistic understanding used to develop these three biogeochemical and ecological states was gathered from science conducted in the GBR and its catchments, as well as from other

marine ecosystems. We then describe some major stressors that may alter OC dynamics and outline how the source, transformation and fate of DOC and POC likely occur in two important GBR lagoon environments: coral reefs, and seagrass and macro-algae communities.

6.4.1 Scenario 1: "Normal" state (weeks to months) (Figure 16)

This period can be summarised by the following characteristics:

1. "Normal" scenario where the availability of DOC and POC in the majority of the GBR is largely controlled by the resuspension and delivery of OC (mainly POC) by tides and currents (mainly wind-driven) from sediment, rivers, mangrove, saltmarshes and from the deep ocean, as well as phytoplankton production;
2. Most DOC and POC, whether of terrestrial or marine origin, is consumed within the GBR in this highly oxidative and mixed environment, and very little is stored in sediment or exported to the Coral Sea; and,
3. Rates of sediment DOC and POC mineralisation will decrease with distance from the coast due to a reduced availability of terrestrial OC in coastal waters.

In the absence of monsoonal and cyclonic weather systems, a "normal" biogeochemical and ecological scenario characterises the GBR (Figure 16). This "normal" scenario is largely identified by oligotrophic conditions throughout the inner, middle, and outer shelf of the GBR. Although nutrients and OC are relatively scarce, highly productive components of the GBR (e.g. seagrass and coral) lead to rapid cycling and thus sufficient availability of limiting resources for primary and secondary production (Hatcher, 1990; Silveira *et al.*, 2017). Rivers deliver DOC and POC from land, and from autotrophic and heterotrophic processes within rivers. This terrestrial OC will only have a major influence on the inner shelf of the GBR, as evidenced by a decreasing availability of terrestrial-derived OM in sediment in a transect from west to east (Alongi *et al.*, 2011). DOC is also delivered to the GBR lagoon via groundwater discharge (Hunter, 2012), along with nutrients and aqueous CO_2. These components may further promote DOC production via enhanced phytoplankton productivity (Gagan *et al.*, 2002). Relatively refractory DOC and POC are also delivered from mangrove forests and possibly also saltmarshes, via tides and currents to the inner shelf of the GBR (Alongi, 1987; Alongi *et al.*, 1989; Alongi, 1990; Kandasamy and Nagender Nath, 2016). The spatial influence of this refractory OC does not, however, extend more than a few kilometres from the coast (Rodelli *et al.*, 1984; Alongi, 1990; Chong *et al.*, 2001). Tides and currents likely deliver DOC from the open ocean to the mid and outer shelf.

Most of the pelagic POC within the GBR is derived from sediment via sediment resuspension (Larcombe *et al.*, 1995; Larcombe and Woolfe, 1999). Phytoplankton production is typically rapidly grazed and remineralised (Furnas *et al.*, 2005). Rates of sediment POC and pelagic DOC mineralisation decrease with distance from the coast as terrestrial OM loads decrease (Alongi *et al.*, 2008). Phytoplankton production is also highest closer to the coast (Furnas and Mitchell, 1988; Brodie *et al.*, 2007; Alongi *et al.*, 2008). In coral reef ecosystems, the DOC processing of bacterioplankton is largely dependent on the production of labile OC by benthic primary producers in the form of photosynthates, rather than OC production by phytoplankton (Torréton *et al.*, 2002; Rochelle-Newall *et al.*, 2008) (see section 3.6.3). Elsewhere in the reef, it is likely that bacterioplankton processing is constrained and largely dependent on OC from: (1) coupled bacterioplankton-phytoplankton

processes (Croft *et al.*, 2005; Prieto *et al.*, 2016); and (2) the delivery and resuspension of sediment via tides and currents (Furnas *et al.*, 2005; Furnas *et al.*, 2011). In coupled bacterioplankton-phytoplankton processes, the bacterioplankton production has been shown to increase the pelagic concentrations of labile nutrients and CO_2 (Prieto *et al.*, 2016), as well as essential vitamins that many autotrophs cannot produce (Croft *et al.*, 2005). This is then assimilated by phytoplankton promoting their growth.

Water mixing and circulation via tides, winds and currents resuspend any terrestrial or marine-produced POC that is stored on the sediment surface (Larcombe *et al.*, 1995; Larcombe and Woolfe, 1999; Lønborg *et al.*, 2016). The resuspension of POC, along with refractory DOC in the water column, increases its OET. A greater OET is associated with increased rates of OC mineralisation (Blair and Aller, 2012). The exposure of more refractory DOC to sunlit waters increases the potential for photochemical degradation (Shen and Benner, 2018). The wide and shallow nature of the GBR likely enhances the opportunity of refractory (i.e. terrestrial) and labile DOC and POC to be exposed to greater resuspension activity, a greater OET, and thus mineralisation. A consequence of the high rates of OC mineralisation in this highly oxidative environment, is the relatively low storage of terrestrial POC in sediment (Alongi and McKinnon, 2005; Alongi *et al.*, 2011). Further, little OC delivered to, or produced in, the GBR is exported to the Coral Sea, with the majority of the DOM (>83%) and POM (>96%) consumed on the GBR shelf (Lønborg *et al.*, 2016).

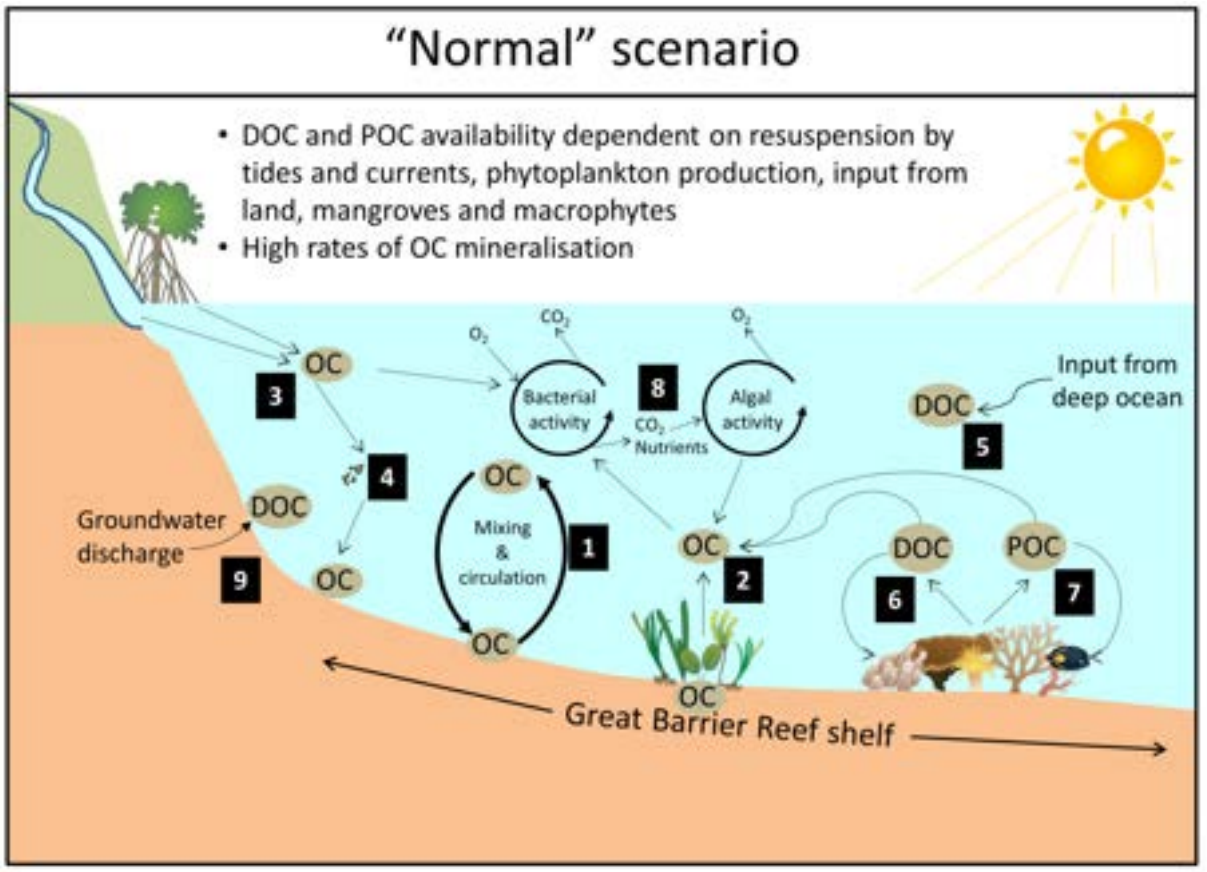

Figure 16. A conceptual models displaying the key organic carbon (OC) processes in a more "Normal" scenario on the Great Barrier Reef shelf system. DOC=dissolved organic carbon, POC=particulate organic carbon. Numbers refer to important fluxes, processes, or statements and are described in detail in a narrative Table (2) below.

6.4.2 Scenario 2: Extreme weather-based increase in terrestrial OC, via freshwater discharge, and marine OC, via sediment resuspension (days to weeks) (Figure 17)

This period can be summarised by the following characteristics:

1. river plume remains suspended in the water column, and there is an increase in the proportion of terrestrial DOC and POC in pelagic waters and sediment of coastal marine environments of the GBR;
2. erosion and resuspension of GBR shelf sediment may increase DOC and POC in pelagic waters;
3. potentially enhanced activities of bacterioplankton, which may elevate pelagic concentrations of DOC;
4. constrained rates of primary production, and thus POC derived from phytoplankton, relative to other times; and,
5. potentially greater algal productivity on the fringe of the suspended river plume.

The tropical and sub-tropical coast of Queensland is subject to monsoonal and cyclonic weather systems, concentrated between the months of November and April (Commonwealth of Australia, 2018). These tropical weather systems lead to dramatic increases in river discharge during storm events that rapidly export large quantities of terrestrial sediment and organic matter into estuaries and near-shore environments of the GBR shelf (Carter *et al.*, 2009) (Figure 17). This large flux of sediment and organic matter from rivers causes visible turbid “plumes” that extend beyond a river mouth and estuary (Great Barrier Reef Marine Park Authority, 2011; Howley *et al.*, 2018). Concentrations of DOC and POC increase in inner-shelf waters which will be mostly associated with increased quantities of terrestrial OC in the river plume (Lønborg *et al.*, 2016). Concentrations of DOC and POC may also increase further offshore, in mid- and outer-shelf waters, due to the erosion and resuspension of pre-storm sediment on marine benthic surfaces (Gagan *et al.*, 1990). During this period, rates of POC sedimentation may also increase due to the elevated terrestrial material associated with the plume (Gagan *et al.*, 1990; Hilton *et al.*, 2008). Adsorption of some DOC to sediment particles in the plume may reduce its biological uptake and increase rates of sedimentation (Hedges *et al.*, 2000). Despite the large flux of terrestrial sediment and organic matter in river plumes, the influence of these plumes, in relation to both distance offshore and rates of sedimentation of terrestrial material, does not often extend beyond the inner shelf of the GBR (Figure 17) (Gagan *et al.*, 1990). It is worth noting that while sedimentation may increase during ‘plume events’, the quantity of suspended sediment in large plumes is still insignificant compared to sediment resuspended by waves, currents, and tides (Larcombe and Woolfe, 1999). It is also worth noting that tropical cyclones cause substantial shelf-wide erosion, resuspension and deposition of pre-storm marine sediment (Gagan *et al.*, 1990). This shelf-wide disturbance can lead to up to 30% of the inner-shelf sediment comprised of sediment transported from the mid-shelf (Gagan *et al.*, 1990). A small amount of refractory DOC may be shunted off the GBR shelf to the deep ocean.

