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Catchment Soils Supply Ammonium to the Coastal Zone – Flood Impacts on Nutrient Flux in Estuaries

Kaitlyn O'Mara^{a*}, Jon M. Olley^a, Brian Fry^a, Michele Burford^a

^a*Australian Rivers Institute, Griffith University, 170 Kessels Rd, Nathan, Brisbane, Australia*

*Corresponding author: kaitlyn.omara@griffithuni.edu.au

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Abstract

Erosion of soil from catchments during floods can deliver large quantities of sediment to the coastal zone. The transformations and processes of nutrient release from catchment soils during flooding are not well understood. To test the hypothesis that catchment soils supply nutrients to the coastal zone, we examined nutrient release and transformation following wetting of soils formed from three distinct rock types (basalt, granite and sandstone) with fresh and marine water. The soil samples were collected from eroding areas of a subtropical river catchment. We simulated runoff, transport and deposition by tumbling the fine fraction of the soils in freshwater for three days and settling in seawater for four weeks. We also collected and incubated cores from an adjacent coastal bay and added a layer of catchment soil to simulate deposition of new sediment following flood plume settling. Dissolved nutrients were measured in both simulations. Basalt soils were relatively nutrient rich and released substantial quantities of organic and inorganic dissolved nutrients, particularly phosphate. However when soils were added to estuarine sediment cores and incubated, there was a net influx of phosphate from the overlying water. All soils continually released ammonium in both experiments, indicating that catchment soils may be an important source of ammonium to fuel productivity within the coastal zone. This study provides new insights into increased nitrogen availability in a nitrogen-depauperate coastal zone and identifies catchment geology as an important influence in coastal productivity through delivery of soil nitrogen to downstream estuaries.

Keywords

Sediment, nitrogen, phosphorus, basalt, granite, sandstone

1 Introduction:

Large storms and associated floods facilitate the erosion and transport of material from catchments to estuaries and coastal bays, with very little erosion and transport occurring during dry weather periods. This is particularly true in tropical and subtropical areas in which river flows are driven by major rainfall events. Much of this eroded material remains in the coastal zone (Lowes et al., 2008). Sediment derived from the erosion of catchment soils are the main source of organic carbon in marine sediments in the coastal zone (Li et al., 2016). Biogeochemical cycling within this zone is therefore strongly linked to hydrology and erosion within the catchment (Smith et al., 1996). Nutrients associated with sediments may play an important role in regulating the productivity of ecosystems in receiving estuaries (Lowes et al., 2008). Nitrogen is typically a key limiting nutrient in coastal systems, and catchment inputs provide an important source fuelling productivity (Glibert et al., 2010; Saeck et al., 2013). Sediment particles are exposed to several abrupt chemical and hydrological changes during erosion and transport in floodwaters, influencing the amount of nutrients released from or absorbed by these particles (Uncles, 2003). Once they enter an estuary, these sediment particles are exposed to new complex biogeochemical and hydrological dynamics, as well as sharp chemical gradients, again influencing the flux of nutrients and other materials (Uncles, 2003). During large floods, rapid sedimentation can occur, forming a new surface layer that can act as a source or sink for nutrients and trace metals.

An increased awareness of fine sediments as a carrying medium for nutrients, trace metals and other contaminants to the coastal zone has drawn attention to the importance of catchment sources (Slattery and Burt, 1997). The properties of different soil types influence organic matter content and how they bind and retain nutrients (Asselman and Middelkoop, 1995). Hence, nutrient cycling and availability in estuaries is influenced by catchment geology. Estuaries and coastal bays that have modified catchments are often degraded by increased nutrient input and accelerated erosion,

particularly in agricultural areas (Worrall et al., 2012). Several studies from modified catchments demonstrate that nutrient-rich fine particles of terrigenous origin are being transported from catchments and deposited in oceans and coastal bays during floods (Chaston et al., 2008; Garzon-Garcia et al., 2017; Warrick et al., 2005). The majority of flood deposit material is comprised of fine particles due to preferential deposition of the coarser fraction during sediment transport (Kerr et al., 2011; Slattery and Burt, 1997). Fine particles have a high surface area to volume ratio, meaning an increased nutrient carrying capacity (Horowitz and Elrick, 1987). However, the influence of catchment derived fine sediment on estuarine biogeochemistry and contribution to coastal productivity remains poorly understood and this study is the first of its kind.

