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Published

2018

Journal Title

Marine and Freshwater Research

Version

Accepted Manuscript (AM)

DOI

[10.1071/MF17009](https://doi.org/10.1071/MF17009)

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# Assessment of water quality from the Normanby River catchment to coastal flood plumes on the northern Great Barrier Reef, Australia

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**Abstract.** Understanding the flux and fate of nutrients and sediments from rivers is of global importance because of the effects of these materials on coastal ecosystems. The present study followed three flood events from upper tributaries of the Normanby River to Princess Charlotte Bay in the northern Great Barrier Reef (GBR) lagoon, Australia. During each event, nutrients and suspended sediment concentrations were measured along a freshwater to marine transect. The upper catchment provided the majority of suspended sediments and nutrients supplied to the river system, although concentrations of most materials decreased by 52–85% between the upper catchment and estuary. As an exception, ammonium concentrations doubled within the estuary, indicating that undisturbed coastal ecosystems can provide a significant source of dissolved inorganic nitrogen to tropical river flood plumes. The dissolved nutrients in floodwaters stimulated phytoplankton blooms that inundated seagrass meadows and coral reefs. Northern GBR marine ecosystems are increasingly threatened by climate change and catchment development. The results of this study show that increased anthropogenic loads of nutrients and sediments from the upper Normanby catchment have the potential to affect the condition of marine ecosystems at Princess Charlotte Bay.

Received 15 January 2017, accepted 14 September 2017, published online 7 February 2018

## Introduction

Riverine floodwaters supply vital nutrients to coastal ecosystems. However, anthropogenic activities have significantly altered the loads of nutrients and sediments discharged from the world's rivers into adjacent coastal systems (Green *et al.* 2004; Syvitski *et al.* 2005; Walling 2006). Increased sediment and nutrient loads, and associated changes in nutrient ratios, have modified the composition, function and values of coastal ecosystems, including seagrass meadows and coral reefs (Orth *et al.* 2006; Hughes 2009; Schaffelke *et al.* 2013; Costanza *et al.* 2014). Climate change may further alter the flux of sediments and nutrients into coastal waters, as well as the resilience of marine ecosystems to these changes. Understanding the flux and fate of nutrients and sediments from rivers is of global significance because of the effects of these materials on ecosystem processes, and the important environmental, economic and cultural services provided by these ecosystems (Barbier *et al.* 2011; de Groot *et al.* 2012).

Catchments adjacent to the Great Barrier Reef (GBR) have experienced significant changes since European settlement. Increased loads of nutrients and sediment discharged to the GBR lagoon are considered to have contributed to the 50%

decline in total coral cover across the central and southern GBR (De'ath *et al.* 2012; Brodie *et al.* 2013). In contrast, coral reefs in the far northern (Cape York) region of the GBR have maintained moderate to high (20–50%) live coral cover (De'ath *et al.* 2012; Miller and Sweatman 2013), and rivers in this region may provide the best example of pre-anthropogenic sediment and nutrient loads discharged to the GBR (Furnas 2003). However, there have been few empirical studies documenting the loads and fate of pollutants discharged from Cape York rivers.

Early studies of Cape York flood events focused on the small (2065 km<sup>2</sup>) Annan–Endeavour Basin in south-east Cape York Peninsula (CYP). These studies documented high concentrations of suspended sediments in the upper catchment, estuary and at a coral reef 15 km offshore (Hart *et al.* 1988; Davies and Eyre 2005; Davies and Hughes 1983). More recent Annan River flood monitoring also measured high SS concentrations in the estuary (>1400 mg L<sup>-1</sup>; Shellberg *et al.* 2015) and adjacent flood plume (50 mg L<sup>-1</sup>; C. Howley, unpubl. data, 2016). In contrast with the assumed low level of disturbance of Cape York catchments and associated low level of risk to the GBR (Furnas 2003; Waterhouse *et al.* 2012; Reef Water Quality Protection Plan Secretariat 2013), these studies highlight both the high

erodibility of soils and the land use effects that have elevated SS and nutrient concentrations in at least one CYP river and adjacent coastal waters (Eyre and Balls 1999; Davies and Eyre 2005; Shellberg *et al.* 2015). Aside from these south-eastern CYP studies, there remains little information on within-river or flood plume processing or the fate of nutrients and sediment discharged from Cape York rivers.

Recent climate-driven coral bleaching (Great Barrier Reef Marine Park Authority 2016) and outbreaks of crown-of-thorns starfish (<http://data.aims.gov.au/waCOTSPage/cotspage.jsp>, accessed 1 May 2017) have drawn global attention to the vulnerability of reefs in the northern GBR region and the need to protect their resilience by maintaining pristine marine water quality. Documenting the flux of sediment and nutrients from Cape York rivers, and the role of estuaries and plumes in trapping, releasing and modifying these materials, is crucial to our understanding of the effects of these fluxes on GBR ecosystems and the potential effects of changes in land use and climate.

The objectives of the present study were to assess the sources and fate of sediments and nutrients transported by the Normanby River, the largest river system in eastern CYP, to the GBR lagoon during flood events. This system provides the unique opportunity to assess changes in nutrient and sediment concentrations from a large, undeveloped GBR catchment (relative to the more developed southern catchments) through an unmodified coastal zone. We tested the hypothesis that the upper catchment is a significant source of sediment and associated nutrients to flood plumes by measuring nutrient and suspended sediment concentrations across transects from upland freshwater tributaries to marine waters during three flood events over consecutive years. We also examined changes in chlorophyll (*Chl*)-*a* concentrations and phytoplankton communities in receiving waters. This was the first study of catchment and plume processes over large magnitude flood events in the Cape York region.

## Materials and methods

### Study area

The Normanby Basin in south-eastern CYP (15°08'52.8"S, 144°21'32.4"E) is the fourth largest catchment (24 550 km<sup>2</sup>) discharging to the GBR lagoon. The Basin includes the Normanby, Laura, Kennedy, Hann, Mossman, Morehead and Annie rivers, plus three distributaries, namely the North Kennedy, Normanby and Bizant (Fig. 1). Annual discharge from the Normanby distributary between 2005 and 2015 ranged from 1148 to 5965 GL (median 2398 GL). A similar volume may be discharged from the ungauged North Kennedy distributary each year. The Basin is located in the dry tropics, where climate is characterised by distinct wet (summer) and dry (winter) seasons, with 95% of its annual rainfall occurring between November and April. Mean annual rainfall varies from 920 to 1240 mm and mean monthly temperatures range from 16–28°C in July to 21–35°C in November.

The Basin supports a small human population (<500), with native vegetation covering 95% of the land (Queensland Department of Science, Information Technology, Innovation and the Arts 2012). Conservation areas covered 46% of the Basin in



Fig. 1. Normanby Basin water quality sampling sites. DNRM, Department of Natural Resources and Mines, Queensland Government, Australia.

2013, whereas cattle grazing land tenure covered 53% (State of Queensland 2015); however, feral cattle also populate formerly grazed conservation lands. In upper catchment areas where grazing occurs on erosion-prone soil types, rates of alluvial gully erosion have been accelerated by up to 10-fold above pregrazing rates, contributing to increased sediment loads (Brooks *et al.* 2013). The area under cultivation is expanding, but currently covers less than 1% of the Normanby Basin, in the upper catchment near Lakeland (Fig. 1). As of 2010, this small area of horticulture had already significantly affected water quality in the Laura River, where nutrient concentrations were up to 10-fold higher than background concentrations (Howley 2010).

The Normanby River discharges into the GBR lagoon at Princess Charlotte Bay (PCB; Fig. 1). PCB is recognised as a valuable marine habitat that includes over 11 500 ha of coastal and reef-top seagrass meadows and 25 000 ha of coral reefs (Carter *et al.* 2012). Riverine sediment and nutrient loads are primarily delivered to the marine environment following cyclonic conditions and major rain events (Devlin and Brodie 2005). Normanby River flood plumes can extend over 70 km to the outer-shelf reefs of the GBR, transporting sediment and nutrients into the marine environment, where chemical and biological transformation processes occur over rapid time scales.

**Table 1. Number of river and plume samples collected for determination of suspended sediment (SS) and nutrient concentrations for each flood event**

Upper catchment nutrients are total nitrogen, total phosphorus, nitrate + nitrites, NH<sub>4</sub>, filterable reactive phosphorus, dissolved organic nitrogen, dissolved organic phosphorus, particulate phosphorus and particulate nitrogen. Chl-*a*, chlorophyll-*a*; PCB, Princess Charlotte Bay

Flood event (year)	Upper catchment		Mid-catchment		Estuary		PCB plume samples				
	SS	Nutrients	SS	Nutrients	SS	Nutrients	SS	Nutrients	Chl- <i>a</i>	Phytoplankton	Si
2012	11	3	6	5	5	5	13	13	13	5	0
2013	38	38	12	3	5	5	31	31	29	16	31
2014	18	18	7	3	3	3	10	10	10	8	0

### Event sampling and plume mapping

Major flood events in the Normanby Basin (event discharge ranging from 544 to 1084 GL) in March 2012, January 2013 and April 2014 created visible plumes of turbid water extending into PCB. During each of these events, samples were collected along transects from upland tributaries to the coastal flood plumes to assess the changes in water quality parameters. The extent and direction of the flood plume was estimated using moderate-resolution imaging spectroradiometer (MODIS) imagery from the Aqua and Terra satellites (the edge of each of the visible turbid plumes was traced in ArcGIS), aerial mapping of the plume from a helicopter and by measuring surface water salinity.