Concentrations of DOC, POC, inorganic carbon, as well as organic and inorganic nutrients are greatest during high-flow events in both small and large rivers (Medeiros *et al.*, 2015; Rue *et al.*, 2017). Further, the rapid water residence times experienced during large rainfall events has been shown elsewhere to increase the proportion of relatively unprocessed or

"fresh" (i.e. less oxidised), and potentially more bioavailable, terrestrial OM (Medeiros *et al.*, 2015). The large input of relatively unprocessed DOC and POC, along with other nutrients, may promote the productivity of bacterioplankton, especially in areas directly affected by river plumes (Ducklow and Kirchman, 1983; Bainbridge *et al.*, 2012). Indeed, increased bacterial activities have been associated with a larger availability of "fresh" terrestrial OM in both freshwater (Burrows *et al.*, 2013) and marine (Chin-Leo and Benner, 1992; Amon and Benner, 1998) environments elsewhere.

While the productivity of bacterioplankton may increase during this period, the productivity of phytoplankton may be suppressed (Bainbridge *et al.*, 2012). Higher suspended sediment loads throughout the reef (Gagan *et al.*, 1990) may reduce light availability and constrain phytoplankton productivity in the short-term (until sediment particles settle or are transported elsewhere), as has been observed elsewhere (Jochem, 2003). Further, organic compounds in the plume, which originate from terrestrial material (i.e. leaves and sediment) leachate, may inhibit phytoplankton productivity, as has been observed for freshwater algal species in a laboratory experiment (Neilen *et al.*, 2017). It is possible that phytoplankton productivity may increase on the margins of the river plume, as has been observed elsewhere (McKinnon and Thorrold, 1993; Lohrenz *et al.*, 1999), where turbidity is low enough for sufficient light penetration, but there is still an increased availability of river-transported dissolved nutrients and aqueous CO_2 (Devlin *et al.*, 2001; Chen *et al.*, 2017; Howley *et al.*, 2018).

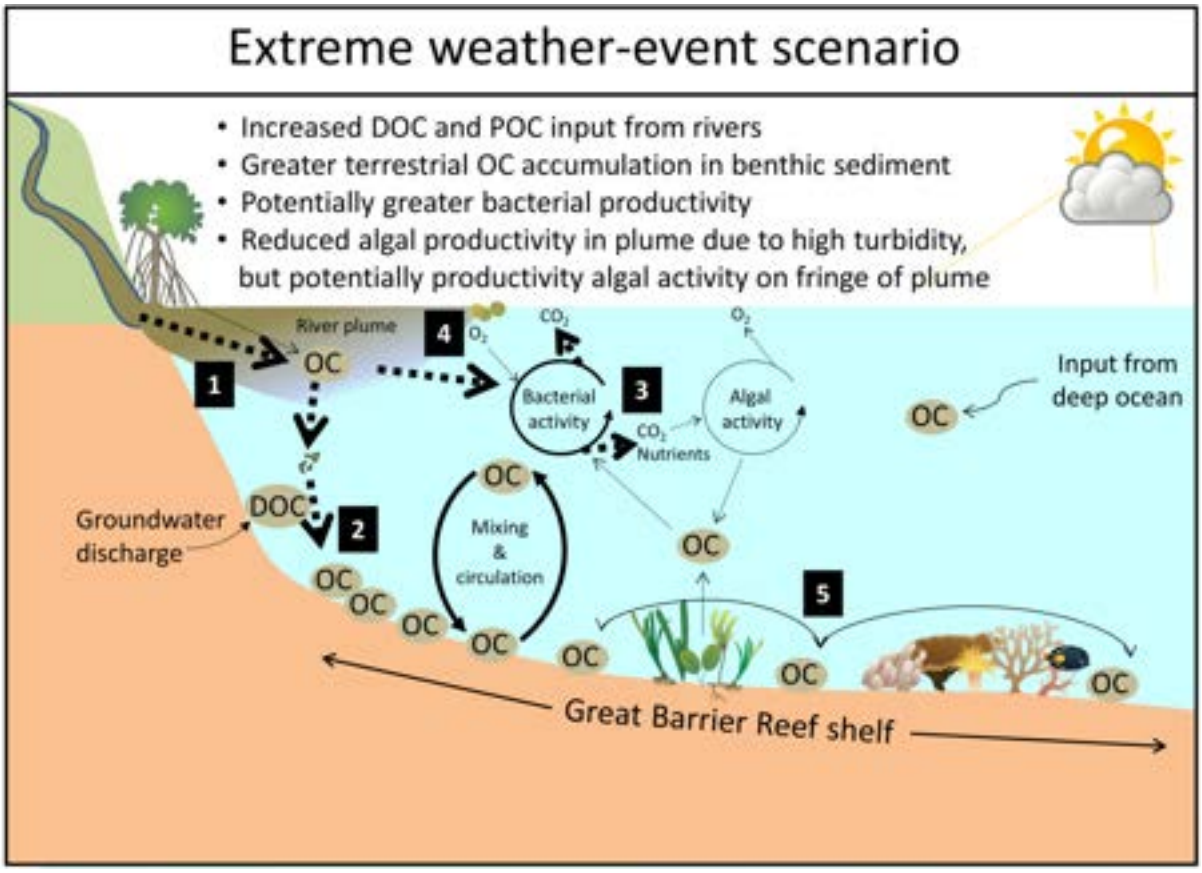

Figure 17. A conceptual model displaying the key organic carbon (OC) processes during an extreme weather event scenario on the Great Barrier Reef shelf system. DOC=dissolved organic carbon, POC=particulate organic carbon. Numbers refer to important fluxes, processes, or statements and are described in detail in a narrative Table (2) below.

6.4.3 Scenario 3: Post-extreme weather scenario (days to weeks) (Figure 18)

This period can be summarised by the following characteristics:

1. decrease in the input of terrestrial DOC and POC from rivers relative to the event scenario
2. decreasing water column and sediment concentrations of terrestrial DOC and POC due to an increasing oxygen exposure time (OET) caused by tides and currents that increases mineralisation by bacterioplankton
3. elevated phytoplankton productivity in coastal areas, leading to elevated autochthonous DOC and POC concentrations

In the days to weeks following significant rainfall events, river discharge decreases along with the input of higer concentrations of terrestrial DOC and POC. River plumes disperse, and water column clarity improves in coastal waters, aided by the relatively short (~15 and 365 days) water-residence time on the GBR shelf (Brodie *et al.*, 2012). Tides, waves, and currents continuously resuspend plume-associated terrestrial OC that has settled on the shelf floor (Larcombe and Woolfe, 1999), increasing its oxygen exposure time (OET). Greater OET times are associated with higher rates of OM mineralisation, including of more refractory DOC and POC compounds (Blair and Aller, 2012). Consequently, most of the remaining terrestrial DOC and POC delivered during storm events are likely mineralised by bacterioplankton in this highly oxidative environment.

The dispersion of the river plume, the settling of mobilised OM on the marine floor, and the removal of pelagic DOC and POC by bacterial mineralisation, leads to a gradual return to clear and oligotrophic waters. With a greater light availability, and the residual terrestrial dissolved inorganic and organic nutrients delivered during the storm event, phytoplankton productivity increases in coastal areas affected by the plume (Bainbridge *et al.*, 2012). Greater phytoplankton productivity leads to elevated concentrations of marine-produced DOC, due to passive (i.e. leakage) and active (i.e. exudation) extra-cellular processes, and POC (i.e. the phytoplankton themselves) (Thornton, 2014). Additionally, elevated bacterioplankton activities, associated with residual terrestrial OC and nutrients delivered during elevated river discharge, may also increase phytoplankton productivity due to coupled bacterioplankton-phytoplankton processes (Croft *et al.*, 2005; Prieto *et al.*, 2016).

Overall, much of the terrestrial OC associated with the storm-event has been mineralised and exported as DIC or CO_2, incorporated into algal (via coupled bacterioplankton-phytoplankton processes) and bacterial biomass, or deposited as sediment-associated DOC or POC on the benthic floor (Figure 18).

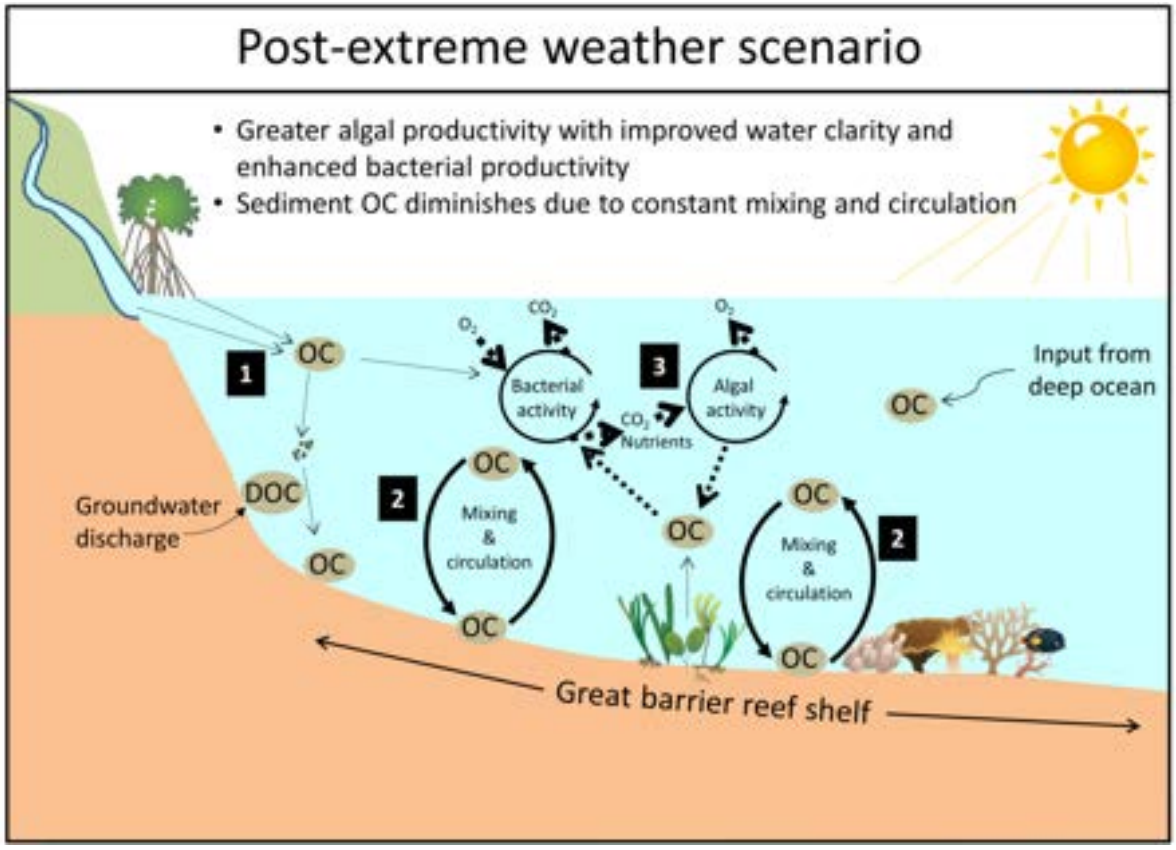

Figure 18. A conceptual model displaying the key organic carbon (OC) processes in the weeks to months following an extreme weather event on the Great Barrier Reef shelf system. DOC=dissolved organic carbon, POC=particulate organic carbon. Numbers refer to important fluxes, processes, or statements and are described in detail in a narrative Table 3 below.