Our study was conducted in subtropical Queensland Australia where a legacy of rapid land-use change and associated soil erosion has placed the receiving waters of Moreton Bay, a RAMSAR wetland, at risk of significant ecological degradation and decline in conservation value through increased nutrient and sediment delivery (Leigh et al., 2013). To test the hypothesis that catchment soils are important contributors of nutrients to the coastal zone, we conducted two experiments in parallel. Firstly, we examined nutrient release from soils developed from three distinct rock types (basalt, granite and sandstone) during simulated flood sediment transport and deposition. A second experiment examined the interaction between marine sediments and fine soil particles by simulating deposition of eroded catchment soil on existing Moreton Bay sediments and measuring nutrient fluxes.

2 Materials and methods:

The Brisbane River catchment covers over 13,600 km² with sandstone, granite and mafic to felsic volcanic rocks comprising the main geologies (Barton et al., 2015; Geoscience, 2015). Long term

monitoring data shows higher nutrient load delivery to Moreton Bay during periods of heavy rainfall in the catchment, with total nitrogen loads up to ten times higher in flood years than in dry years, which is mostly accounted for by increased sediment loads (Leigh et al., 2013). Moreton Bay provides diverse and ecologically important habitats to a variety of endangered or economically important species of wildlife ranging from migrating wetland birds to commercially harvested fish and prawns to larger protected species such as turtles and dugongs. Over the past 50 years an expanding human population and land use change has caused the decline of water quality in the bay, with flow on effects including reduction of seagrass coverage (Roelfsema et al., 2009).

2.1 Flood simulation experiment

2.1.1 Soil collection

Three soil types (derived from basalt, granite and sandstone) were collected from eroding natural or lightly grazed catchment areas surrounding the Brisbane River (Fig. 1). Soil collection details, including soil lithologies, are given in Table 1. When collecting granite and sandstone soils a soil profile was clearly visible, hence both topsoil and subsoil were collected. However, the basalt soil profile was uniform with no subsoil evident, hence only surface sample was collected. Each soil sample was passed through a 2 mm sieve and poured onto black plastic sheeting to be dried naturally in sunlight. Granite and sandstone soils were dry-sieved to $< 63 \mu\text{m}$. Basalt soil was wet sieved due to its adhesive properties. The water used to wet sieve the basalt soil was sampled for nutrient release during sieving and initial release corrections were applied.

2.1.2 Experimental methods

Since larger, heavier sediment particles first settle out during transport, flood plumes usually contain mostly fine sediment particles from the $< 63 \mu\text{m}$ size fraction (Slattery and Burt, 1997). To simulate the period of turbulent water transport, three replicates of approximately 130 g of the $< 63 \mu\text{m}$ fraction of each soil type were placed into plastic cylinders containing 1 L of reverse osmosis deionized (RODI) water. Lids were placed on the cylinders and a mechanical tumbling apparatus (16 revolutions per minute) was used to invert the cylinders continuously for 72 h. During this time, water samples were taken and filtered through $0.45 \mu\text{m}$ membrane filters (Sartorius) at regular time intervals of 1, 4, 24, 48 and 72 h following commencement of tumbling.

Following tumbling, the soil from each sample was separated from the freshwater by settling and the soil was then left to air-dry in the laboratory so that the weight of soil in each replicate could be standardised. Approximately 25% of each sample (20-30 g dry weight) was placed in a clean plastic cylinder containing 1 L of natural seawater collected from south-eastern Moreton Bay (temperature 23.12°C , salinity 34.1, pH 8.00, dissolved oxygen 83 % saturated (5.82 mg L^{-1})). The soil samples were subdivided to dilute them beyond sediment loads typically in freshwater because once floodwaters reach an estuary or coastal bay, the sediment to water volume ratio decreases. Three splits (one dilution of each replicate used in the tumbling) of each soil type were left to settle in the cylinders for four weeks to simulate flood plume settling in seawater. To simulate water movement, the water above the soil layer in each tube was stirred briefly without stirring through the soil layer, once daily for the first three days then once weekly thereafter. During this four week seawater exposure, filtered water samples were taken using plastic syringes and $0.45 \mu\text{m}$ membrane filters at regular time intervals of 1 h, 4 h, 24 h, 1 wk, 2 wk and 4 wk. In addition, filtered samples of RODI and seawater used in the experiment were collected and analyzed to determine dissolved nutrient concentrations prior to addition of soils. The entire experiment was carried out in a dark room so

that microalgae would not assimilate the nutrients. All samples were frozen immediately for storage prior to analysis.