Discharge to PCB during each event was calculated from the Queensland Department of Natural Resources and Mines Gauging Station 105107A (Kalpowar Crossing), which is situated ~70 km upstream from the mouth of the Normanby River (sample location NR-02; Fig. 1). Discharge calculations from the 105107A gauge do not represent total Normanby Basin discharge to PCB (Wallace *et al.* 2012; Brooks *et al.* 2013), but provide a comparison of relative flood magnitude in the Normanby River. Total annual discharge (water year 1 October–30 September), total event discharge (calculated from visual estimates of the initial rapid rise of the hydrograph until river height returned to base flow), peak discharge and antecedent discharge (total discharge for the water year before the start of the flood event) were calculated from gauge measurements taken at 15-min intervals.

### River sampling

Suspended sediment and nutrient (total, particulate, dissolved inorganic and dissolved organic nitrogen and phosphorus) samples were collected from 10 upper and mid-catchment sites during the three flood events (Fig. 1). Upper catchment sampling sites were located at the Laura (LR-02 to LR-07), East Normanby (NR-05), and West Normanby (NR-06) rivers and the Normanby River at Battlecamp Crossing (NR-04). Mid-catchment samples were collected from the Normanby River at 12 Mile Waterhole (NR-03) and Kalpowar Crossing (NR-02). Samples were collected manually from the river banks or bridges (mid-channel) during the rising and falling flood stages (where possible). Manual surface water samples were collected from the riverbanks using a 2.5-m extended pole with a pre-rinsed wide-mouth sampling cup (nutrients) or Rickly Hydrological Co. DH-48 isokinetic sampler (Columbus, OH, USA)

(suspended sediments) and the appropriate acid-washed polyethylene sample bottles. Automatic rising stage samplers (RSS) also collected suspended sediment samples at upper catchment sites LR-02, NR-05, NR-06 and NR-04 during the 2012 event (described in Brooks *et al.* 2013). The number of samples collected at each site and the distribution across each event varied due to access and other logistical constraints; two to five samples were collected from each site in 2012 (primarily rising and peak stages), compared with seven to nine samples collected from each site across the 2013 event (well-distributed rising and falling stage) and three to six samples collected from each site across the rising and falling stages of the 2014 event. The number of samples collected from each region and event are listed in Table 1.

Eleven paired suspended sediment samples were collected from bridges (mid-channel) and the adjacent riverbanks (with the extended sampling pole) to compare mid-channel and edge concentrations. The mean relative percentage difference (RPD) between the paired samples was 11%, indicating that samples collected from riverbanks are underestimating the average (width- and depth-integrated) SS concentrations.

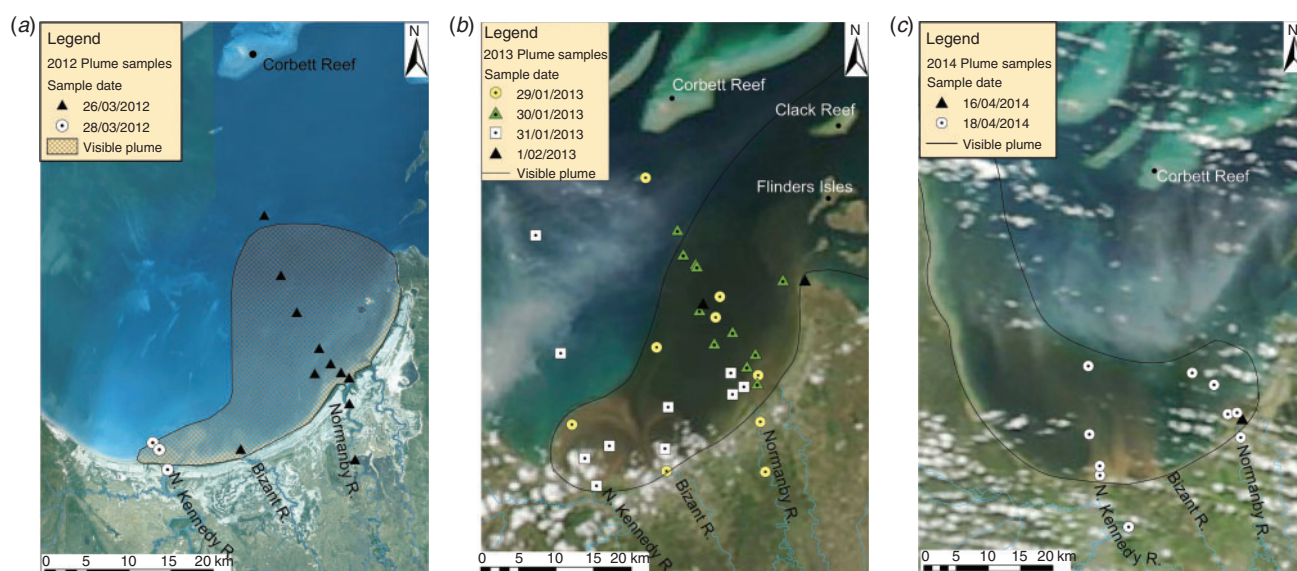
### Estuary and flood plume sampling

Estuarine and flood plume sampling during the March 2012, January 2013 and April 2014 flood events was timed to commence when peak floodwaters reached the Normanby River mouth, 2–3 days after the flood peak at upstream Gauge 105107A (Fig. 1). Floodwater travel time from Gauge 105107A to PCB was estimated based on measurements of the time between the peak of a flood hydrograph at the gauge and peak river height measured on a pressure transducer temporarily installed at the Normanby River mouth (J. Shellberg, unpubl. data, 2013), as well as daily observations of the movement of turbid floodwaters through the catchment and into PCB using satellite images. The duration of plume transect sampling over the course of each event ranged from 2 to 4 days (Table 2), with only the 2013 event capturing changes within the plume over multiple days. For each event, samples were collected from the Normanby estuary and along a transect from the Normanby River mouth to the outer edge of the visible plume (Normanby plume transect), with a maximum transect length of 35 km (Fig. 2). Samples were also collected from the mouths of the Kennedy and Bizant rivers and the plumes discharged from these rivers. Background samples were collected from PCB outside the visible plume.

**Table 2. Annual and event discharge metrics in 2012, 2013 and 2014, plus event duration, wind speed, wind direction and plume area**

The water year is calculated from 1 October to 30 September. Peak discharge was measured at Department of Natural Resources and Mines Gauge 105107A (NR-02). The estimated floodwater travel time from NR-02 to Princess Charlotte Bay is 2 days. Antecedent discharge is the total discharge for the water year before the start of the flood event. The area of visible plume was estimated from aerial surveys (2012) and moderate-resolution imaging spectroradiometer (MODIS) satellite images (2013 and 2014). SE, south-east; NW, north-west

Water year	Annual discharge (GL)	Event duration	Plume sampling dates	Peak discharge ( $\text{m}^3 \text{s}^{-1}$ ) and date	Total event discharge (GL)	Antecedent discharge (GL)	Average wind speed (knots ( $\text{km h}^{-1}$ ))	Average wind direction	Area of visible plume ( $\text{km}^2$ )
2011–12	1148	14 March–3 April 2012	26 and 28 March 2012	516.78 (23 March 2012)	555	380	13.6 (~25.2)	134° (SE)	350
2012–13	1822	22 January–9 February 2013	29 January–1 February 2013	1860.49 (27 January 2013)	860	0.3	13.0 (~24.0)	300° (NW)	>1400
2013–14	2663	11–29 April 2014	16 and 18 April 2014	2055.89 (16 April 2014)	1082	1390	27.2 (~50.4)	130° (SE)	>1100



**Fig. 2.** (a) Flood plume sample locations in 2012, with the visible plume drawn from an aerial survey on 26 March 2012 (no clear moderate-resolution imaging spectroradiometer (MODIS) satellite image available). (b) Plume sample locations in 2013 from a MODIS image from 30 January 2013. (c) Plume sample locations in 2014 with MODIS imagery from 17 April 2014.

Estuary and plume samples were collected from a helicopter, with additional samples collected by boat during the 2013 event. Plume samples were analysed for nutrients, Chl-*a* and suspended sediment. Phytoplankton counts and taxa were analysed from select plume sites chosen to represent the variations across the salinity gradient. Silicate (Si) samples were collected in 2013 only. Salinity, temperature and turbidity were also recorded. Salinity values presented are based on the Practical Salinity Scale of 1978 (<http://salinometry.com/pss-78/>, accessed 1 May 2017). The number of samples collected for each analyte and event is listed in Table 1.

To test for potential helicopter downdraft effects on surface sample concentrations, four paired suspended sediment samples were collected from the estuary mid-channel by helicopter and from the adjacent bank with the extended sampling pole. On average, helicopter sample concentrations were 9% higher than

bank samples, which is comparable to the mean RPD calculated for the mid-channel (bridge)–bank sample pairs from the upper catchment (11%). These results indicate that the helicopter downdraft did not significantly alter suspended sediment concentrations.

#### Sample processing and laboratory analysis

All river and plume samples were stored on ice immediately and frozen (nutrients, Chl-*a*) or refrigerated (suspended sediment, phytoplankton) within several hours of collection. Dissolved nutrient samples were filtered *in situ* through a single-use 0.45- $\mu\text{m}$  cellulose acetate filter. Chl-*a* samples (plume only) were filtered through Whatman glass fibre filters (GE Healthcare, Parramatta, NSW, Australia), preserved with 0.01 g of magnesium carbonate preservative and wrapped in aluminium foil before being frozen. Water samples for

phytoplankton cell counts and species identification were preserved in Lugol's iodine.