Table 3. This narrative table describes the important fluxes, processes, or statements, as well as references, for each scenario that highlights the mechanisms that may increase DOC and POC concentrations in coastal waters of the GBR.

Narrative table		
Scenario 1		
Number	**Flux, processes, or statement**	**Supporting references**
1	The majority of the suspended POC and DOC within the GBR, and other tropical waters, is likely derived from benthic sediment via resuspension events.	Larcombe et al., 1995; Larcombe & Woolfe (1999); Walsh et al., 1988
2	Macro-algae and seagrasses are often net sources of DOC to tropical marine environments.	Barrón et al., 2014
3	Rivers, mangroves, and saltmarshes deliver POC and DOC to coastal regions of the GBR.	
4	Terrestrial OC input from rivers, mangroves, and saltmarshes only has a major physical (sedimentation) and ecological (biological uptake) influence in the inner shelf of the GBR.	Alongi et al., 1989; Alongi and McKinnon, 2005; Alongi et al., 2011; Brunskill et al., 2002; Loneragan et al., 1997
5	DOC from the open ocean can be delivered to coastal regions via tides, currents, and storm events.	

6	Most DOC and POC in coral reefs is produced by benthic primary producers, including coral-associated symbiotic zooxanthellae, macro-algae, algal turfs and endolithic algae.	
6	Degraded coral reefs can be a source of DOC and POC to tropical waters, but in healthy reefs most of this C is assimilated and recycled.	Silveira et al., 2017
7	POC from sloughed coral mucus can be a net source of OC to benthic surfaces.	Wild et al., 2004
8	In marine environments away from coral reefs, bacterioplankton and phytoplankton processes are rapid and tightly coupled. Bacterioplankton can assimilate riverine DOM, and the CO_2 and labile nutrients produced can then promote the productivity of phytoplankton. Phytoplankton also produce DOM which can be assimilated by bacterioplankton. This rapid cycling and tight coupling leads to low concentrations of inorganic and organic pelagic nutrients.	Croft et al., 2005; Furnas et al., 2005; Furnas et al., 2011; Prieto et al., 2016
9	Groundwater discharges into the GBR lagoon and can contain high concentrations of DOC.	Stieglitz, 2005; Hunter, 2012
9	Elevated concentrations of dissolved inorganic nitrogen and aqueous CO_2 may increase DOC production via enhanced phytoplankton production.	Hunter, 2012; Gagan et al., 2002; Sorrell et al., 2013

Scenario 2

Number	Flux, processes, or statement	Supporting references
1	Extreme weather events (i.e. cyclones) increase precipitation on land. This leads to elevated river discharge and the export of large quantities of terrestrial sediment and organic matter into estuaries and near-shore environments of the GBR shelf.	Carter et al., 2009
2	Rates of sedimentation will increase due to the elevated terrestrial material associated with the plume, increasing the quantity of OC stored on benthic surfaces.	Bainbridge et a., 2012; Gagan et al., 1990; Hilton et al., 2008;
3	Heterotrophic productivity increases in areas affected by river plumes and sediment resuspension, due to the increased availability of carbon substrates and nutrients	Amon and Benner, 1998; Chin-Leo and Benner, 1992; Ducklow and Kirchman, 1983; Jochem, 2003
4	Elevated DIN and aqueous CO_2 concentrations in river plumes may increase phytoplankton production, but only in regions (e.g. plume margin) where there is sufficient light availability	Chen et al., 2017; McKinnon and Thorrold 1993; Devlin et al. 2001; Lohrenz et al. 1999

5	Pelagic concentrations of DOC and POC may increase in mid- and outer-shelf waters, due to the erosion and resuspension of pre-storm sediment on marine benthic surfaces. Tropical cyclones cause substantial shelf-wide erosion, resuspension and deposition of pre-storm marine sediment.	Gagan et al., 1990

Scenario 3		
Number	**Flux, processes, or statement**	**Supporting references**
1	River plumes disperse and pelagic DOC and POC concentrations begin to decline, aided by the relatively short (~15 and 365 days) water-residence time on the GBR shelf and reduction in river discharge.	Brodie et al., 2012
2	Tides, waves, and currents continuously resuspend plume-associated terrestrial OC that has settled on the shelf floor, increasing its oxygen exposure time and thus its mineralisation.	Blair and Aller, 2012; Larcombe and Woolfe, 1999
3	As river plumes disperse, pelagic light availability increases and phytoplankton productivity increases, aided by the residual terrestrial dissolved and inorganic nutrients delivered during the storm event.	Bainbridge et al., 2012.

6.4.3 Natural factors and anthropogenic stressors influencing GBR organic carbon dynamics

6.4.3.1 Extreme weather events

Extreme weather events can directly increase DOC and POC concentrations in coastal waters via two main mechanisms:

1. cyclones and extreme rainfall events on land can increase the riverine export of terrestrial-derived sediment (Carter *et al.*, 2009), leading to elevated DOC and POC concentrations in coastal waters of the GBR (Great Barrier Reef Marine Park Authority, 2011; Howley *et al.*, 2018), and;
2. cyclones can mobilise marine benthic sediment, leading to higher pelagic OC concentrations and the transport of POC in sediment across large areas of the GBR shelf (Gagan *et al.*, 1990).

The increased export of terrestrial OC was one mechanism that was hypothesised by Lønborg *et al.* (2016) to help explain the recent trend for elevated DOC and POC in coastal waters of the GBR (see section 0). The recent trend (~2009 onwards) trend for increasing DOC at many sites, and POC concentrations at some sites, in coastal waters of the GBR corresponds with the occurrence of several extreme weather events along the Queensland coast. For instance, the period between 2009 and 2012 corresponded with a period of extreme weather events along the Queensland coast, including unusually strong La Nina events between 2010-2012 (Great Barrier Reef Marine Park Authority, 2011; Commonwealth

of Australia, 2012). Cyclone Hamish (4-16 March 2009), Ului (19-21 March 2010), and Yasi (2-4 February 2011) were all severe category cyclones that impacted the GBR shelf and coastal environments (Great Barrier Reef Marine Park Authority, 2011), and they may have contributed to the elevated DOC and POC concentrations observed.

A study investigating changes in the frequency of flood plume events extending beyond inshore areas of the reef found that high-flow events, that are caused by extreme weather events, are becoming more frequent (Lough *et al.*, 2015). In fact, the frequency of high-flow events (i.e. freshwater flood plumes of a high intensity) has increased in the GBR from 1 in every 20 years (1748-1847) to 1 in every 6 years (1948-2011). The authors postulated that climate shifts will most likely increase the occurrence of extreme weather events which may increase sediment loads to the GBR.

The study by Lough et al. (2015) highlights the potentially large role that extreme weather events can have on the biogeochemistry of the GBR shelf. However, several questions remain, including:

- how long does the DOC and POC delivered to GBR coastal waters remain in the water column and on benthic surfaces? and,
- how do successive extreme weather events impact on the pelagic concentrations of DOC and POC?

The flushing time of fresh water in the GBR varies between 15 and 365 days (Hancock *et al.*, 2006; Luick *et al.*, 2007; Wang *et al.*, 2007; Choukroun *et al.*, 2010), with most investigations estimating a flushing time of less than ~2 months. However, Brodie et al. (2012) stated that there is no justification to assume that fresh water resident times are the same as solute resident times, because many solutes are subject to non-conservative transportation (i.e. they are affected by many physical and biological processes). The authors synthesised existing data on the flushing time of many materials in the GBR, including sediments and nutrients, and concluded that the residence time of fine sediment (10's of years), coarse sediment (1000's of years), and reactive nutrients (years to decades) is much greater than that of fresh water (Brodie *et al.*, 2012).

Sediments and nutrients may be flushed into the GBR during high-flow events, but they are then subject to multiple physical and biological processes that may enhance particle settling on benthic surfaces or sorption to inorganic and organic compounds (Brodie *et al.*, 2012). Importantly, these solutes that were once input on to the GBR shelf during a high-flow event can then be re-suspended during subsequent extreme weather events. Numerous extreme weather events over just a few years may increase (1) the quantity of terrestrial sediment (and OC) deposited on benthic surfaces, (2) the quantity of OC resuspended during these subsequent extreme weather events, and (3) coupled bacterioplankton-phytoplankton processes that increase pelagic concentrations of DOC and POC. All-in-all, it is possible that the successive extreme weather events between 2009 and 2012 may have contributed to the recent observation of elevated DOC and POC concentrations in coastal waters of the GBR.

6.4.3.2 Groundwater discharge

Groundwater discharges directly to the GBR lagoon (Stieglitz, 2005; Hunter, 2012). Groundwater, and groundwater discharge, in this region can be, but is not always,

characterised by relatively high DOC and DIN concentrations (Hunter, 2012) and be supersaturated in CO_2 (Gagan *et al.*, 2002). The discharge of high-DOC groundwater to coastal waters may thus directly increase pelagic DOC concentrations. Further, since the availability of DIN and aqueous CO_2 can control rates of primary and secondary production in marine environments (Sorrell *et al.*, 2013), the discharge of groundwater to coastal waters was suggested by Gagen et al. (2002) to potentially stimulate DOC production in the photic zone via enhanced phytoplankton productivity.

It must be noted that very little is currently known about the magnitude of, and spatial and temporal trends in, groundwater inputs to the GBR lagoon (Stieglitz, 2005; Hunter, 2012). Even less is known about the ecosystem effects of direct groundwater discharge to the GBR lagoon environment. However, it has been reported that groundwater levels have been rising in many coastal regions of Queensland, including in the lower Burdekin, Barron Delta, lower Johnston, Don, Proserpine and Pioneer Valley (McNeil and Raymond, 2011; Hunter, 2012). This rise in groundwater levels is likely due to land clearing since European colonisation, which results in enhanced groundwater infiltration due to reduced loss via vegetation transpiration (Hunter, 2012).