2.1.3 Sample analysis

To analyze soil nutrient composition prior to wetting, a subset of $<63\ \mu\text{m}$ dry soil samples were analyzed for total Kjeldahl nitrogen (TkN) and phosphorus (TkP)(digestion), organic carbon (OC) (combustion), and extractable nitrate (extNO_3) (Aqueous Cl). Filtered water samples were analyzed for ammonium (NH_4^+), nitrite and nitrate ($\text{NO}_2^- + \text{NO}_3^-$), phosphate (PO_4^{3-}), total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) on a segmented flow analyzer (AA3-HR Auto Analyzer, Seal Analytical) and standard colorimetric methods were used (Eaton et al., 2005). In the case of TDN and TDP, samples were first persulfate digested (Hosomi and Sudo, 1986). Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were calculated by subtracting inorganic dissolved nitrogen concentrations ($\text{NH}_4^+ + (\text{NO}_2^- + \text{NO}_3^-)$) from TDN and subtracting PO_4^{3-} from TDP, respectively. Dissolved organic carbon (DOC) content was determined for freshwater samples by high-temperature catalytic oxidation (HTCO) and are presented here, however a determination of DOC in seawater samples was confounded by enriched DOC from the soils and interference from salt ions in seawater, therefore there are no results reported.

2.2 Nutrient and oxygen fluxes in bay sediment with soil additions

To study the flux of nutrients from Moreton Bay sediments after settling of the flood plume, catchment soil ($<63\ \mu\text{m}$) was added to core samples taken from central Moreton Bay. Using a box corer, cores were collected in Perspex core tubes (47 mm diameter) from a site known to have high sediment deposition following previous floods (latitude 27.266122° , longitude 153.339572°). The

physico-chemical characteristics of the site were measured using a Hydrolab sensor, and subsamples were taken from bottom waters using a van Dorn sampler for nutrients (method of analysis outlined below). The site of collection was 20 m deep, salinity 35.13 PSU, bottom temperature 20.52°C, bottom dissolved oxygen concentrations 7.34 mg L⁻¹, and average bottom ammonium, nitrate plus nitrite and phosphate concentrations were 0.023, 0.001 and 0.011 mg L⁻¹ respectively. Cores contained approximately 5 cm of Moreton Bay bottom sediment with overlying water and were transported to the laboratory where they were equilibrated over 24 h at 24°C and kept in the dark. Approximately 3 g of topsoil of one of the three geologies, i.e. sandstone, granite and basalt (three replicates of each) was added to a core so that 2 cm surface layer was created. This depth was based on estimates of sediment deposition from the 2011 flood in Moreton Bay (Coates-Marnane et al., 2016). The topsoils collected and sieved (to <63 µm) for the flood simulation experiment described above were used as additions to the cores collected from Moreton Bay. There was also a control with no soil addition (3 replicates). Cores were kept in a water bath maintained at a temperature of 21°C. The cores were sealed with no airspace. Small circulating pumps were attached to the side of the core tubes for circulating water before each sampling occasion via a surface port. Dissolved oxygen concentrations were measured on each sampling occasion with an optical oxygen sensor kit (Presens) where water column oxygen could be measured through the Perspex wall. Water samples were taken before the soil addition and at 6, 22, 30, 47, 53, 78, 103 and 118 h after soil addition and filtered through 0.45 µm membrane filters then frozen for subsequent ammonium, oxides of nitrogen and phosphate analysis. Removed water was replaced with water collected at the site. Samples were analyzed on a segmented flow analyzer (AA3-HR Auto Analyzer, Seal Analytical) and standard colorimetric methods were used (Eaton et al., 2005).

In order to calculate nutrient and oxygen fluxes, changes in concentrations were graphed over time. To ensure flux rates were not affected by low oxygen conditions, a cutoff of 2 mg L⁻¹ DO was used

as the minimum for rate measurements. If oxygen levels in the cores fell below 2 mg L^{-1} , data beyond the time point at which this occurred was not used. The slope of the linear curve for each analyte was used to give an influx or efflux hourly rate ($\text{mg L}^{-1} \text{ h}^{-1}$), with net influx to sediments given as a negative rate and net efflux to the water given as a positive rate.