Nutrient samples were analysed for total and dissolved Kjeldahl nitrogen (TKN and DKN respectively), ammonium nitrogen ( $\text{NH}_4$ ), and nitrate + nitrites ( $\text{NO}_x$ ), total and dissolved phosphorus (TP and DP respectively) and filterable reactive phosphorus (FRP) according to Methods 4500-N<sub>org</sub> D, 4500-NH<sub>3</sub>, 4500-NO<sub>3</sub>, and 4500-P B and 4500-P G of the American Public Health Association and American Water Works Association–Water Environment Association (2005). Total nitrogen (TN), particulate nitrogen (PN), dissolved organic nitrogen (DON), particulate phosphorus (PP) and dissolved organic phosphorus (DOP) were calculated from the results of TKN, TDN, TP, DP,  $\text{NH}_4$ ,  $\text{NO}_x$  and FRP. Detection limits were as follows:  $\text{NO}_x$  and FRP,  $0.001 \text{ mg L}^{-1}$ ;  $\text{NH}_4$ ,  $0.002 \text{ mg L}^{-1}$ ; TP, PP and DOP,  $0.02 \text{ mg L}^{-1}$ ; and TN, PN and DON,  $0.03 \text{ mg L}^{-1}$ . Analytical uncertainty (the 95% confidence interval of the s.d.) was  $\pm 8\%$  for  $\text{NH}_4$ ,  $\text{NO}_x$  and FRP,  $\pm 12\%$  for TN and  $\pm 15\%$  for TP, PN, PP, DON and DOP.

River suspended sediment samples were analysed for suspended sediment concentration (SSC) using ASTM D3977–97 Method C (American Society for Testing and Materials 2002) or for total suspended sediment (TSS) using American Public Health Association and American Water Works Association–Water Environment Association (2005) Method 2540 D (detection limit  $1 \text{ mg L}^{-1}$ ; uncertainty  $\pm 12\%$ ). Twenty-seven duplicate samples were analysed for both SSC and TSS to compare the two methods that were used to analyse river samples. SSC results were, on average, 1.3-fold higher than TSS results and are considered to be more accurate (Gray *et al.* 2000). However, no adjustment has been made to the TSS data presented here to be consistent with other GBR plume monitoring programs using TSS methods. (Both TSS and SSC are hereafter referred to as 'TSS'.)

Chl-*a* and phaeophytin concentrations were determined using a spectrophotometer after grinding of samples in 90% acetone according to American Public Health Association and American Water Works Association–Water Environment Association (2005) Method 10200H. Water samples for phytoplankton cell counts and species identification were concentrated by gravity-assisted membrane filtration and examined under a Leica light microscope (Wetzlar, Germany) (phase contrast) to a maximum magnification of  $400\times$ . Phytoplankton was enumerated to the lowest possible taxon using the Lund Cell technique (Hötzel and Croome 1999) to a minimum of 100 cells per sample. For some taxa, species-level identification was not possible using routine light microscopy. In such instances, individuals were identified to genus level. The counting method underestimates picoplankton densities, so interpretation of data is limited to larger species.

#### Data analysis

Sampling locations were grouped as 'upper catchment' (LR-02 to LR-07 and NR-04 to NR-06), 'mid-catchment' (NR-02 and NR-03), 'estuary' (NR-00, NR-01, KR-01, BR-01) and flood plume. Statistical analyses of these groups were conducted using SPSS, ver. 22 (IBM Corp., Armonk, NY, USA). Most catchment and flood plume water quality parameters failed the

Kolmogorov–Smirnov and Shapiro–Wilk tests for normality; therefore, the datasets were analysed for spatial and temporal (event) statistical differences ( $P < 0.05$ ) using non-parametric Kruskal–Wallis *H*-tests followed by pairwise comparisons using Dunn's (1964) procedure with Bonferroni correction. Statistically significant variations identified by this method refer to differences between median values (where the variable distributions are similar) or mean ranks.

Concentrations in the upper catchment were not assessed for temporal variations because of differences in sampling methods (RSS *v.* grab sample) and the number of samples collected per event. Flood plume nutrient, SS and Chl-*a* concentrations and phytoplankton counts were assessed for correlations with salinity and discharge metrics using Spearman's rank order correlation test with significance assigned at  $P < 0.01$ , Spearman's rho ( $r_s$ )  $> 0.5$ . Correlations between parameters were assessed both for individual plumes and for all plumes combined.

The behaviour (conservative *v.* non-conservative) and fate of materials in the flood plumes were investigated by plotting SS, nutrient, Chl-*a* and phytoplankton concentrations against salinity, as per Devlin and Brodie (2005) and Devlin and Schaffelke (2009). Water quality parameters were plotted against salinity and analysed for both annual events and individual sampling days (2013) to assess variations through different stages of the plume. Similar trends were evident at both the daily and event scales; therefore, only the event-scale mixing plot results are presented here.

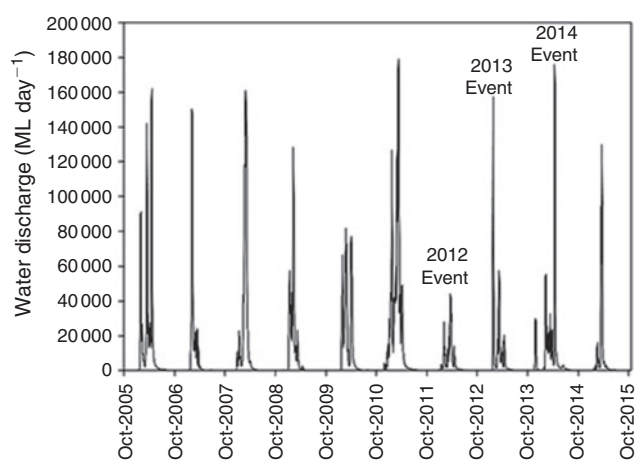
## Results

### Flood event discharge and plume characteristics

The March 2012 flood event had a total event discharge of 555 GL over 21 days, preceded by several smaller events (Table 2; Fig. 3). On 26 March 2012 (3 days after peak discharge upstream at Gauge 105107A), a freshwater flood plume flowed north from the mouths of the Normanby, Bizant and North Kennedy rivers, extending  $\sim 22 \text{ km}$  north into PCB (Fig. 2a). The area of the plume of turbid floodwater was estimated by aerial survey and salinity tests as  $350 \text{ km}^2$ . Surface water temperatures within the plume ranged from  $31.6$  to  $32.8^\circ\text{C}$  and salinity ranged from  $1.0$  to  $32.1$  (see Table S1 and Fig. S1, available as Supplementary material to this paper). The depth of the freshwater plume was not measured.

The January 2013 flood (total event discharge 860 GL over 19 days), associated with ex-Tropical Cyclone Oswald, was the first event in the catchment for the 2013 water year (Table 2; Fig. 3). The flood plume flowed north from Normanby Basin distributaries, inundating coastal seagrass meadows and several mid-shelf reefs. Strong north-westerly winds (Table 2) forced the plume  $75 \text{ km}$  to the east towards outer-shelf reefs, covering an area of over  $1400 \text{ km}^2$  (Fig. 2b). Vertical sampling showed that the freshwater plume remained  $1.5 \text{ m}$  deep  $4 \text{ km}$  from the mouth of the Normanby River. Surface water salinity measured on 29 January 2013 ranged from  $1.7$  at the mouth of the Normanby River to  $28.3$  at a point  $33 \text{ km}$  north-west from the Normanby River mouth. Between 30 January and 1 February 2013, salinity increased along the Normanby plume transect (Fig. S1). Salinity outside the flood plume ranged from  $35.1$  to  $35.3$ .

In April 2014, the passage of Cyclone Ita across the south-eastern Normanby catchment resulted in a total event discharge of 1082 GL over 18 days (Table 2). Numerous smaller events preceded this flood event (Fig. 3), with total antecedent discharge for the water year totalling 1388 GL (Table 2). The April 2014 flood plume extended 18 km north from the Kennedy River and 10.5 km north-west from the Normanby River on 18 April 2014. Salinity within the Normanby plume transect ranged from 0.2 at the river mouth to 29.8 (Fig. S1). Salinity in the transect out from the Kennedy River ranged from 3.5 to 26.7. The mean temperature within the plume was 29.0°C. Outside the visible plume, salinity ranged from 32.9 to 33.5 (Table 3). Strong



**Fig. 3.** Hydrograph showing daily discharge at the Kalpowar Crossing gauge (105107) for the period of record (2005–15) showing the 2012, 2013 and 2014 flood events. (Data from the Department of Natural Resources and Mines (DNRM) water monitoring information portal; see <http://watermonitoring.dnrm.qld.gov.au/host.htm>, accessed 1 May 2017.)

south-easterly winds (Table 2) pushed the plume 70 km to the north-west, covering an area of at least 1100 km<sup>2</sup> based on MODIS imagery from 20 April 2014 (Fig. 2c).

#### Catchment to coast nutrient and sediment concentration gradients

##### Suspended sediment

TSS concentrations were significantly higher in the upper catchment than at the mid-catchment and estuary sites for all events (Table 3; Fig. S2). Maximum TSS concentrations were detected at the West Normanby River (1586 mg L<sup>-1</sup>) during the 2012 event and at the Laura River (1217 mg L<sup>-1</sup>) during the 2013 event. A mid-catchment maximum TSS of 126 mg L<sup>-1</sup> was detected at NR-02 in 2013 and an equivalent estuary maximum (126 mg L<sup>-1</sup>) was recorded in the lower Normanby estuary in 2014. Mean SS concentrations for the three combined events were 344 mg L<sup>-1</sup> (upper catchment), 67 mg L<sup>-1</sup> (mid-catchment) and 52 mg L<sup>-1</sup> (estuary; Table 3).