6.4.3.3 Sea surface temperature

There has been an increasing trend for sea-surface temperatures in the GBR over the past century (Figure 19). The increase in sea surface temperature corresponds with the general trend for increasing DOC concentrations since ~2005 (see Figure 15), but also peaks in both DOC and POC concentrations during high-water temperatures periods. For instance, a period of high sea-surface temperatures recorded in 2012-2013 corresponds with peaks in both DOC and POC concentrations recorded at many GBR monitoring sites (see Figure 15). It is possible that rising sea-surface temperature may be one factor contributing to altered physical and biological processes that are responsible for the observed increasing trends of water-column DOC and POC concentrations.

Rising sea surface temperatures in the Coral Sea are already affecting the GBR ecosystem (Great Barrier Reef Marine Park Authority, 2017). One of the most visible and published ecosystem effects of rising sea temperatures is coral bleaching. Coral bleaching occurs when the thermal stress leads to a breakdown in the symbiotic relationship between the coral host and zooxanthellae (Great Barrier Reef Marine Park Authority, 2017). As zooxanthellae can provide corals with up to 90% of their energy needs, the loss of zooxanthellae often causes the coral host to starve. Elevated sea water temperatures can cause corals to alter their export of DOC and POC (see sections 3.6.3 and 6.4.4.1), with one study recording a reduced flux of DOC from once species of coral but an increased flux of POC (Levas *et al.*, 2015). However, it is likely that there will be species-specific effects in terms of how OC dynamics of coral species will respond to increasing water temperature (see sections 3.6.3 and 6.4.4.1).

Rising sea surface temperatures also affect numerous other biotic processes that can increase water column concentrations of DOC and POC, including autotrophic and heterotrophic production (Riegl *et al.*, 2015; Striebel *et al.*, 2016; Rasconi *et al.*, 2017) as well as seagrass (Barrón and Duarte, 2009; Apostolaki *et al.*, 2010) and macro-algae productivity (Barrón *et al.*, 2014). However, the temperature dependence of many biotic processes are controlled by the availability of resources, such as nutrients in the water

column. For instance, it has been demonstrated that phytoplankton production will only increase with rising temperatures if nutrient availability also increases (Riegl *et al.*, 2015; Striebel *et al.*, 2016). The fact that biotic processes are co-limited by multiple resources highlights the complexity in the drivers that may underpin changes in DOC and/or POC concentrations in the water column of the GBR.

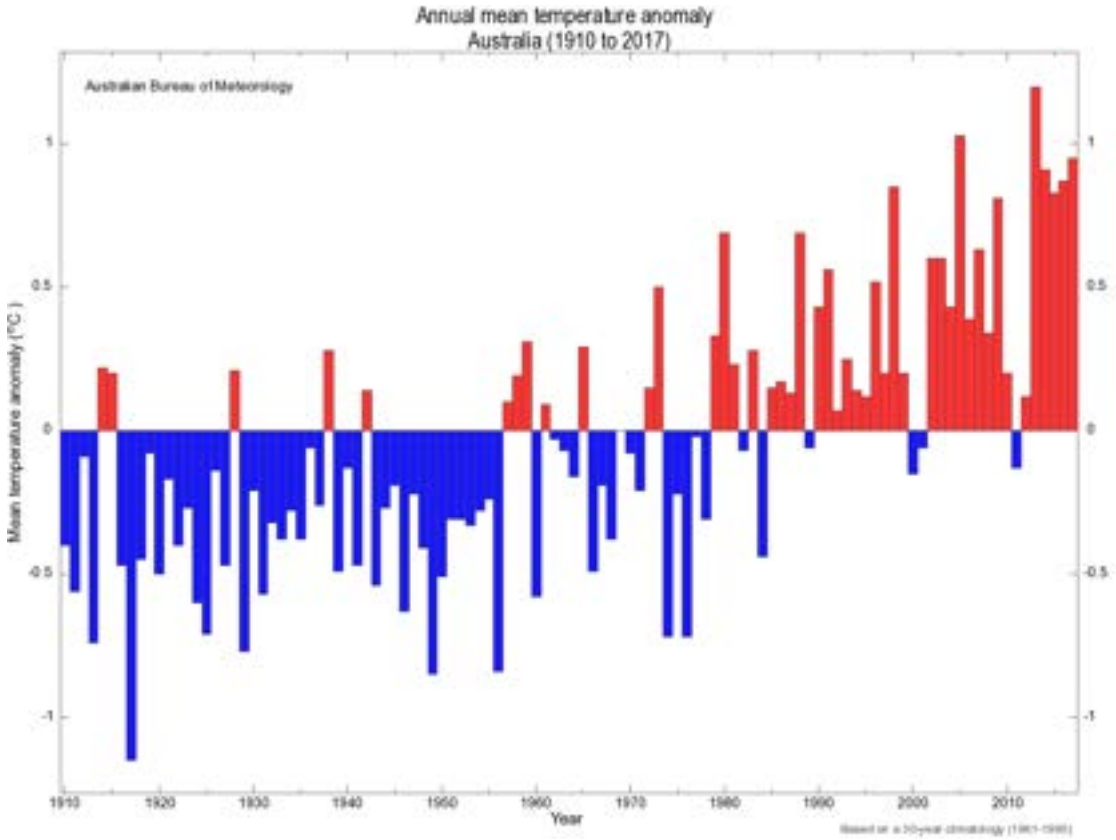

Figure 19. Annual sea surface temperature anomalies between 1910 and 2017, based on a 30-year climatology (1961-1990). Source: Australian Bureau of Meteorology (Australian Bureau of Meteorology, 2018).

6.4.4 Organic carbon dynamics of reef communities in response to environmental change

Tropical coastal oceans are under increasing pressure globally due to many natural and anthropogenic pressures, including increased water temperatures, ocean acidification (i.e. elevated aqueous CO_2), and greater nutrient and other chemical inputs from land. The specific and cumulative consequences of these pressures for OC fluxes and transformations in specific environments (i.e. coral reefs or seagrass beds) in tropical coastal oceans is very difficult to unravel and understand at the scale of ecosystems because (1) species-specific effects often manifest (Alldredge *et al.*, 2013; Levas *et al.*, 2015), (2) results from laboratory-mesocosm experiments may not describe true responses in nature, and (3) many studies do not investigate cumulative responses. Below we highlight the potential changes in OC dynamics that may manifest under current or future environmental change for several important environments in the GBR: coral reefs, and seagrass and macro-algae communities, and benthic cyanobacterial matts.

6.4.4.1 Coral reefs

There are over 3000 coral reefs in the broader GBR, containing more than 600 species of coral polyps (Hutchings *et al.*, 2008). In healthy coral reefs, zooxanthellae translocate excess photosynthetically fixed C to their coral host. The majority of this fixed C is stored as energy reserves, with the remainder either released directly into the water column as DOC or excreted as POC in mucus (Wild *et al.*, 2004). This mucus-POC is eventually sloughed off, with up to 80% converted back to DOC via biological and physical processes and a small quantity stored as POC on benthic surfaces (Wild *et al.*, 2004). Under stressed conditions, however, the flux of OC from coral reefs can be altered. Levas et al. (2015) found that, under elevated water temperature and acidic conditions, a significant decrease in the flux of DOC, but not POC, was evident for two coral species. It was hypothesised that corals conserve DOC losses to sustain energy reserves under these stressful conditions (Levas *et al.*, 2015). Additionally, the authors postulated that limiting POC flux in mucus would be detrimental to corals as mucus protects coral from many environmental conditions, including UV exposure, increased sedimentation, and elevated temperatures (Levas *et al.*, 2015). It is worth emphasising that coral species may respond differently to external pressures, which is why ecosystem-scale predictions in reef OC dynamics are difficult. Overall, understanding how the OC dynamics of coral will respond to natural and anthropogenic stressors will require targeted research for individual species as well as at larger scales (i.e. coral platforms and whole coral reefs). Further, research is required into how the OC dynamics of coral will respond to individual and multiple stressors, including in responses to both pulse (short-term) and press (long-term) disturbances.

6.4.4.2 Seagrass and macro-algae communities

The extent of OC release from marine seagrass and macro-algae (visible autotrophs that are not a seagrass) communities, and the factors influencing this release, is becoming increasingly clear. Using existing and unpublished experimental data, Barrón et al. (2014) found that 85% of seagrass communities, and all the macro-algae communities assessed, were net sources of DOC to the surrounding marine environment. Additionally, they found a global pattern of increasing net DOC flux from seagrass communities with increasing water temperature. This positive association between water temperature and net DOC flux is supported by other studies that report greater DOC flux from seagrasses in summer compared to winter (Barrón and Duarte, 2009; Apostolaki *et al.*, 2010). The mechanisms for DOC release from macrophyte communities are varied and may include leaching, decomposition of detritus, organismal excretion, and respiration from the plants themselves or associated bacteria, micro-algae, phytoplankton and epiphytes, as well as sediment beneath plants (Barrón *et al.*, 2014). Further, it is largely unknown whether temperature-related increases in DOC release are due to biotic stress or the enhancement of metabolic processes. Seagrasses and macro-algae in the tropics grow at close to their thermal limits (Koch *et al.*, 2013), and it is therefore conceivable that biotic stress may account for some DOC release from degrading seagrass or from resuspended OC stored in benthic sediment when seagrass extent is reduced or productivity declines. At the same time, elevated aqueous CO_2 concentrations, due to ocean acidification, may enhance seagrass and macro-algae productivity (Koch *et al.*, 2013; Ow *et al.*, 2016), as occurs in terrestrial environments, which may enhance DOC release via autotrophic leaching, decomposition of detritus, organismal excretion, and respiration. Regardless, there is the potential for an increased DOC flux from marine plants with increasing water temperatures and under future climate change scenarios.

6.4.4.2.1 Seagrass and macro-algae status on the GBR

There has been a general decrease in the abundance and area inhabited by seagrasses in coastal regions of the GBR since 2007 (Coles *et al.*, 2015), with large declines during severe weather events between 2009 and 2011 (McKenzie *et al.*, 2017). The decline has been directly attributed to a series of severe tropical cyclones that cause large terrestrial runoff, elevated pelagic pollutants, reduced light availability due to increase turbidity, and physical damage (Coles *et al.*, 2015). It is worth noting, however, that since 2015 the condition of many seagrass communities has stabilised or slightly improved (McKenzie *et al.*, 2017). Most seagrass monitoring in the GBR is conducted in coastal waters and often in close proximity to ports and river estuaries. Very little is known about the population dynamics of seagrasses in the mid and outer shelf of the GBR (Great Barrier Reef Marine Park Authority, 2012). Predicting how seagrass beds influences the DOC and POC concentrations in the GBR will require a better understanding of changes in seagrass extent over the whole GBR, as well as how elevated water temperatures will impact seagrasses, as increasing water temperature is associated with increased DOC flux from seagrass communities (Barrón *et al.*, 2014).