2.3 Statistical methods

For the first experiment, nutrient concentrations were standardized to micrograms of dissolved nutrient per gram of soil per litre of water. To visualise release of nutrients from each soil type over time, scatterplots were created in R. The highest rates of release were identified in these graphs as three different release phases: quick release in the first hour of exposure to freshwater (FW quick release) and saltwater (SW quick release), and a slower release after 1-2 weeks in saltwater (SW slow release). Release fluxes were calculated for these periods and general linear models (ANOVA) were used in R to determine differences in release rates between soil types and between release phases. These differences were graphed in Microsoft Excel. For the second experiment involving core incubations, differences in fluxes of inorganic dissolved nutrients were also determined using ANOVA with R software and graphed in Microsoft Excel.

3 Results

3.1 Flood simulation experiment

3.1.1 Dry soil initial nutrient composition

Analysis of initial nutrient composition in collected soils showed that extractable nitrate concentrations ranged from 1 to 12 mg kg⁻¹ (Table 2) and total organic carbon concentrations ranged from 0.46 to 2.38%. Total kjeldahl nitrogen concentrations ranged from 0.04 to 0.16% and total kjeldahl phosphorus concentrations ranged from 0.02 to 0.07%.

3.1.2 Nutrient release during flood simulation

Nutrients were released upon initial wetting (0-1 h) in freshwater (FW) for most soil types in the flood simulation experiment (Fig. 2-3). This release phase is referred to as the 'FW quick release phase' hereafter. A slight decrease in all dissolved nutrient water concentrations was measured for most soil types following the FW quick release phase (1-4 h). Further responses varied between nutrients and soil types for the remainder of the fresh water exposure (4-72 h), with variable responses for inorganic nutrients NH₄⁺, NO₂⁻ + NO₃⁻ and PO₄³⁻ (Fig. 2), and little to no further release of DON, DOP and DOC (Fig. 3-4). Basalt and sandstone subsoil initially released more than twice the amount of dissolved organic carbon than the other soil types (Fig 4). After the first hour of exposure to freshwater, dissolved organic carbon concentrations in the water remained relatively constant for all soil types except basalt, which fell from 250 to 100 µg carbon g⁻¹ soil between 1-24 h and remained relatively constant after 24 h. The FW quick release phase upon initial wetting of soils with freshwater was the highest release rate of all dissolved nutrients measured over the experiment, with the exception of NH₄⁺, which exhibited release rates when first exposed to seawater that were more than double the NH₄⁺ FW quick release rates (Table 3).

Dissolved nutrients were also released in the first hour of exposure to saltwater (referred to as SW quick release phase hereafter) at a faster rate than the remainder of the saltwater exposure (Fig. 2-3). Similar to the freshwater exposure, a slight decrease in dissolved water nutrient concentrations

was measured subsequent to the initial SW quick release phase (1-4 h). Ammonium was continually released from soil particles of all soil types over the remainder of the saltwater exposure (Fig. 2). Nitrite and nitrate ($\text{NO}_2^- + \text{NO}_3^-$) concentrations remained relatively steady from 24 to 336 h, followed by increased release of $\text{NO}_2^- + \text{NO}_3^-$ by basalt topsoil and both granite topsoil and subsoil, with sandstone topsoil and subsoil having very little release (Fig. 2). Phosphate release into saltwater was negligible after the first hour of exposure for the granite and sandstone topsoils and subsoils. However, the basalt soil treatment had the highest and most distinct continued release of PO_4^{3-} until the end of the experiment (Fig. 2). After a slight increase at 24 h, DON concentrations decreased for all soil types until 336 h, where basalt and granite topsoils released further DON into the water until the end of the experiment, and the remaining soil types did not release further DON (Fig. 3). Subsoils released little to no DOP during the saltwater exposure, and topsoils followed a similar pattern of release to DON, except only basalt soils exhibited substantial DOP release after 336 h of exposure to saltwater (Fig. 3). Rates of prolonged release (2-4 wks) were calculated and are referred to hereafter as SW slow release phase.