The coastal flood plumes had a combined mean TSS concentration of 14 mg L<sup>-1</sup>. Mixing diagrams of salinity and TSS show a rapid decrease in TSS within the 0–5 salinity zone for all events (Fig. 4), with one exception in 2014 where 150 mg L<sup>-1</sup> was measured at a salinity of 20, 2 km offshore (potentially due to resuspension). Beyond 6 km from the coast, all SS concentrations were <10 mg L<sup>-1</sup>.

##### Nutrients

Similar to TSS, most nutrient concentrations decreased along a gradient from the upper catchment to the flood plume, but did not vary significantly between the mid-catchment and estuary. PN, PP, NO<sub>x</sub> and FRP concentrations were highest in the upper catchment (with maximum concentrations in the Laura River), decreasing by one-half to one-quarter at mid-catchment sites and remaining constant between the mid-catchment and estuary

**Table 3.** Mean ( $\pm$  s.d.) concentrations from combined 2012, 2013 and 2014 flood events for catchment regions, Princess Charlotte Bay (PCB) flood plumes and in PCB outside the flood plumes

Within rows, different lowercase superscript letters indicate significant differences ( $P < 0.05$ ) between river regions (a, b), as well as between plume and background (outside plume) concentrations (x, y). SS, suspended sediments; NO<sub>x</sub>, nitrate + nitrite; DON, dissolved organic nitrogen; FRP, filterable reactive phosphorus; DOP, dissolved organic phosphorus; Chl-*a*, chlorophyll-*a*; NA, not analysed

Analyte	Upper catchment	Mid-catchment	Lower estuary/river mouths	Plume	PCB outside plume
SS (mg L <sup>-1</sup> )	344 $\pm$ 353 <sup>a</sup>	67 $\pm$ 32 <sup>b</sup>	52 $\pm$ 41 <sup>b</sup>	14 $\pm$ 25 <sup>x</sup>	5 $\pm$ 4 <sup>x</sup>
Total N ( $\mu$ M)	77.7 $\pm$ 40.7 <sup>a</sup>	36.0 $\pm$ 6.8 <sup>b</sup>	37.4 $\pm$ 8.5 <sup>b</sup>	20.6 $\pm$ 7.7 <sup>x</sup>	7.97 $\pm$ 4.6 <sup>y</sup>
NO <sub>x</sub> ( $\mu$ M)	9.40 $\pm$ 7.38 <sup>a</sup>	2.02 $\pm$ 2.82 <sup>b</sup>	3.22 $\pm$ 1.99 <sup>b</sup>	2.00 $\pm$ 1.33 <sup>x</sup>	0.43 $\pm$ 4.6 <sup>y</sup>
NH <sub>4</sub> /NH <sub>3</sub> ( $\mu$ M)	0.90 $\pm$ 1.28 <sup>a</sup>	1.05 $\pm$ 0.93 <sup>a</sup>	2.47 $\pm$ 1.96 <sup>b</sup>	0.92 $\pm$ 0.66 <sup>x</sup>	0.64 $\pm$ 0.54 <sup>x</sup>
DON ( $\mu$ M)	19.9 $\pm$ 10.4 <sup>a</sup>	22.8 $\pm$ 3.2 <sup>a</sup>	18.5 $\pm$ 7.4 <sup>a</sup>	13.4 $\pm$ 5.7 <sup>x</sup>	5.4 $\pm$ 4.5 <sup>y</sup>
Particulate N ( $\mu$ M)	46.1 $\pm$ 41.5 <sup>a</sup>	11.34 $\pm$ 4.0 <sup>b</sup>	13.3 $\pm$ 9.5 <sup>b</sup>	4.7 $\pm$ 5.0 <sup>x</sup>	1.5 $\pm$ 1.2 <sup>y</sup>
Total P ( $\mu$ M)	5.7 $\pm$ 4.2 <sup>a</sup>	2.4 $\pm$ 0.8 <sup>b</sup>	2.0 $\pm$ 1.2 <sup>b</sup>	0.6 $\pm$ 0.3 <sup>x</sup>	0.2 $\pm$ 0.1 <sup>y</sup>
FRP ( $\mu$ M)	0.56 $\pm$ 0.41 <sup>a</sup>	0.29 $\pm$ 0.25 <sup>a</sup>	0.32 $\pm$ 0.14 <sup>a</sup>	0.16 $\pm$ 0.09 <sup>x</sup>	0.11 $\pm$ 0.05 <sup>x</sup>
DOP ( $\mu$ M)	0.33 $\pm$ 0.29 <sup>a</sup>	0.47 $\pm$ 0.23 <sup>a</sup>	0.19 $\pm$ 0.21 <sup>a</sup>	0.22 $\pm$ 0.15 <sup>x</sup>	0.02 $\pm$ 0.02 <sup>y</sup>
Particulate P ( $\mu$ M)	4.7 $\pm$ 4.2 <sup>a</sup>	1.7 $\pm$ 0.9 <sup>b</sup>	1.5 $\pm$ 1.1 <sup>b</sup>	0.3 $\pm$ 0.3 <sup>x</sup>	< 0.1 $\pm$ < 0.1 <sup>y</sup>
Si ( $\mu$ M)	NA	NA	167.1 $\pm$ 45.8	74.3 $\pm$ 39.1 <sup>x</sup>	8.9 $\pm$ 11.1 <sup>y</sup>
Chl- <i>a</i> ( $\mu$ g L <sup>-1</sup> )	NA	NA	NA	1.7 $\pm$ 1.8 <sup>x</sup>	0.3 $\pm$ 0.1 <sup>y</sup>
Phaeophytin ( $\mu$ g L <sup>-1</sup> )	NA	NA	NA	0.8 $\pm$ 0.3 <sup>x</sup>	0.3 $\pm$ 0.2 <sup>x</sup>
Phytoplankton (cells L <sup>-1</sup> , $\times 10^4$ )	NA	NA	26 $\pm$ 25	378 $\pm$ 862 <sup>x</sup>	80 $\pm$ 80 <sup>y</sup>
Salinity	NA	NA	NA	21.3 $\pm$ 8.9	33.5 $\pm$ 1.3
Temperature (°C)	NA	NA	NA	30.9 $\pm$ 1.8	30.5 $\pm$ 2.0

sites (Table 3). Median DON and DOP concentrations did not vary significantly along the freshwater to marine gradient (Table 3).  $\text{NH}_4$  showed significantly higher mean concentrations in the estuary ( $2.47 \mu\text{M}$ ) than at mid-catchment ( $1.05 \mu\text{M}$ ) or upper catchment ( $0.90 \mu\text{M}$ ) sites (Table 3). A maximum  $\text{NH}_4$  concentration of  $7.6 \mu\text{M}$  was detected in 2014 adjacent to mudflats at the mouth of the Normanby River.

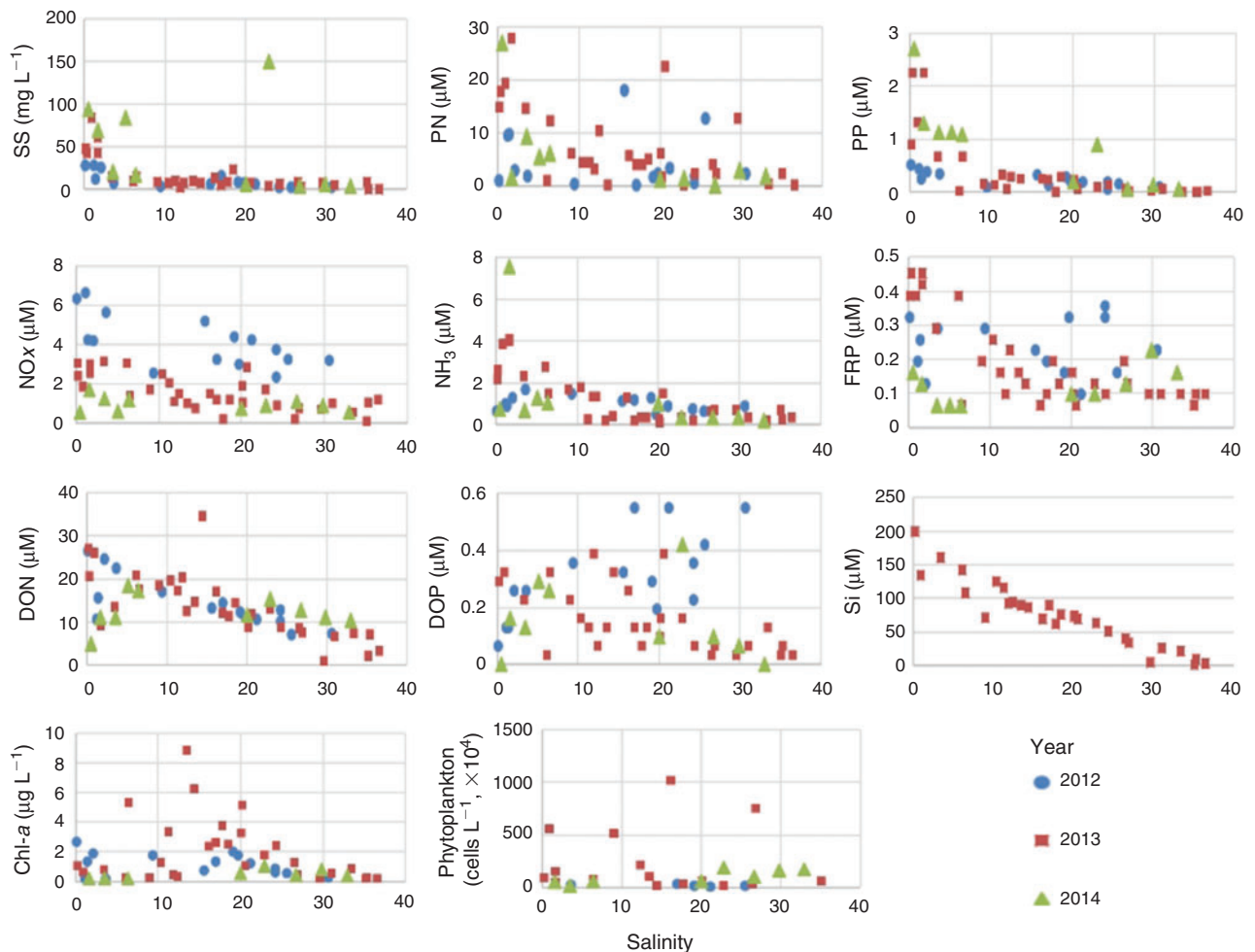
Within the flood plumes, TN,  $\text{NH}_3$ , DON, TP and PP concentrations were negatively correlated with salinity (Table 4). Mixing diagrams of nutrients against salinity showed varied patterns across the three years. Si (2013;  $r^2 = 0.9$ ) exhibited conservative behaviour, decreasing linearly with salinity (Fig. 4). DON concentrations decreased with increasing salinity, although variations were observed in the low-salinity range. DON increased at salinities  $<10$  in 2012 and 2014. These increases were less evident in 2013 when riverine end-member concentrations were higher. PN and PP declined rapidly with increasing salinity, but there were several PN increases at mid-salinity sites and PP remained low ( $<1 \mu\text{M}$ ) across the 2012