Although there has been no regular monitoring of changes in macro-algae coverage on the GBR, many reefs have shifted globally from a coral dominated to a macro-algae dominated environment (McCook, 1999; Dell *et al.*, 2016). Much of this change has been due to an increased advantage of macro-algae over coral under elevated nutrients loads (McCook, 1999) and decreased herbivory (Dell *et al.*, 2016) which can promote macro-algal fecundity and growth (Nordemar *et al.*, 2007). Further, increased ocean acidity (Diaz-Pulido *et al.*, 2011; Ober *et al.*, 2016) is predicted to enhance the competitive advantage of macro-algae over coral. All-in-all, the abundance of macro-algae on reef structures increases under a variety of stressors. Given that, macro-algae are likely net sources of DOC to pelagic waters, so changes in macro-algae extent on the GBR may have a substantial impact on DOC concentrations.

6.4.4.3 Benthic cyanobacterial mats

Benthic cyanobacterial mats can represent up to 79% of the DOC release from reef communities (Brocke *et al.*, 2015b). Further, there has been an increase in the formation of dense benthic cyanobacterial mats in tropical reefs around the world (Albert *et al.*, 2005; Brocke *et al.*, 2015a; de Bakker *et al.*, 2017; Ford *et al.*, 2018). The causes of the increase in benthic cyanobacterial mats is varied and complex but is thought to be associated with climate change, poor water quality, increased iron input to coastal regions, and the overexploitation of keystone species (Ford *et al.*, 2018). Consequently, benthic cyanobacterial mats are increasingly becoming a major source of DOC in many tropical reef ecosystems.

6.5 Summary of potential factors that may alter concentrations of DOC and POC in coastal waters of the GBR

A mechanistic understanding of the factors mediating changes in DOC and POC concentrations in inshore waters of the GBR is presented above (See Section 0). This mechanistic understanding highlights many potential sources of DOC and/or POC in coastal waters of the GBR shelf. Further, many natural and anthropogenic factors and pressures

that may alter the flux of DOC and/or POC have been outlined. In Table 3, these sources of DOC and/or POC are presented, along with the main vector(s) responsible for its release, the natural and anthropogenic factors and drivers exacerbating these vectors, and the likely responses of DOC and/or POC concentrations to these natural and anthropogenic factors and pressures.

Table 4. The DOC and/or POC sources, likely current state, the main vector mediating the flux, the driver(s) involved, and the overall flux response.

Source	Likely current state	Main vector	Driver(s)	Flux response
Seagrass community	Net source of DOC	Exudates released during autotrophic production, DOC and POC released during senesce & decomposition	Ocean acidification, rising water temperature	Potentially greater primary production and increased DOC flux
Seagrass community	Net source of DOC	Exudates released during autotrophic production, DOC and POC released during senesce & decomposition	Greater water column nutrient concentrations	Reduced primary productivity and decreased DOC flux Potentially short-term flux of DOC and POC from seagrass communities and sediment as they die
Macro-algae	Net source of labile DOC to heterotrophic bacteria on tropical reefs	Algae exudates released during autotrophic production	Ocean acidification, rising water temperature, greater water column nutrient concentrations, overfishing	Greater competitive advantage of macro-algae over coral in reef communities Increased DOC flux from macro-algae in reef communities
Benthic cyanobacterial mats	Net source of DOC	Algae exudates released during autotrophic production	Climate change, poor water quality, increased iron input to coastal regions, and the overexploitation of keystone species	Potentially greater primary production and increased DOC flux
Sediment	Major source of POC and DOC	Resuspension by currents (mainly wind driven), storms, and tides	Increased resuspension events due to more frequent extreme weather events	Greater flux of POC and DOC from sediment to the water column
Sediment	Major source of POC and DOC	Resuspension by dredging	Greater spatial and temporal extent of dredging	Greater flux of POC and DOC from sediment to the water column
Sediment	Major source of POC	Resuspension by	Decreased resuspension	Reduced flux of POC and DOC from sediment to the

	and DOC	currents (mainly wind driven), storms, and tides	events due to altered water currents	water column Increased OM (and OC) storage in benthic sediment
Coral reefs	Source of DOC and POC to reef community, but most is recycled	Release of DOC by coral polyps or flux of POC via sloughing of polyp mucus	Ocean acidification, rising water temperature, greater pelagic nutrient concentrations	Pulse disturbance: coral stress; reduction in DOC flux; no change in POC flux Press disturbance: coral bleaching and death; flux of DOC and POC from decomposition coral organisms; altered macro-algae dynamics (see above)
Land	Major source of POC and DOC to inner shelf of the GBR	Rivers, especially during high-rainfall events	Greater frequency of extreme weather events (i.e. cyclones) due to climate change	Greater flux of terrestrial DOC and POC to inner shelf of GBR
Phytoplankton	Primary source of labile POC, but also some DOC, in pelagic waters	Primary production	Sustained increase in riverine bioavailable-nutrient export from land	Greater phytoplankton-derived POC and DOC concentrations caused by greater primary production associated with increased availability of labile nutrients. Note: greater phytoplankton productivity may not be detected by chlorophyll measures if algal biomass doesn't increase alongside productivity
Phytoplankton	Primary source of labile POC, but also some DOC, in pelagic waters	Primary production	Increase in sea water temperatures	Greater phytoplankton-derived POC and DOC concentrations caused by increased cellular processes and production with greater water temperature
Phytoplankton	Primary source of labile POC in pelagic waters	Primary production	Greater pelagic nutrient concentrations at times of extreme weather events (i.e. cyclones)	Reduced phytoplankton-derived POC concentrations in nearshore environments affected by river plumes, caused by supressed rates of primary production Potentially greater phytoplankton-derived POC concentrations on edge of river plumes, caused by greater primary production associated with increased availability of labile nutrients
Mangrove forests and saltmarshes	Source of refractory but large concentrations of POC and DOC to near-	Tides and currents	Reduced mangrove forest extent due to human disturbance and/or	Reduced nearshore concentrations of DOC and POC Potentially less POC stored in sediment over longer

	shore environments of the GBR		extreme weather events (i.e. cyclones)	timescales
Coral Sea	Minor source of refractory DOC and POC to outer shelf of the GBR	Tides and currents	Ocean acidification, rising water temperature	Elevated pelagic concentrations of DOC and POC associated with greater rates of ocean primary production, leading to increased flux of DOC and POC to GBR shelf
Coral Sea	Minor source of refractory DOC and POC to outer shelf of the GBR	Primary production	Increased supply of nutrients from the Coral Sea and enhanced phytoplankton production	Elevated pelagic concentrations of DOC and POC
Groundwater	Net source of DOC	Groundwater discharge	Land clearing increases groundwater levels Agricultural practices (i.e. cane production) can enhance DOC and nutrient concentration in groundwater	Greater groundwater discharge of water containing high DOC concentrations to coastal environments of the GBR lagoon Greater groundwater discharge of water containing high DIN and aqueous CO_2 concentrations to coastal environments of the GBR lagoon that may promote DOC production via enhanced phytoplankton productivity

7.0 HYPOTHESES FOR TESTING POTENTIAL SOURCES AND DRIVERS

Numerous drivers were identified to alter the flux of DOC and POC in coastal waters of the GBR shelf (see Table 4). Below we examine some of the main drivers that could be examined using existing water quality monitoring data or be examined after additional data collection.

7.1 Hypothesis with terrestrial sources driving DOC and POC concentrations

Based on the hypothesis that the increases in POC and DOC concentrations are a result of terrestrial inputs the following would provide evidence for this:

1. Marine DOC and POC concentrations will be highest at monitoring points closest to the coast, particularly near river estuaries and mangrove forests.
    a. Examining the spatial extent of the trend of increasing marine DOC and POC concentrations to determine terrestrial vs. marine drivers. For instance, if the trend for increasing DOC and POC concentrations is persistent across the whole reef, it is more likely that drivers impacting the whole reef are primarily responsible, such as: elevated primary production or greater benthic sediment resuspension from tides, waves, and currents. Alternatively, if the trend for increasing DOC and POC concentrations is localised to coastal regions, it is more likely that terrestrial processes are primarily responsible, such as: greater riverine input of DOC and/or POC, greater coastal sediment erosion/resuspension, or groundwater discharge. Models could be run that test the correlation between DOC and POC concentrations with distance from the coast. The majority of the Marine Monitoring Program data collection is, however, limited to within 30 km of the coast. This coastal bias may restrict investigations of land versus marine influences in the inner shelf of the GBR.
2. Marine DOC and POC concentrations will be highest in the days and weeks following high-rainfall events on land.
    a. Using only data from monitoring points nearby river estuaries; examine the correlation between marine DOC and POC concentrations with river discharge.
3. Marine DOC and POC concentrations will be highest near known locations of direct groundwater discharge to coastal waters along the GBR coast.
    a. Obtain latest data on the location of groundwater discharge to the GBR shelf. At monitoring points near locations of known groundwater discharge, is there less seasonal variability in marine DOC and POC concentrations and are these concentrations elevated compared to non-groundwater influenced locations? Less temporal variability in DOC and POC concentrations may be expected at locations near groundwater discharge because, while surface river discharge can be highly seasonal, groundwater discharge (i.e. baseflow) is often more constant and can be a constant subsidy of nutrients and carbon to aquatic ecosystems.

7.2 Hypothesis with marine sources driving DOC and POC concentrations

This alternative hypothesis states that increases in DOC and POC concentrations are driven from marine sources. The following would provide evidence for this:

1. Marine DOC and POC concentrations will be highest immediately following weather events that lead to greater wave action and increased benthic sediment resuspension.
    a. Examine whether DOC and POC concentrations are greater during periods of known sediment resuspension events. Suspended sediment data can be used to provide further support for any suspected periods of greater sediment resuspension.
2. Periods of greater marine DOC and POC concentrations will be associated with higher phytoplankton production.
    a. Monitoring data could be examined to assess associations between concentrations of DOC and POC with measured variables that are related to phytoplankton activity (i.e. Chl-*a*, coloured dissolved organic matter, water temperature).
    b. Suspended sediment data may help rule-out, or account for, the potential confounding influence of sediment resuspension events for elevating pelagic DOC and POC concentrations.
3. Marine DOC concentrations will be greater in close proximity to more productive seagrass and macro-algae communities.
    a. Seagrass and macro-algae communities are commonly net DOC sources. Data collected from monitoring points in close proximity to seagrass and/or macro-algae communities, which are also regularly monitored, could be investigated for associations between indices of community health (i.e. greater spatial extent, productivity, etc) with variation in local DOC concentrations through time.
4. Marine DOC and POC concentrations will be greater in close proximity to seagrass and macro-algae communities that are in a state of decline.
    a. A decline in the health and extent of seagrass and macro-algae communities may increase the flux of DOC and POC from the plants themselves, and from the sediment where they are located. It may be problematic to associate variation in seagrass and/or macro-algae community health with variation DOC and POC concentration because both increases and decreases in productivity and extent can increase the flux of DOC and POC to the surrounding water column. However, any flux of DOC from seagrass and macro-algae communities in poor health (i.e. due to senescence) would likely be short-lived – examining both short- and long-term temporal trends may be vital in differentiating impacts from productive (i.e. point 3 above) versus unproductive seagrass and macro-algae communities.
5. Marine DOC and POC concentrations will be greater during periods of higher sea surface temperatures.
    a. Greater sea surface temperatures can increase phytoplankton productivity, if sufficient nutrients are also available. Greater phytoplankton production may increase the DOC and POC concentrations in the water column.

b. Greater sea surface temperature can also increase seagrass senescence and thus flux of DOC and POC to the water column.