3.1.3 Comparison of rates of nutrient release during flood simulation

Statistical analysis of nutrient release rates in the flood simulation experiment identified significant differences between release rate phases and soil types, as well as an interaction between release rate phase and soil type at the $p < 0.001$ significance level for all nutrients (aside from DOC, only soil type is used as a predictor due to missing SW data) (Table 3). Post-Hoc tests (Tukey's HSD) revealed that basalt soils had significantly higher release rates than other soil types for all nutrients except NH_4^+ (Fig S1-S3). Basalt NH_4^+ release rates were higher than all other soil types except granite topsoil. Granite subsoil showed the lowest or equal lowest release rates for all nutrients (Table 3). Sandstone subsoil generally had low release rates compared to the topsoil types, except

for DOC in FW, where sandstone subsoil had the second highest release rate behind basalt topsoil. The SW quick release phase had the highest release rates for NH_4^+ , followed by the FW quick release phase, with the SW slow release phase having the lowest rates of release (Table 3). In fact, the SW slow release phase was significantly lower than both the FW and SW quick release phases for all nutrients (aside from DOC, for which SW data is unavailable). The FW quick release phase had significantly higher release rates than the SW quick and slow release phases for $\text{NO}_2^- + \text{NO}_3^-$ and DON, but similar release rates to the SW quick release phase for PO_4^{3-} and DOP.

3.2 Inorganic nutrient fluxes from soil additions to Moreton Bay sediment

Concentrations of $\text{NO}_2^- + \text{NO}_3^-$ and PO_4^{3-} in the water column decreased over time in all treatments including the control, whereas dissolved NH_4^+ concentrations increased (Fig. 5). Nutrient flux rates were not significantly different between soil and control treatments for NH_4^+ ($\text{df} = 3$, $F = 2.00$, $p = 0.202$) or $\text{NO}_2^- + \text{NO}_3^-$ ($\text{df} = 3$, $F = 2.79$, $p = 0.119$), however, a difference between treatments was measured for PO_4^{3-} fluxes ($\text{df} = 3$, $F = 5.50$, $p = 0.024$). Specifically, phosphate influx to sediment was higher in basalt compared to control and sandstone treatments, but not significantly different to the granite treatment (Fig. 5). Water column dissolved oxygen concentrations decreased faster in soil treatments compared to the control treatment ($\text{df} = 3$, $F = 14.13$, $p = 0.002$).

4 Discussion

4.1 Soil nutrient composition and nutrient release

This study showed that nutrient release from inundated soils during the experiment generally matched the initial nutrient content of each soil type. Consistent with general predictions from the

literature, subsoils were observed to have the lowest initial nutrient composition, which is likely due to lower organic matter content than the surface layers and use of limiting nutrients by plant roots at greater depths causing a shallow vertical nutrient distribution (Jobbágy and Jackson, 2001). Subsoils are dominant in the supply of catchment soil to Moreton Bay and other subtropical Queensland catchments (Garzon-Garcia et al., 2017; Wallbrink, 2004). Therefore, while our results from the flood simulation experiment show lower nutrient release from subsoils than topsoils, subsoils are still likely to be important contributors to nutrient fluxes in Moreton Bay during floods. Organic carbon concentrations also appeared to play a role in nutrient release: soils with a lowest initial organic carbon concentration had a lower release of nitrate, i.e. sandstone and granite subsoils compared to topsoils. In a floodplain soil re-wetting experiment, Heffernan and Sponseller (2004) also found that soil organic matter was strongly correlated with nitrate losses. Even though basalt, granite and sandstone topsoils had similar initial nitrogen content, basalt soil released more NH_4^+ , $\text{NO}_2^- + \text{NO}_3^-$ and DON during the experiment. Basalt soil also had the highest phosphorus content and released more PO_4^{3-} and DOP than other soil types. Basalts are among the most easily weathered rocks compared to other crystalline silicate rocks and are naturally rich in phosphorus due to their mafic igneous origins (Porder and Ramachandran, 2013; Suchet and Probst, 1993; Toplis et al., 1994). Nutrient content of eroded material is also likely to be affected by recent drought or flood cycles, with studies showing soil particles to have higher nutrient content after longer dry periods (Baldwin and Mitchell, 2000; Heffernan and Sponseller, 2004; Schönbrunner et al., 2012). Prior to soil collection in 2016, the most recent major flood in the Brisbane River catchment occurred in 2011, with minor floods in 2008 and 2013.