plume (Fig. 4).  $\text{NO}_x$  concentrations tended to show conservative behaviour, particularly in 2012, when riverine end-member concentrations were highest and there was no significant increase in Chl-*a* concentrations.  $\text{NO}_x$  remained low ( $<2 \mu\text{M}$ ) across the 2014 plume (Fig. 4).  $\text{NH}_3$  decreased at low salinities ( $<10$ ) in 2013, but increased at low salinities in 2014. FRP concentrations generally decreased at lower salinities, particularly in 2013, when a corresponding increase in Chl-*a* was observed. FRP was removed at both low salinities and salinities above 30 in 2014, whereas some concentrations were high across the 2012 plume (Fig. 4).

$\text{NO}_x$ , DON, PN, FRP, PP and Si concentrations within the plumes were significantly elevated compared with concentrations outside the plumes in PCB (Table 3).

#### Flood plume Chl-*a* concentrations and phytoplankton densities

Chl-*a* concentrations within the three PCB flood plumes ranged from  $0.2$  to  $8.8 \mu\text{g L}^{-1}$  (mean  $1.7 \mu\text{g L}^{-1}$ ). Concentrations



**Fig. 4.** Suspended sediments (SS), particulate phosphorus (PP), particulate nitrogen (PN),  $\text{NH}_3$ , nitrate + nitrites ( $\text{NO}_x$ ), dissolved organic nitrogen (DON), filterable reactive phosphorus (FRP), dissolved organic phosphorus (DOP), Si, chlorophyll (Chl)-*a* and phytoplankton plotted as a function of salinity for the 2012, 2013 and 2014 Princess Charlotte Bay flood plumes. An outlying 2013 phytoplankton value ( $4141 \times 10^4 \text{ cells L}^{-1}$ ) has been omitted for improved clarity.



**Table 4.** Spearman's Rank correlation coefficients for combined 2012, 2013 and 2014 Princess Charlotte Bay flood plume constituents (suspended sediments (SS), nutrients, chlorophyll (Chl)-a, phaeophytin (Phaeo), phytoplankton (Phyto)), total event discharge (TED), antecedent discharge for the water year (ANTD), salinity (SAL) and turbidity (TURB)

The number of samples for each analysis varied from 47 to 59, whereas phytoplankton only had 27 samples. Bold values are significant at  $P < 0.01$  level ( $r_s > 0.5$ ). TN, total nitrogen;  $\text{NO}_x$ , nitrate + nitrite; DON, dissolved organic nitrogen; PN, particulate nitrogen; TP, total phosphorus; DIP, dissolved inorganic phosphorus; DOP, dissolved organic phosphorus; PP, particulate phosphorus

	SAL	SS	TURB	TN	$\text{NH}_3$	$\text{NO}_x$	DON	PN	TP	DIP	DOP	PP	Si	Chl-a	Phaeo	Phyto	TED	ANTD
SAL	1.00	<b>-0.65</b>	<b>-0.87</b>	<b>-0.74</b>	<b>-0.57</b>	-0.29	-0.46	-0.50	-0.74	-0.23	-0.43	<b>-0.71</b>	-0.45	0.05	-0.44	0.40	0.07	-0.22
SS	<b>-0.65</b>	1.00	<b>0.55</b>	<b>0.63</b>	0.42	0.02	0.40	0.44	<b>0.65</b>	0.13	0.11	<b>0.76</b>	0.56	0.09	<b>0.56</b>	-0.06	0.27	0.07
TURB	<b>-0.87</b>	<b>0.55</b>	1.00	<b>0.57</b>	<b>0.57</b>	0.32	0.37	0.28	<b>0.69</b>	0.24	0.43	<b>0.50</b>	0.11	-0.21	0.31	<b>-0.77</b>	-0.22	<b>0.51</b>
TN	<b>-0.78</b>	<b>0.63</b>	<b>0.57</b>	1.00	<b>0.72</b>	0.48	<b>0.64</b>	<b>0.67</b>	<b>0.75</b>	<b>0.39</b>	<b>0.51</b>	<b>0.68</b>	<b>0.82</b>	-0.01	0.31	-0.29	-0.12	-0.04
$\text{NH}_3$	<b>-0.57</b>	0.42	<b>0.57</b>	<b>0.72</b>	1.00	<b>0.52</b>	0.42	0.40	<b>0.57</b>	0.36	0.37	0.37	0.41	-0.36	0.04	<b>-0.57</b>	-0.12	-0.03
$\text{NO}_x$	-0.29	0.02	0.32	0.48	<b>0.52</b>	1.00	0.20	0.17	0.42	0.41	0.45	0.24	<b>0.57</b>	-0.11	0.27	-0.29	<b>-0.71</b>	0.07
DON	<b>-0.54</b>	0.40	0.37	0.64	0.42	0.20	1.00	0.08	0.43	0.22	0.42	0.39	<b>0.84</b>	0.24	0.25	0.34	-0.03	-0.07
PN	-0.50	0.44	0.28	0.67	0.40	0.17	0.08	1.00	0.42	0.10	0.13	0.48	0.36	-0.07	-0.01	-0.11	0.05	-0.17
TP	<b>-0.77</b>	<b>0.65</b>	<b>0.69</b>	<b>0.75</b>	<b>0.57</b>	0.42	0.43	0.42	1.00	0.36	<b>0.74</b>	<b>0.85</b>	<b>0.87</b>	-0.06	0.45	-0.33	-0.10	0.33
DIP	-0.23	0.13	0.24	0.39	0.36	0.41	0.22	0.10	0.36	1.00	0.05	0.15	<b>0.58</b>	-0.03	-0.03	-0.02	-0.39	-0.05
DOP	-0.43	0.11	0.43	<b>0.51</b>	0.37	0.45	0.42	0.13	<b>0.74</b>	0.05	1.00	0.39	0.50	0.15	0.18	-0.31	-0.41	0.23
PP	<b>-0.75</b>	<b>0.76</b>	<b>0.50</b>	<b>0.68</b>	0.37	0.24	0.39	0.48	<b>0.85</b>	0.15	0.39	1.00	<b>0.74</b>	0.08	<b>0.55</b>	-0.09	0.13	0.28
Si	-0.45	<b>0.56</b>	0.11	<b>0.82</b>	0.41	<b>0.57</b>	<b>0.84</b>	0.36	<b>0.87</b>	<b>0.58</b>	<b>0.50</b>	<b>0.74</b>	1.00	0.26	0.24	0.41		
Chl-a	0.05	0.09	-0.21	-0.01	-0.36	-0.11	0.24	-0.07	-0.06	-0.03	0.15	0.08	0.26	1.00	0.31	<b>0.62</b>	-0.17	-0.36
Phaeo	-0.44	<b>0.56</b>	0.31	0.31	0.04	0.27	0.25	-0.01	0.45	-0.03	0.18	<b>0.55</b>	0.24	0.31	1.00	-0.05	-0.23	0.23
Phyto	0.40	-0.06	<b>-0.77</b>	-0.29	<b>-0.57</b>	-0.29	0.34	-0.11	-0.33	-0.02	-0.31	-0.09	0.41	<b>0.62</b>	-0.05	1.00	0.16	-0.41

outside the plume ranged from 0.2 to 0.9  $\mu\text{g L}^{-1}$  (Table 3). Phaeophytin concentrations ranged from  $<0.1$  to 16.8  $\mu\text{g L}^{-1}$  (mean 1.1  $\mu\text{g L}^{-1}$ ), with maximum values recorded at the mouth of the Normanby River in 2012. Plume phytoplankton densities ranged from 10 100 to 4 140 800 cells  $\text{L}^{-1}$  (mean 377 600 cells  $\text{L}^{-1}$ ), with a maximum density of 35 900 cells  $\text{L}^{-1}$  outside the freshwater plume (Table 3). The maximum density was recorded 5 km from the Normanby mouth (salinity 29, SS 10.6  $\text{mg L}^{-1}$ ). Phytoplankton sample counts are likely to underestimate the total cell densities because picoplankton, which can dominate ambient waters of the GBR Lagoon (Devlin et al. 2012a), were not recorded.