7.3 Confounding factors

Determining the precise contribution that particular drivers or vectors have for explaining the trend of increasing OC concentrations in coastal waters of the GBR is problematic due to a number of confounding factors, including:

1. laboratory analysis techniques that do not clearly differentiate marine versus terrestrial OC compounds (see 'Conjecture in the determination of terrestrial versus marine OC');
2. uncertainty around whether something is of terrestrial or marine origin. For example, should OC contained within benthic sediment resuspension be considered of marine origin if it contains OC from both recent and older terrestrial sources? Additionally, should new marine autotrophic and heterotrophic production be considered of terrestrial or marine origin if the inorganic and/or organic nutrients synthesised are from terrestrial sources?
3. the largely unknown spatial and temporal influence of groundwater discharge along the GBR shelf; and,
4. the difficulty in separating sustained, long-term (i.e. press disturbances such as rising sea temperatures) pressures from more periodic, but large ecosystem-wide pressures (i.e. tropical cyclones).

8.0 WATER QUALITY DATA ANALYSIS

8.1 Objective

The objective of this water quality data analysis is to investigate the water quality data from inshore GBR monitoring to determine the factors correlating with DOC and POC increases over time. We achieve this by exploring the associations of various environmental parameters, collected as part of the Great Barrier Reef Marine Park Authority Marine Monitoring Program, with concentrations of DOC and POC.

8.2 Methods

We followed a structured and statistically rigorous procedure to determine which environmental factors correlate with DOC and POC increases over time (Figure 20). First, we used Spearman-rank correlation plots to visualise correlations between DOC/POC and other variables. We eliminated non-significant correlations using the Spearman test statistic (null hypothesis - correlation happened by chance). We report only significant Spearman-rank correlations. Second, we performed an all-subsets stepwise regression (using AIC modelling procedure) to guide the final selection of the explanatory environmental parameters in the final model predicting variation in DOC or POC. All-subsets stepwise regression selects only those explanatory variables that form the most parsimonious model. In this procedure, we created an initial model that included only those explanatory variables that had a significant Spearman rank correlation with DOC or POC. Finally, we determined the relative importance of each explanatory variable (as percentage of the coefficient of determination in the final model) in the final models predicting variation in DOC or POC, using the R package *relaimpo*. In this procedure, four different relative importance metrics (LMG, PMVD, FIRST, BETASQ) are reported; a description of each of these metrics is available in Grömping (2006). Bootstrapping (bootstrap runs = 10,000) was used to produce confidence intervals.
All analyses were stratified according to sample collection depth in order to investigate spatial patterns in the relationship between DOC and POC with environmental factors. The data was analysed in the following groups: all available data (sample size = 1244), samples collected between 0 and 1 m water depth (i.e. ‘surface water’) (sample size = 970), and samples collected below a water depth of 1 m (i.e. ‘deeper water’) (sample size = 1274). Spearman-rank correlations were also performed on a subset of the Marine Monitoring Program data to investigate differences in the correlations between DOC/POC and other variables for data collected in near-shore (sample size = 141) versus open-water (sample size = 241) environments. To avoid collinearity and redundancy between the explanatory and response variables in our models, we excluded particulate phosphorus (PP) from analyses as it was highly correlated with particulate nitrogen (PN) (Spearman's rank correlation coefficient = 0.77).

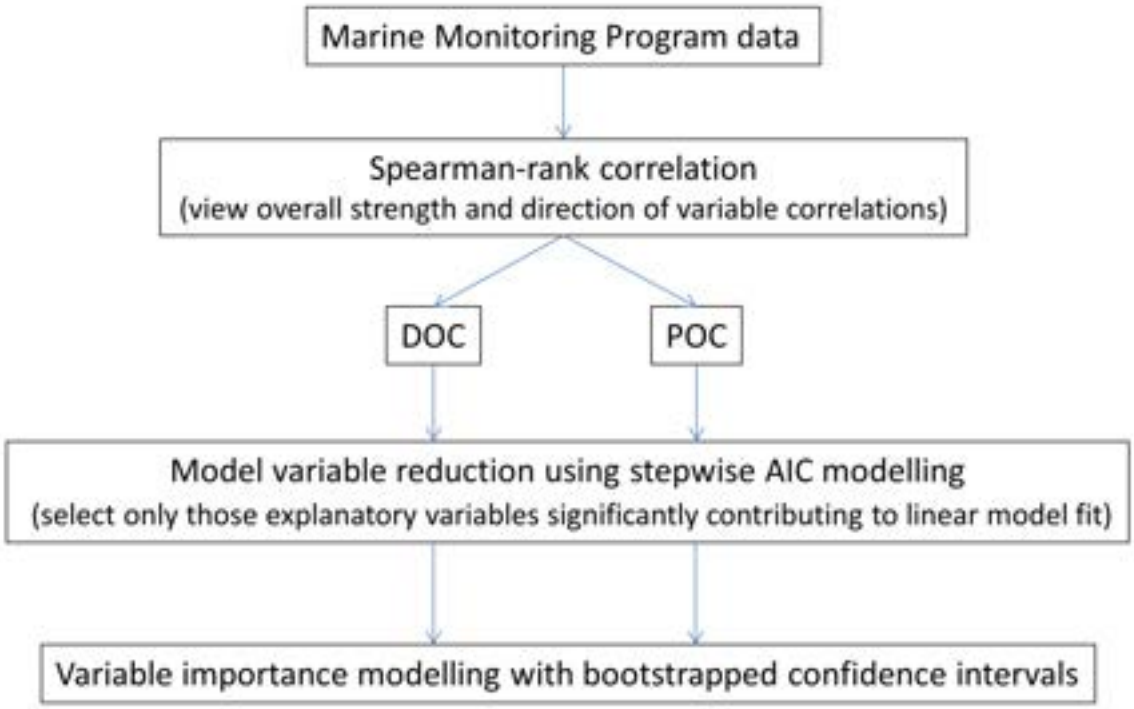

Figure 20. The statistical procedure taken to analyse the Marine Monitoring Program data to determine which environmental parameters are associated with increases in DOC and POC concentrations over time

8.3 Results

8.3.1 Overall model characteristics

Particulate organic carbon (POC) was more strongly correlated with Marine Monitoring Program data environmental parameters compared to DOC, as evidenced by stronger Spearman rank correlation coefficients for POC than DOC (Figure 21) and a greater predictive power (i.e. higher R^2) of the final linear models for POC than DOC (Figure 22 and Figure 23).

8.3.2 Dissolved organic carbon

Variation in DOC concentrations was most strongly correlated with variations in PN and PP (positive correlation), salinity (negative association), and Si (positive correlation) (Figure 21). The strength of these correlations was greater in surface-water samples compared to deeper-water samples (Figure 21b,c). DOC and POC were positively correlated with each other in both surface water and deeper water (Figure 21b,c). Particulate nutrients (PN, and PP due to its high correlation with PN) were the most important factors predicting variation in DOC concentrations in the relative importance modelling for all the data, and the data subset according to sample depth (Figure 22a,b,c). Salinity was more important in the surface data compared to the sub-surface data, as indicated by its greater relative contribution in surface-water models (Figure 22b) compared to deeper water models (Figure 22c). TDP and POC were also important in all models predicting variation in DOC concentrations.

8.3.3 Particulate organic carbon

Variation in POC concentrations was most strongly correlated with variation in PN and PP concentrations (positive correlation), Secchi and acoustic depths (negative correlation), TSS and chlorophyll *a* concentrations (both positive correlations) (Figure 21). The strength and direction of these correlations were generally very similar in both surface and deeper water samples (Figure 21b,c). Similarly to the DOC results, particulate nutrients (PN and PP) were the most important factors predicting variation in POC concentrations in the relative importance modelling (Figure 23a,b,c). Secchi depth, chlorophyll *a*, TSS concentrations, silica, and DOC concentrations were also included as important factors predicting variation in POC concentrations, but their relative contribution was generally less than 20% to the overall model fit (Figure 23a,b,c).

8.3.4 Nearshore and open water patterns

There is a strong positive correlation between DOC and POC in nearshore samples (P=1.00) but this correlation weakened in open-water samples (P=0.64) (Figure 21). Almost all correlations of DOC and POC with the environmental parameters become weaker in open-water samples compared to nearshore samples (Figure 21). However, the strength of the correlation between DOC and POC with salinity and chlorophyll *a* does not diminish in nearshore versus open-water samples (Figure 24). The positive correlation of DOC and POC with TSS became stronger in open-water samples compared to nearshore samples (Figure 24).

8.3.5 Correlation among environmental parameters

Particulate nutrients (PN and PP) were negatively correlated with salinity, indicating that PN and PP concentrations are higher in fresher water. PN and PP are also negatively correlated with Secchi and acoustic depth, indicating that locations with more turbid and shallower water were associated with higher PN and PP concentrations. Chlorophyll *a* was positively correlated with PN and PP in both nearshore and open-water samples (Figure 24). Further, there is only a strong positive correlation between TSS and chlorophyll *a* in open-water samples.