4.2 Nutrient release from soils during flood transport

Similar to wetland and floodplain soil inundation experiments (Lowes et al., 2008), initial wetting in freshwater triggered a rapid release of all nutrient forms. A second rapid release occurred when

the same particles are exposed to saltwater. This indicates that freshwater running into estuaries during flooding is likely to contain high nutrient concentrations. Further nutrients will be dissolved in estuarine waters once the soil particles reach saline water, where nutrients that are retained by soil particles through several days of turbulent transport in freshwater are released upon exposure to the different ionic composition of seawater. Release rates from the initial exposure to both freshwater and saltwater were significantly higher than long-term release rates (2 – 4 weeks of saltwater exposure) for all nutrients measured. Much of these rapidly released nutrients are likely to be flushed out of estuaries into coastal waters, producing a short peak of nutrient supply during and immediately after flooding (Mitchell et al., 1997; Warrick et al., 2005). This stimulates phytoplankton growth as has been demonstrated in southern Moreton Bay and other estuaries (Bruesewitz et al., 2013; Drupp et al., 2011; Murrell et al., 2007; Saeck et al., 2013). An increase in benthic metabolism in Moreton Bay has also been observed following flood-induced phytoplankton blooms, which is likely a result of input of allochthonous organic carbon and abundant phytodetritus from the post-flood bloom (Ferguson et al., 2007).

4.3 Nutrient flux in seawater following flood plume settling

Following the initial release upon exposure to seawater, most dissolved nutrients appeared to be re-sorbed to soil particles or taken up by bacteria, only to be released again after two weeks of exposure to seawater. The exception to this was PO_4^{3-} release from basalt soil and NH_4^+ release from all soils, which showed a continuing gradual release over the four-week seawater exposure.

Addition of $<63 \mu\text{m}$ soil to marine sediments (incubated cores) had a different trend, with an efflux of NH_4^+ but an influx of $\text{NO}_2^- + \text{NO}_3^-$ and PO_4^{3-} into the sediment. Although basalt soils showed high PO_4^{3-} release during the flood simulation experiment, they actually adsorbed the highest amount of PO_4^{3-} during the core incubations. The tendency of estuarine sediment to retain or

release phosphorus will affect nutrient cycling in the coastal zone. This tendency depends on the physical, chemical and biological properties of the sediment as well as conditions at the sediment-water interface (Maher and DeVries, 1994). Under oxidizing conditions, sediments retain inorganic phosphorus at considerably greater concentrations than in that of sediment pore water because phosphorus is trapped by iron oxyhydroxides in the surface oxygenated layer (Pant and Reddy, 2001). However, under reducing conditions or high carbon input, appreciable amounts of phosphorus can be released from the sediment (Maher and DeVries, 1994). This is because of the reduction of Fe(III) to the more soluble Fe(II) under anaerobic conditions and consequent release of iron-bound phosphorus (Roden and Edmonds, 1997). Reducing conditions in the water column are uncommon in the coastal zone and high initial oxygen levels in cores taken from Moreton Bay in this study indicate oxidizing conditions. Surface sediments in large tidal systems such as Moreton Bay are therefore more likely to sequester phosphorus. However, it is possible for phosphorus to be released under oxidizing conditions through re-suspension of sediments in shallow areas of coastal bays, which can create sharp gradients of soluble phosphorus at the sediment-water interface (Pant and Reddy, 2001). Phosphate sorption to calcium ions in carbonates within sediments may also account for some of the phosphate retention observed (Azzouz et al., 2012). Zessner et al., (2005) found there to be no immediate influence of flood events in upstream parts of the Danube River basin on the transport of phosphorus from the catchment to the receiving sea, due to retention by sedimentation.

The results of this study show that catchment soils are likely to be an important contributor of NH_4^+ to the saline waters of the coastal zone. Upon exposure to seawater in both the flood simulation and core incubation experiments, continual release of NH_4^+ was measured for all soil types. These results are supported by field measurements of post-flood NH_4^+ increases in estuaries and coastal bays in both modified (Bally et al., 2004; Eyre and Twigg, 1997) and natural catchments (Howley

et al., 2018). Immediate release of NH_4^+ upon exposure to freshwater or seawater is via chemical reactions. Salinity directly affects ammonium release from soil particles through ion exchange, where more NH_4^+ is generally released at higher salinities (Giblin et al., 2010). Microbes are believed to be mostly responsible for long-term NH_4^+ release over days to months post flood. Microbial processes such as nitrification, de-nitrification and dissimilatory nitrate reduction to ammonium contribute to nitrogen cycling in the coastal zone (Ferguson et al., 2007). Nitrogen cycling is complex and the prevalence of one of these processes over another is affected by water and sediment conditions, which determine abundances of bacterial communities that are present (Bernhard et al., 2007; Weston et al., 2010). Sediment bacteria are generally effective at mineralizing organic matter, both aerobically and anaerobically, releasing dissolved nutrients into the water column where they are taken up by algae and macrophytes and enter the food web (Sinkko et al., 2013).