Chl-a concentrations in the 2012 and 2013 plumes increased or remained stable in low to mid-salinities ( $\sim 20$ ) and decreased from mid- to high salinities. Chl-a (and phytoplankton densities) were low across the 2014 plume ( $<1.1 \mu\text{g L}^{-1}$ ; Fig. 4). Increases in Chl-a generally occurred at SS concentrations below 10  $\text{mg L}^{-1}$ ; however, the peak phytoplankton density in 2014 (188 700 cells  $\text{L}^{-1}$ ) occurred at TSS concentrations of 150  $\text{mg L}^{-1}$ .

Bacillariophytes (diatoms) were the dominant class all years, comprising up to 97% of phytoplankton. *Chaetoceros* spp. was the most abundant genus (up to 9400 cells  $\text{L}^{-1}$ ) in the 2012 plume. The diatoms *Navicula* sp. and *Thalassionema nitzschioides* and the dinoflagellate *Gymnodinium* sp. also occurred at similar densities (4700–9400 cells  $\text{L}^{-1}$ ) in some samples. The diatom *Skeletonema* sp. was the most prevalent genus in the 2013 plume, comprising over 50% of most samples, with a density of 3 892 000 cells  $\text{L}^{-1}$  in one sample. *Skeletonema* sp. was not detected in 2012 or 2014 samples or outside the freshwater plume. Dinoflagellates, coccolithophorids and unidentified nanoplankton also occurred in the 2013 plume, as well as several freshwater taxa such as the cryptophyte

*Mallomonas* sp. Dominant species in the 2014 flood plume included the cyanobacterium *Trichodesmium erythraeum*, which was recorded at a maximum density of 70 800 cells  $\text{L}^{-1}$ , but was not found in 2012 or 2013.

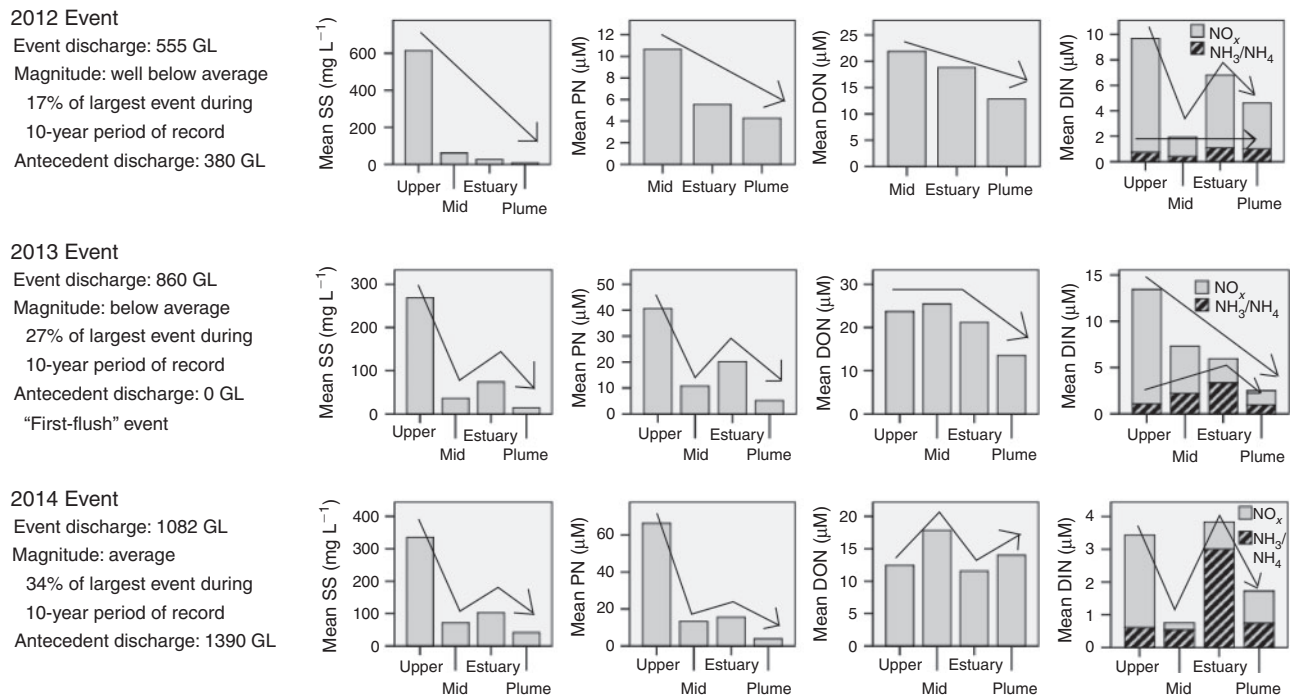
#### Variations between flood events and correlations with discharge

The 2012 flood event had a total discharge of 555 GL, compared with 860 and 1082 GL for the 2013 and 2014 events respectively. Both the 2012 and 2014 events were preceded by significant antecedent discharge compared with the 2013 'first flush' event, which had only 0.3 GL antecedent wet season discharge at Gauge 105107A (Table 2).

Owing to variations in the sampling methods (RSS v. manual sampling) and timing, variations between events in the upper catchment were not evaluated. Mid-catchment TSS concentrations did not differ significantly between flood events, but estuary concentrations were significantly higher in 2014 (mean 102  $\text{mg L}^{-1}$ ) than in 2012 (26  $\text{mg L}^{-1}$ ; Table S1). TSS concentrations at Normanby estuary sites were highly correlated ( $r_s = 0.9$ ) with both total event discharge and peak event discharge measured upstream at Gauge Site 105107A. Despite the strong correlations observed in the estuary, TSS concentrations within the plumes were not correlated with discharge (Table 4) and did not differ significantly between events, most likely due to rapid sedimentation rates (Table S1).

PN and PP concentrations in the estuary were significantly higher in 2013 and 2014 than in 2012 (Table S1; Fig. S2). Estuary PP concentrations were positively correlated with total event discharge ( $r_s = 0.8$ ) and SS ( $r_s = 0.8$ ).

Dissolved nutrient concentrations were generally higher at freshwater sites during the 2013 'first flush' event than in 2012 or 2014 (Table S1; Fig. S2). In contrast, estuary  $\text{NO}_x$



**Fig. 5.** Conceptual diagram showing variations in suspended sediment (SS) and nitrogen concentrations from the upper catchment to the flood plume during three flood events in 2012, 2013 and 2014. PN, particulate nitrogen; DON, dissolved organic nitrogen; DIN, dissolved inorganic nitrogen.

concentrations were significantly higher in 2012 (mean  $5.43 \mu\text{M}$ ) than they were in 2013 or 2014 ( $2.58$  and  $0.21 \mu\text{M}$  respectively), and were negatively correlated with both total and peak event discharge ( $r_s = -0.9$ ). Consistent with estuary trends,  $\text{NO}_x$  concentrations within the plumes were significantly higher in 2012 (mean  $3.60 \mu\text{M}$ ) than in 2013 or 2014 ( $1.57$  and  $0.99 \mu\text{M}$  respectively; Table S1) and were negatively correlated ( $r_s = -0.7$ ) with discharge (Table 4). FRP and DOP plume concentrations were also significantly elevated in 2012 compared with 2013 (DOP) and 2014 (FRP; Table S1). There were no significant differences in dissolved nutrients between the 2013 and 2014 flood plumes, although riverine end-member concentrations were higher in 2013.

Maximum Chl-*a* concentrations were detected in the 2013 plume (Fig. S2), but there were no significant differences between the three events (Table S1). Maximum phytoplankton densities were also recorded in 2013 (Table S1; Fig. S2) and a greater diversity of phytoplankton species was identified in 2013 plume samples (45) than in 2012 or 2014 (26 and 28 respectively).

## Discussion

The present study provides data on the export of material from the Normanby River to the far northern section of the GBR, about which there is limited knowledge. The results showed that flood events in the Normanby Basin are a source of nutrients and sediments to PCB and the northern GBR lagoon. During each of the three events studied, PCB seagrass and coral ecosystems were exposed to plumes of floodwater containing  $\text{NO}_x$ , DON, PN, FRP and PP at concentrations that were significantly elevated above ambient concentrations. Elevated concentrations

of dissolved nutrients discharged to PCB stimulated phytoplankton blooms, with densities up to an order of magnitude higher than ambient densities. Research on other GBR flood plumes has shown that the high levels of primary production associated with flood events also lead to subsequent increases in zooplankton, fish and other aquatic organisms (Devlin *et al.* 2012a).

### Catchment sources and temporal variations

Monitoring across the catchment during three flood events showed that TSS, PN, PP,  $\text{NO}_x$  and FRP concentrations decreased along a gradient from the upper catchment to the flood plume at PCB (Table 3; Fig. 5). From this we infer that the upper catchment is the primary source of both sediment and nutrients to the flood plumes. This may be attributed to both natural and anthropogenic factors; greater slope and erosion-prone sodic and dispersive soils in the upper Normanby River catchment make this region more susceptible to effects from land use disturbances (Biggs and Pain 1995; Brooks *et al.* 2013). Cattle grazing and horticultural land use is currently concentrated in the upper catchment region. Concentrations and loads of suspended sediment and nutrients in the upper catchment are estimated to have at least doubled since European settlement (Cape York Natural Resource Management and South Cape York Catchments 2016).