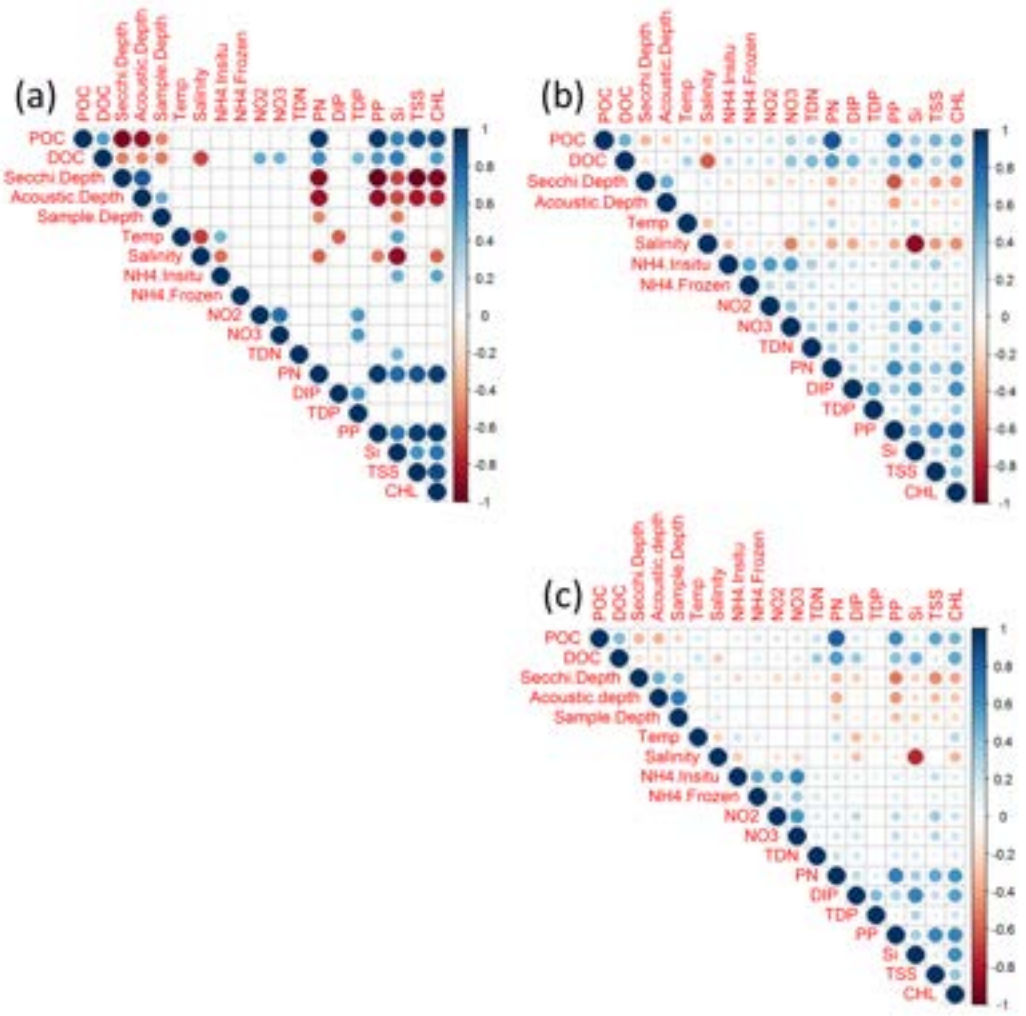

Figure 21. The Spearman rank correlation coefficients for correlations among GBR marine monitoring data for (a) all data, (b) surface (0-1 m water depth) and (c) deeper (1+ m water depth). Only significant correlations (at α=0.05) are presented. The strength of each Spearman rank correlation is colour coded, with dark blue indicating a strong positive correlation, white indicating no correlation, and dark red indicating a strong negative correlation. POC = particulate organic carbon; DOC = dissolved organic carbon; Secchi = Secchi depth; Temp = temperature; NH4.Insitu = ammonium measured in-situ; NH4.Frozen = ammonium measured from a frozen water sample; NO2 = nitrite; NO3 = nitrate; TDN = total dissolved nitrogen; PN = particulate nitrogen; DIP = dissolved inorganic phosphorus; TDP = total dissolved phosphorus; PP = particulate phosphorus; Si = silicon; TSS = total suspended solids; CHL = chlorophyll *a*. All nutrient data, TSS and chlorophyll a data is expressed as concentrations.

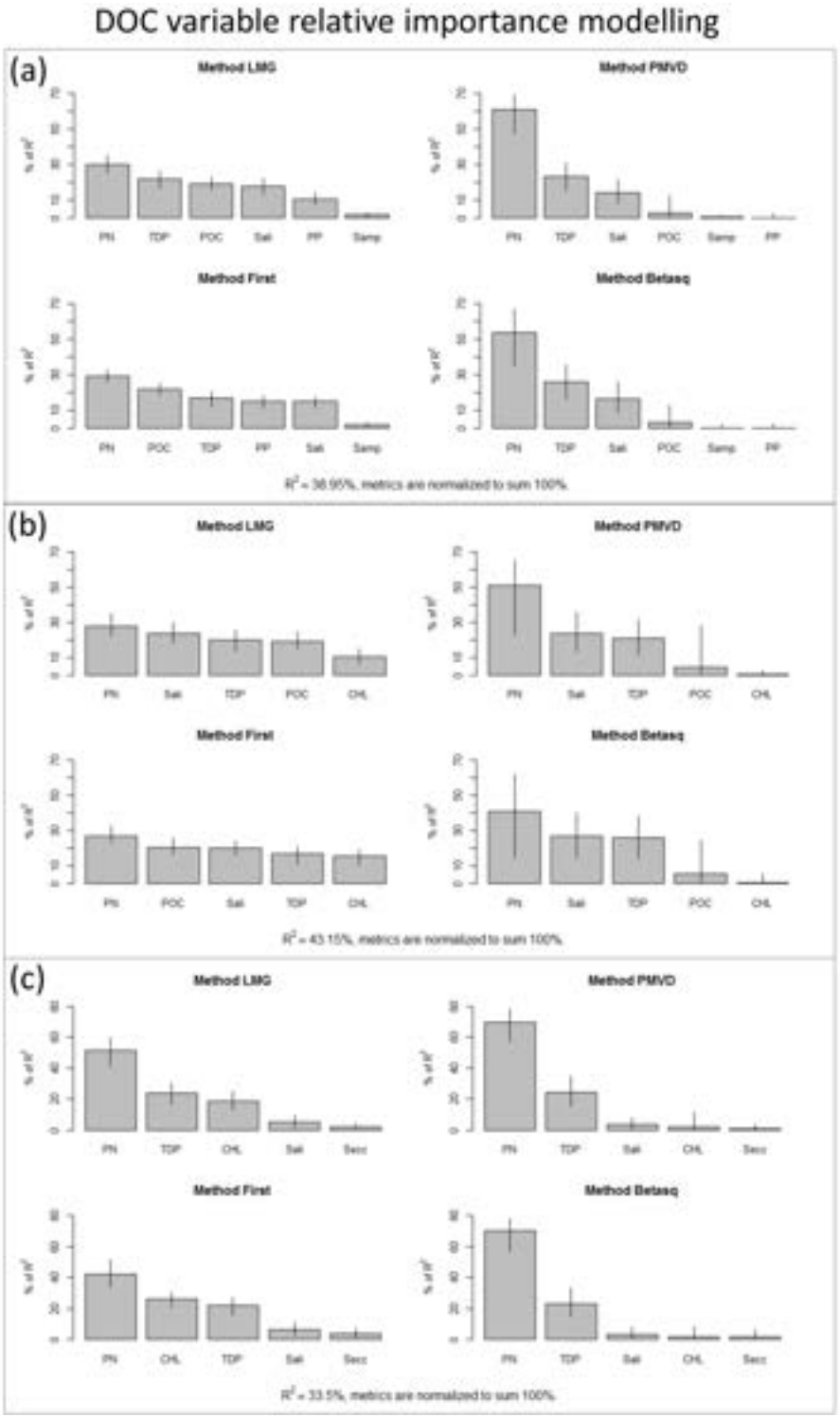

Figure 22. The outcome of the modelling procedure determining the relative importance of explanatory variables for explaining variation in dissolved organic carbon (DOC) concentrations for (a) all data, (b) surface data only (0-1 m water depth), and (c) deeper data only (>1 m water depth). The y-axis displays the mean percentage (and 95% confidence intervals) of the final model R^2 explained by each variable. The model R^2 is given below each tile and this model includes all variables listed on the x-axis. PN = particulate nitrogen; TDP = total dissolved phosphorus; POC = particulate organic carbon; Sali = salinity; PP = particulate phosphorus; Samp = sample depth; Secc = Secchi depth.

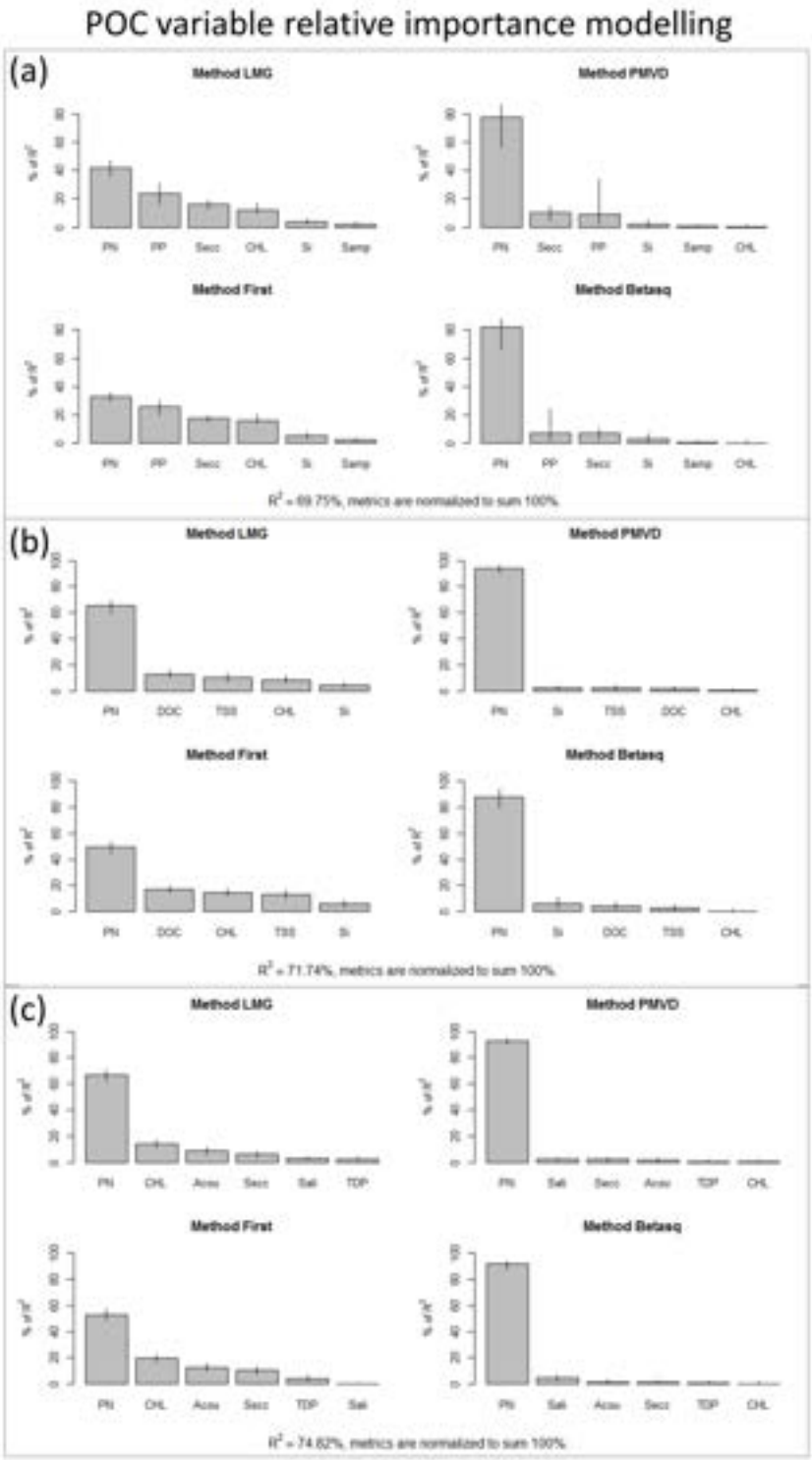

Figure 23. The outcome of the modelling procedure determining the relative importance of explanatory variables for explaining variation in particulate organic carbon (POC) concentrations for (a) all data, (b) surface data only (0-1 m water depth), and (c) deeper data only (>1 m water depth). The y-axis displays the mean percentage (and 95% confidence intervals) of the final model R^2 explained by each variable. The model R^2 is given below each tile and this model includes all variables listed on the x-axis. PN = particulate nitrogen; TDP = total dissolved phosphorus; DOC = dissolved organic carbon; Sali = salinity; PP = particulate phosphorus; Samp = sample depth; Secc = Secchi depth; TSS = total suspended solids; Acou = acoustic depth; Si = silica.