Primary production in Moreton Bay, like most marine coastal bays, is nitrogen limited (Glibert et al., 2006; Saeck et al., 2016) and identifying sources of nitrogen forms such as NH_4^+ is important for understanding nitrogen cycling and coastal productivity. While nitrogen is essential for phytoplankton production, an overabundance of nitrogen leads to algal blooms and hypoxia in estuarine and coastal ecosystems (Howarth et al., 2011; Valiela et al., 1997; Vitousek and Howarth, 1991). Although nutrient input controls the intensity of phytoplankton blooms, frequency of storm events, wind speed, flushing rates, tidal mixing, incident solar radiation and turbidity can influence whether an environment can initiate and sustain a bloom (Drupp et al., 2011). During base flow conditions, water column nitrogen is recycled in the microbial loop and is closely linked to the carbon cycle (Bruesewitz et al., 2013). High sedimentation rates can also reduce the contact time between organic matter and dissolved oxygen in the water column, contributing to higher concentrations of carbon and nutrients in sediment (Hilton et al., 2008; Li et al., 2016).

This study demonstrates that newly deposited catchment-derived sediment is a more sustained source of NH_4^+ than the flood itself. Post-flood resuspension of sediment through wind and waves or tidal mixing is likely to supply long-term fluxes of NH_4^+ from sediment to the water column, particularly in areas with low water residence time (Dunne et al., 2010; Morin and Morse, 1999). Eyre and Twigg (1997) found that sediments transported into the Richmond River estuary (New South Wales, Australia) from its catchment during a small flood supplied NH_4^+ to the water column, sustaining primary production for almost 10 months after the flood.

4.4 Experiment limitations

The two experiments in this study were conducted simultaneously, and the soil used in the core incubation experiment had not undergone a flood simulation first, therefore the rates of NH_4^+ release in the cores are likely to be higher than expected and may represent an extreme scenario. Furthermore, smothering effects on existing sediment and resulting death of some organisms could affect the rates of NH_4^+ or $\text{NO}_2^- + \text{NO}_3^-$ flux. However this should have little influence on our results since our cores were collected from a muddy prodelta with high suspended sediment loads, where many of the organisms would be tolerant to a fine sediment environment, and loss of abundance and diversity of taxa is expected to be low compared to coarser sediments (Lohrer et al., 2006). Core incubations are useful for experimenting with microcosms of the natural environment and much can be learnt from these manipulations, although they have limitations that need to be considered. Oxygen depletion over time is expected in these closed systems but may have been exacerbated by microbial processes such as release of nutrients from soil particles and possible smothering of existing sediment. By ending measurements in each core if they reached water dissolved oxygen levels of 2 mg L^{-1} or less, we ensured that anoxic conditions were not present and although sediment oxygen levels were not measured it is unlikely that they became anoxic. While

decreases in sediment oxygen levels may occur during flood layer sedimentation, they can return to normal oxygen levels within months after a flood and it is unlikely that Moreton Bay surface sediments (top 5-10 mm) would become anoxic (Cathalot et al., 2010; Hanington et al., 2016). In addition, if sediments became anoxic, we would expect to see some release of phosphate into the water column, particularly by phosphorus rich soils such as basalt. Therefore, while rates of release in this core incubation experiment may vary from natural floods, we believe that the NH_4^+ release and $\text{NO}_2^- + \text{NO}_3^-$ and PO_4^{3-} retention observed is a valuable insight into the behaviour of soil bound nutrients when they are deposited into estuaries.