Reduced nutrient and sediment concentrations in the mid-catchment area (Fig. 5) indicate that the mid-catchment flood plains are a sink for SS, PN, PP,  $\text{NO}_x$  and FRP. Load calculations for the Normanby catchment show nutrient and sediment load reductions of between 65 and 85% between the upper and mid-catchment regions (Howley 2016), confirming

that sediments and nutrients are settling out or biologically used in the central and lower Normanby flood plains. The downstream decline is also consistent with the decline in specific sediment yield reported for the Normanby Basin by Brooks *et al.* (2013). This decline is likely to be a combined function of dilution by floodwater from lower-gradient areas with reduced sediment contributions and increased flood plain and in-channel sediment deposition, as has been demonstrated in Australian and global river systems (Walling 1983; Wasson 1994; Prosser *et al.* 2001).

In contrast with the mid-catchment region, the estuary provides a source of sediments, particulate nutrients and dissolved inorganic nutrients (DIN) to flood plumes (Fig. 5). Some Normanby estuary SS and particulate nutrients may be resuspended materials originating from the upper catchment. The Daintree estuary, located 230 km to the south of PCB, was also found to provide a source of SS during a flood event, either from clearing in the lower catchment or resuspension of estuarine sediments (Davies and Eyre 2005).

Maximum concentrations of  $\text{NH}_4$  were detected adjacent to intertidal mudflats near the mouth of the Normanby River, suggesting that mudflats may be a significant source of  $\text{NH}_4$  to coastal waters. Alongi and McKinnon (2005) showed that PCB intertidal mudflats release  $\text{NH}_4$  to the water column in the order of  $950 \mu\text{mol N m}^{-2} \text{ day}^{-1}$  under non-event conditions. Other potential coastal sources of  $\text{NH}_4$  include waters draining from inundated freshwater flood plains, supratidal mudflats (Burford *et al.* 2016), the flux of  $\text{NH}_4$  from mangrove sediment porewaters (Dittmar and Lara 2001), ammonification of particulate organic nitrogen (PON), remineralisation from DON and dissimilatory nitrate reduction to ammonium (DNRA) by anaerobic bacteria in sediments or the water column (Dagg *et al.* 2004). Davies and Eyre (2005) also found  $\text{NH}_4$  increased near the mouths of the Annan and Daintree rivers (northern GBR) during flood events, which they associated with the flushing of mangrove channels or the decomposition of PON. Although the exact sources remain uncertain, these findings indicate that undisturbed coastal zones can provide a significant natural source of DIN to tropical river flood plumes.

Antecedent discharge had a strong effect on dissolved nutrient concentrations in the river, particularly when comparing events of similar magnitude (2013 and 2014). The January 2013 flood was a 'first-flush' event, with only 0.3 GL antecedent discharge, whereas there had been 1390 GL discharge preceding the April 2014 flood event. Estuary DON,  $\text{NO}_x$ ,  $\text{NH}_4$  and FRP concentrations in 2013 were at least double the concentrations in 2014. Of the three flood events monitored, the most significant increase in phytoplankton biomass was also measured during the 2013 plume. These temporal differences in nutrient concentrations and resulting phytoplankton blooms are likely to be related to the varying antecedent discharge, although it is possible that phytoplankton densities may have increased within the 2014 plume after the sampling period. Events that occur later in the wet season after significant rainfall tend to have lower riverine SS and DIN concentrations than first-flush events (Devlin and Schaffelke 2009; Kuhnert *et al.* 2012). First-flush events in dry tropical regions have higher amounts of erosion due to low levels of vegetation ground cover during the start of the wet season (Bartley *et al.* 2006; Silburn *et al.* 2011) and the

depletion of readily erodible sediment and surface organic matter (Morehead *et al.* 2003).

A more detailed evaluation of the factors affecting water quality (sediment and nutrient concentrations and loads) at gauged sites across the Normanby Basin will be the focus of future papers.

#### Plume transformations

Nutrient concentration trends within the plumes were complex and varied for each event, often reflecting different riverine end-member concentrations. In some cases, apparent trends within the mixing plots of nutrients against salinity may reflect changes in riverine end-member concentrations over the course of the event (Eyre 1994).

Phosphorus entered the plume primarily as PP during the larger-magnitude events, and was subjected to rapid sedimentation at low salinities. FRP entered the plumes at maximum concentrations during the 'first-flush' event of 2013 and was removed at salinities  $<20$ , associated with an increase in phytoplankton (Fig. 4). The removal of FRP at low salinities in 2014 did not correspond to increasing Chl-*a* or phytoplankton densities, thus was likely due to adsorption onto suspended sediments, flocculation and precipitation with iron and humic materials or a combination of both processes (Eyre and Twigg 1997; Dagg *et al.* 2004). Mid-salinity increases in FRP (2012, 2014) suggest desorption from particulates, indicating that sediments may provide an important source of FRP to PCB when high concentrations are not supplied directly from the catchment.

Nitrogen entering the flood plumes was dominated by both particulate and dissolved organic forms. PN concentrations were highest during the first-flush event of 2013 and, like PP, PN was removed by sedimentation at low salinities. The low-salinity zone within the plume was both a sink (2013) and a source (2014) of DIN. In 2013, uptake of  $\text{NO}_x$  and  $\text{NH}_3$  within the plume corresponded to increasing Chl-*a* and phytoplankton densities (Fig. 4). Potential sources of 2012 and 2014  $\text{NH}_3$  increases within the estuary and low-salinity coastal plume were discussed in the previous section.

Mixed DON and DOP trends, including increases at low salinities ( $<10$ ) during the 2012 and 2014 events, may reflect changing riverine end-member concentrations over the course of each event because of changing discharge conditions and sources. Low phytoplankton densities indicate that the observed increases are not likely to be from phytoplankton production; however, flux from coastal mudflats or other estuarine sources could contribute to DON increases (Cook *et al.* 2004). Declining DON concentrations at higher salinities is likely to reflect dilution by ambient seawater with significantly lower DON concentrations (Table 3).

Riverine discharge associated with the flood events supported a phytoplankton bloom that began at low salinities and rapidly reduced nutrient concentrations within the plumes. Chl-*a* concentrations and associated phytoplankton densities increased between salinities of 5 and 25 and declined at salinities above 25, corresponding to depleted DIN and FRP concentrations ( $<1.5$  and  $0.1 \mu\text{M}$  respectively). Rapid sedimentation in the low-salinity zone of PCB flood plumes ( $<6$  km from the river mouths) allowed for increased phytoplankton productivity

at the mid-salinity region of the plumes. Maximum phytoplankton growth has been shown to occur below an SS threshold of 10–15 mg L<sup>-1</sup> (Dagg *et al.* 2004; Devlin *et al.* 2012b). In the present study, this threshold generally applied, but with notable exceptions. Chl-*a* concentrations as high as 5.3 µg L<sup>-1</sup> were detected at SS concentrations of 20 mg L<sup>-1</sup> in 2013, and the maximum phytoplankton density recorded in the 2014 plume (189 000 cells L<sup>-1</sup>) coincided with an SS concentration of 150 mg L<sup>-1</sup>.

Diatoms, which respond quickly to the increased N, P and Si availability associated with flood events (Furnas *et al.* 2005), were the dominant phytoplankton group for all three events, although species composition varied. The 2013 plume supported high densities of diatoms of the euryhaline *Skeletonema* genus, which was not detected in the 2012 or 2014 plumes. The 2014 plume samples were dominated by the common cyanobacteria *T. erythraeum*, which was also only detected that year. A complex array of factors, including salinity, light availability, relative nutrient availability, wind speed, water column mixing or stratification and grazing pressures, can contribute to variations in species composition within flood plumes. Additional research over multiple plumes is required to better understand the development of phytoplankton blooms throughout different plume phases and the factors affecting phytoplankton densities and species composition within PCB flood plumes.

#### *Effects of Normanby Basin flood plumes on PCB ecosystems*

PCB seagrass and coral ecosystems were exposed to plumes of floodwater containing dissolved and particulate nutrients at concentrations that were significantly elevated above ambient concentrations. Although some elevated concentrations of nutrients can increase the productivity of coral zooxanthellae and stimulate coral growth (Fabricius 2005), extended periods of increased turbidity and the deposition of ‘marine snow’ comprised fine clay particles and organic materials can inhibit marine ecosystem productivity (Fabricius and Wolanski 2000; Fabricius 2007; Bainbridge *et al.* 2012). Although the present study monitored plumes for only a short period (up to several days), remote sensing data show that periods of altered water quality and reduced photic depth at inshore, mid-shelf and even outer-shelf waters can last for several months after a PCB flood event (Logan *et al.* 2014). The threshold between increased marine productivity and loss of productivity associated with elevated concentrations and loads of nutrients and sediments discharged to PCB is unknown.

#### *Comparison with other river flood plumes*

A range of factors can complicate comparisons of flood plume concentrations from different events or different river systems, including variations associated with catchment characteristics (e.g. soil type, slope, vegetation, land use), flood magnitude, antecedent rainfall, tidal and wind effects and the timing and location of sampling across the plume. The interpretation of the following comparisons is limited by these factors.

The Normanby estuary TSS concentrations (mean 52 mg L<sup>-1</sup>, maximum 125 mg L<sup>-1</sup>) were an order of magnitude lower than end-of-system event concentrations reported for the two largest

GBR catchments, namely the Burdekin and Fitzroy, which, like the Normanby, are ‘dry-tropical’ catchments dominated by cattle grazing (Table S2). Within the coastal plumes, mean Normanby TSS concentrations (21 mg L<sup>-1</sup>) remained less than those measured over a similar salinity range from Burdekin (33.7 mg L<sup>-1</sup>) and Fitzroy flood plumes (23.7 mg L<sup>-1</sup>); however, they exceeded mean GBR plume concentrations (13.6 mg L<sup>-1</sup>) and plume concentrations from smaller (but higher annual discharge) ‘wet-tropical’ GBR catchments such as the Tully and Herbert rivers (Tables S2, S3). Normanby plume TSS concentrations were low compared with many international river flood plumes, especially those with intensive catchment land use. For example, Yangtze River flood plume suspended sediment concentrations reach 5000 mg L<sup>-1</sup> (Edmond *et al.* 1985) and in a 2011 flood plume in Chesapeake Bay, suspended sediment concentrations reached 2500 mg L<sup>-1</sup> (Cheng *et al.* 2013).