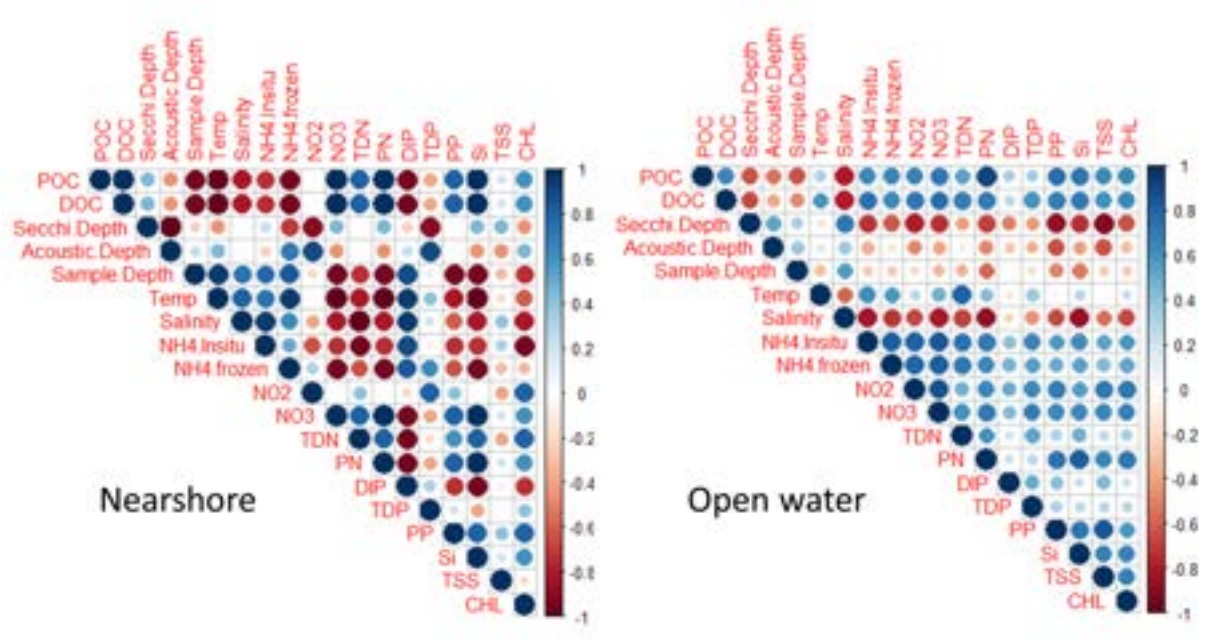

Figure 24. The Spearman rank correlation coefficients for correlations among GBR marine monitoring data for nearshore and open-water water samples. Only significant correlations (at α=0.05) are presented. The strength of each Spearman rank correlation is colour coded, with dark blue indicating a strong positive correlation, white indicating no correlation, and dark red indicating a strong negative correlation. POC = particulate organic carbon; DOC = dissolved organic carbon; Secchi = Secchi depth; Temp = temperature; NH4.Insitu = ammonium measured in-situ; NH4.Frozen = ammonium measured from a frozen water sample; NO2 = nitrite; NO3 = nitrate; TDN = total dissolved nitrogen; PN = particulate nitrogen; DIP = dissolved inorganic phosphorus; TDP = total dissolved phosphorus; PP = particulate phosphorus; Si = silicon; TSS = total suspended solids; CHL = chlorophyll *a*.

8.4 Discussion

8.4.1 Overview

The strongest overall predictors of variation in the concentrations of DOC and POC were those variables (mainly PN and PP, but also salinity, TSS, and silica) that are directly influenced by river discharge. This strong terrestrial influence is perhaps not surprising in coastal waters of the GBR, given that rivers are the primary recipients of terrestrial resources and they strongly influence the biogeochemistry of coastal marine environments (Bianchi, 2011; Kandasamy and Nagender Nath, 2016). Despite this strong terrestrial influence, there was evidence that sediment resuspension and phytoplankton production may be more important for explaining variation in POC concentrations, especially in locations further away from the coast. Therefore, while similar factors appeared to explain variation in DOC and POC concentrations in inshore samples, the weakening of the correlation between DOC and POC concentrations in offshore samples points to an uncoupling in factors driving each of these variables along a gradient from the coast to the ocean. Overall, the modelling work conducted in this study indicates that changes in DOC and POC concentrations in the GBR are probably largely associated with increased discharge of DOC- and POC-rich river water, but that POC concentrations are also influenced by sediment resuspension and phytoplankton biomass.

8.4.2 Factors associated with changes in DOC and POC concentrations

River discharge likely had a large influence on variation in DOC concentrations. This is because a higher DOC concentration was associated with fresher water (i.e. lower salinity values). Further, the association between DOC and salinity was higher in surface-water samples compared to deeper samples, indicative of the lower density freshwater lenses that develop during periods of discharge (Horner-Devine *et al.*, 2015). Although PN, and not salinity, was identified as the most important factor predicting variation in DOC concentrations in the relative importance modelling, salinity was negatively correlated with PN and concentrations of particulate nutrients (PN and PP) are known to be largely associated with freshwater discharge (Cotrim da Cunha *et al.*, 2007; Masotti *et al.*, 2018). To confirm the role of river discharge in influencing variation in DOC concentrations, and specifically river plumes associated with high-flow periods, additional data on river discharge over time, from the major rivers along the Queensland coast, will need to be gathered and incorporated into future data analysis.

While freshwater discharge may also play a role in mediating changes in POC concentrations, variation in POC concentration was strongly linked with variables associated with sediment resuspension and phytoplankton biomass. For instance, POC concentrations were higher when there was more TSS in the water column, and TSS was higher in shallower water (i.e. greater potential for sediment resuspension influence on surface water). TSS values were not strongly associated with salinity, but were higher in shallower and more turbid water, indicating that variation in TSS values were likely more strongly associated with sediment resuspension compared to river discharge.

POC concentrations were also higher when chlorophyll *a* concentrations were higher, suggesting that phytoplankton biomass may play a large role in mediating POC concentrations. Chlorophyll *a* was also positively correlated with particulate nutrients, indicating that the strong associations between POC, PN and PP may also be a consequence of enhanced phytoplankton production. In fact, the influence that phytoplankton biomass has on POC concentrations may be greater in offshore waters, because the correlation between POC and chlorophyll *a* was the only association to remain strong in offshore water samples compared to near-shore samples. Further, chlorophyll *a* was only strongly correlated (positively) with TSS in open-water samples, suggesting that phytoplankton biomass may contribute more to the variation in TSS concentrations in water further from the coast. This pattern, and the fact that the correlation between POC and TSS becomes stronger in more open water, indicates algal biomass was a more important contributor to the POC concentrations in open-water samples compared to nearshore samples.

8.4.3 Appropriateness of the modelling procedure

We stress that the findings from this data analysis procedure are preliminary. More extensive data collection, analysis and modelling are required to confirm any trends identified in this report. In particular, the following data may help provide additional empirical support for the trends identified in this report:

- data on river discharge from the major rivers along the Queensland coast may provide additional empirical support for the likely large influence that river discharge has on coastal DOC and POC dynamics.
- data on the occurrence of large coastal storm events may provide additional empirical support for the likely influence that sediment resuspension has on coastal POC dynamics.

9.0 RECOMMENDATIONS AND CONCLUSIONS

In this review, we summarised the potential sources, transformations, and fate of DOC and POC in coastal marine ecosystems. We applied this understanding to identify the key processes relating to changes in DOC and POC dynamics in near-shore ecosystems of the GBR. Three scenarios were identified that describe the typical biogeochemical and ecological states of near-shore environments of the GBR, in relation to changes in the source, transformation and fate of DOC and POC:

> **Scenario 1.** "Normal" state where the availability of dissolved organic carbon and particulate organic carbon in the majority of the GBR is controlled by the resuspension and delivery of organic carbon by tides and currents (mainly wind-driven) from benthic sediment, rivers, mangrove, and saltmarshes, as well as from phytoplankton production;
> **Scenario 2.** Extreme-weather event-based increase in terrestrial and marine OC due to elevated freshwater discharge from land and the resuspension of marine sediment during storm events; and,
> **Scenario 3.** Post extreme-weather event scenario whereby the organic carbon that was input and/or resuspended during Scenario 2 promotes the activity of bacterioplankton and phytoplankton.

It is possible that other factors exist that describe changes in the source, transformation and fate of DOC and POC concentrations in the water column. For example, elevated sea surface temperatures may alter concentrations of DOC and POC in the water column over both short and long timescales due to changes in a variety of physical and biological processes. Further, it is likely that these scenario-driven changes are not spatially uniform across the GBR, with patchiness in DOC and POC concentrations driven by factors such as distance from estuaries, port facilities and large population centres and also regions of large groundwater discharge to the GBR shelf.

We recommend that the existing monitoring data be used, in conjunction with catchment-scale environmental and river-discharge data, to empirically investigate the spatial and temporal variation in the main sources, vectors, and drivers of changes in the water column DOC and POC concentration in coastal regions of the GBR. This investigation should focus on the hypotheses stated above (see section 0) that aim to unravel the main terrestrial and/or marine sources and drivers of changes to DOC and POC concentrations in the water column of the GBR.

Doing so may uncover additional scenarios that describe changes in the source, transformation and fate of DOC and POC. Further, this targeted investigation may help pinpoint the most likely causes for elevated organic carbon concentrations. A more certain understanding of what is mediating altered organic carbon dynamics in the Great Barrier Reef will help prioritise future research and management actions that aim to minimise (1) future increases in organic carbon concentrations and (2) adverse ecological effects.

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