Owing to the small percentage of horticultural land use in the Normanby Basin (<1%), limited to the upper catchment, estuary and flood plume nutrient concentrations, particularly DIN, were expected to be low compared with more developed GBR and global rivers. Indeed, Normanby estuary DIN concentrations (mean 5.7 µM) were within the range of riverine end-member concentrations from large tropical rivers, including the Amazon (12 µM), Zaire (7.2 µM) and Orinoco (6.6 µM; Dagg *et al.* 2004), but were low compared with discharge from more disturbed rivers such as the Yangtze, Mississippi, Pearl and Los Angeles rivers, where NO<sub>x</sub> ranged from 40 to 207 µM (Edmond *et al.* 1985; Lohrenz *et al.* 1999; Dai *et al.* 2008; Reifel *et al.* 2009).

Surprisingly, mean Normanby flood plume DIN, PN, DON, DOP and Chl-*a* concentrations were among the highest reported for GBR plumes (Table S3) and exceed the mean GBR-wide plume concentrations measured by Devlin *et al.* (2012c), although sampling location and timing variations may contribute to these differences. Mean NO<sub>x</sub> and NH<sub>3</sub> concentrations in PCB plumes exceeded mean concentrations (over a similar salinity range) within plumes from the more intensively farmed Tully and Herbert catchments (Tables S2, S3), where DIN concentrations are elevated because of fertiliser use (Bramley and Roth 2002; Mitchell *et al.* 2007). In contrast, Normanby plume NO<sub>x</sub> concentrations were within a similar range (2012 and 2013) or less than (2014) plume concentrations from the Annan River catchment (Davies and Eyre 2005), which originates in a wet-tropical rainforest and has no commercial horticulture, but a history of mining disturbance, grazing land use and erosion (Shellberg *et al.* 2015). These mixed comparisons show that relatively high DIN concentrations in GBR marine plumes cannot be solely attributed to horticultural land use. Other anthropogenic and natural sources may contribute significantly to DIN in some plumes. Burton *et al.* (2015) demonstrated that fine SS from the Burdekin catchment can produce DIN in both freshwater and marine conditions. The release of nitrogen from particles through desorption or remineralisation has also been shown to contribute to the DIN in global river plumes (Dagg *et al.* 2004). Accelerated erosion and subsequent release of DIN from SS have undoubtedly contributed to nitrogen loads discharged to PCB. However, as observed in the Normanby as well as the Annan and Daintree systems (Davies and Eyre 2005), natural sources, such as organic matter from forested areas and

NH<sub>4</sub> from intertidal and supratidal mudflats and mangroves, can also provide a source of DIN to plumes.

Nutrient and sediment processing within PCB flood plumes followed some common trends exhibited in both GBR and global river plumes. For example, rapid removal of most sediment and particulate nutrients within the nearshore zone occurs in plumes from the Mississippi River (Trefry *et al.* 1994) and GBR rivers, including the Annan, Russell-Mulgrave, Tully, Moresby and Burdekin (Eyre 1994; Davies and Eyre 2005; Devlin and Brodie 2005; Lønborg *et al.* 2016). This removal occurs because of decreasing current velocities and flocculation of clay particles as they encounter saline water (Davies and Eyre 2005). Although less common, an increase in SS has also been observed across northern Australian flood plumes (e.g. Eyre and Balls 1999) and is generally attributed to tidal or wind resuspension of sediments. Because sedimentation reduces light attenuation within a plume, an increase in phytoplankton productivity and corresponding uptake of dissolved nutrient concentrations is observed at mid-range salinities, and decreasing phytoplankton densities occurs at higher salinities because of nutrient depletion. This process was most obvious in the 2013 PCB plume and is measured in many large river plumes (Dagg *et al.* 2004; Boldrin *et al.* 2005; Dai *et al.* 2008).

In contrast with a mid-salinity phytoplankton increase, some GBR plumes have shown maximum phytoplankton densities, Chl-*a* concentrations and uptake of dissolved nutrients occurring in the high-salinity (>25) zone at the plume edge (Devlin and Brodie 2005; Brodie *et al.* 2010). Plume front phytoplankton blooms have also been observed in the Pearl and Yangtze rivers (Tian *et al.* 1993; Harrison *et al.* 2008). Alternatively, maximum Chl-*a* concentrations for both the 2012 PCB event and a small Annan River flood event occurred at the riverine end-member. Chl-*a* remained low (<0.5 µg L<sup>-1</sup>) across the Annan plume due to TSS concentrations above 10 mg L<sup>-1</sup> (Davies and Eyre 2005). In addition to TSS concentrations and associated light availability, factors such as pH, iron and other mineral concentrations, the extent of subsurface mixing or sediment resuspension, nutrient limitations and residence times can contribute to variations in the location and magnitude of primary production and nutrient depletion within plumes (Lohrenz *et al.* 1999; Dagg *et al.* 2004).

The apparent adsorption and sedimentation of FRP at low salinities observed in the 2014 PCB plume has also been observed globally (Dagg *et al.* 2004) and within Australia in plumes from the Annan and Moresby rivers (Eyre 1994; Davies and Eyre 2005) and the Richmond River in northern New South Wales (Eyre and Twigg 1997), but has not been widely reported in GBR plumes. The removal of dissolved inorganic phosphate (DIP) by adsorption to sediments and colloids is regulated by both salinity and pH (Eyre and Twigg 1997). At mid-salinity zones, FRP tends to desorb from sediments, as indicated by increases in the 2012 and 2014 PCB mixing diagrams. This has also been shown to be a significant source of phosphate in Amazon and Yangtze river plumes (Dagg *et al.* 2004). Phosphate desorption in other GBR plumes has been suggested based on mixing diagrams from Daintree and Tully river plumes (Davies and Eyre 2005; Devlin and Schaffelke 2009). However, Edis *et al.* (2002) found that desorption of FRP from Herbert River suspended sediments was likely to occur in the freshwater zone,

but not in the estuary or flood plume. Desorption occurs under conditions of long water residence times (Eyre and Twigg 1997) and therefore may not be common under the high discharge conditions of GBR flood plumes. The appearance of FRP adsorption and desorption within a plume may also be masked or falsely indicated in salinity mixing diagrams by changing riverine sources and end-member concentrations.

Normanby plume DON concentrations were among the highest recorded in GBR plumes, potentially due to differences in soil type, higher vegetation cover within the catchment and estuarine sources (Cook *et al.* 2004; Willett *et al.* 2004; Lehrter 2006). The decline in DON concentrations at higher salinities in the PCB plumes differed from the relatively constant DON concentrations recorded across other GBR plumes, where river and seawater concentrations were similar (Davies and Eyre 2005; Devlin and Brodie 2005) and is most likely explained by the higher riverine end-member DON concentrations in Normanby plumes.

## Conclusion

This study showed that the upper tributaries of the Normanby River (the East Normanby, West Normanby and Laura rivers) are significant sources of sediment and nutrients discharged to PCB during flood events. The estuary provided a source of NH<sub>4</sub>, indicating that undisturbed coastal zones can provide a significant natural source of DIN to tropical river flood plumes. Normanby plume DIN concentrations were relatively high by GBR standards, but globally fall within the range of less-disturbed rivers. Dissolved nutrients within the flood plumes stimulated phytoplankton blooms that inundated mid-shelf and outer-shelf coral reefs, with the area affected determined by flood magnitude, wind direction and wind speed. Increased nutrient concentrations and high levels of primary production associated with riverine flood plumes drive subsequent increases in zooplankton, fish and other aquatic organisms and may stimulate coral growth. However, future increases in anthropogenic loads of nutrients and sediments from the upper Normanby catchment could increase turbidity and muddy marine snow deposition at PCB, leading to declining coral and seagrass conditions or a diminished ability to recover from climate-driven bleaching events. Therefore, careful management and monitoring of development in the upper catchment is required to maintain the health and resilience of aquatic ecosystems at PCB.

## Conflict of interest

The authors declare that they have no conflicts of interest.

## Acknowledgements

This work was completed as part of a Griffith University PhD project for Christina Howley. This project was supported by the Great Barrier Reef Marine Park Authority, through funding from the Australian Government Reef Program. Additional funding and analytical support was provided by the Queensland Department of Science, Information Technology and Infrastructure GBR Loads Program, Balkanu Cape York Development Corporation, South Cape York Catchments and the South Endeavour Trust. Field assistance for catchment and plume monitoring was generously contributed by the Laura Rangers, Jeff Shellberg and Sue Marsh. Bungee Scott Helicopters (Atherton, Qld Australia) helped develop methods of rapidly accessing and sampling remote rivers and flood plumes. Andrew Brooks and

John Spencer (Griffith University) provided the rising stage sampler suspended sediment concentration results. Additional flood plume total suspended sediments data collected in 2013 under the CSIRO eReefs program were provided by Kadira Oubelkheir, Philip Ford and Nagur Cherukuru. The authors thank Jon Olley (Griffith University) and two anonymous reviewers for advice that significantly improved the manuscript.

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