4.5 Implications for nutrient dynamics in Moreton Bay

Clearing of catchment vegetation and land use change associated with European settlement, which started in ~1840, has accelerated export of fine sediment from the catchment to Moreton Bay (Coates-Marnane et al., 2016; Kemp et al., 2015; Olley et al., 2015). All of the different catchment soils used in this experiment appear to behave similarly in terms of timing of nutrient flux during the flood transport and deposition process, but differ in rates of nutrient release or retention. Our study has shown that an increase in the supply of sediment will also have significantly increased the bio-available nutrients delivered in floodwaters, increasing the initial primary production in the bay associated with floods. Over the duration of the first experiment in this study (the flood simulation), we calculated the loss of phosphorus from soils to be approximately 0.4, 1.1, 1.2, 1 and 1.5% for GS, SS, GT, ST and BT respectively and the loss of nitrogen to be approximately 13, 8, 7, 6 and 12% for GS, SS, GT, ST and BT respectively. In the core incubation experiment, we calculated N loss from soils to be 1.6, 2.2 and 0.9% for GT, ST and BT respectively. Phosphorus coming into the bay from the catchment is likely to be sequestered in the bay sediment and the remaining pool of nitrogen in the new sediment layer may be a significant source of nitrogen, particularly ammonium, to the bay for long periods following floods. Since Moreton Bay is a nitrogen-limited system, this

prolonged release of ammonium is also likely to increase primary production in the long term. The experiments conducted here therefore show that in both the short and long term the increase in sediment supply from the catchments to Moreton Bay will have significantly increased the nutrients available for primary production.

5 Conclusions

This study gives insights into the response of sediment-bound nutrients upon exposure to the extreme hydrological and chemical changes of flood erosion, transport and deposition from catchments to the coastal zone. Three phases of nutrient release were identified; rapid release in freshwater and saltwater because of chemical release of nutrients bound to sediment particles and slower long-term release from deposited sediment likely by microbial processes. Soils from the Moreton Bay catchments appear to be an important contributor of nutrients, particularly ammonium, to the receiving coastal waters. Since Moreton Bay is a nitrogen-limited system, this prolonged release of ammonium is an important source of nitrogen to primary producers. Following floods, newly deposited sediment will likely trigger an influx or efflux of nutrients from sediment particles. Although basalt derived soils have high phosphorus content, they appear to sequester phosphorus under oxidizing conditions, which are common in Moreton Bay. A difference in nutrient release between soil types indicates that coastal productivity and biogeochemical cycling may be related to catchment geology. To further understanding of these linkages, we recommend future research to investigate the importance of microbial communities in catchment soil and estuarine sediment on nutrient dynamics and to trace estuarine sediment origins. Measuring estuarine phytoplankton productivity and food web responses to floods will help to identify whether increased sediment input in modified catchments is a benefit or detriment to coastal systems such as Moreton Bay.

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Figure list:

Figure 1. Catchment soil and Moreton Bay core collection location map. Inset map shows location within Queensland, Australia.

Figure 2. Mean ($\pm$ SD) inorganic dissolved nutrient concentrations (from top: ammonium (NH_4^+ $\mu\text{g N g}^{-1}$), nitrite + nitrate ($\text{NO}_2^- + \text{NO}_3^-$ $\mu\text{g N g}^{-1}$), phosphate (PO_4^{3-} $\mu\text{g P g}^{-1}$)) in the water for each soil type for both freshwater and saltwater addition. Different scales were used for ammonium and nitrite + nitrate for salt and freshwater. Basalt soils are represented by a solid line, topsoils of granite and sandstone are represented by a dashed line with triangle and square points, respectively, and subsoils of granite and sandstone are represented by dotted lines with triangle and square points, respectively.

Figure 3. Mean ($\pm$ SD) organic dissolved nutrient concentrations (top: dissolved organic nitrogen (DON $\mu\text{g N g}^{-1}$), bottom: dissolved organic phosphorus (DOP $\mu\text{g P g}^{-1}$)) in the water for each soil type for both freshwater and saltwater addition. Basalt soils are represented by a solid line, topsoils of granite and sandstone are represented by a dashed line with triangle and square points, respectively, and subsoils of granite and sandstone are represented by dotted lines with triangle and square points, respectively.

Figure 4. Mean ($\pm$ SD) dissolved organic carbon concentrations (DOC $\mu\text{g C g}^{-1}$) in the water for each soil type for freshwater addition. Basalt soils are represented by a solid line, topsoils of granite and sandstone are represented by a dashed line with triangle and square points, respectively, and subsoils of granite and sandstone are represented by dotted lines with triangle and square points, respectively.

Figure 5. Mean inorganic nutrient fluxes ($\text{mg}^{-1} \text{L}^{-1} \text{h}^{-1}$) in incubated Moreton Bay sediment cores with dry catchment soil addition. Error bars represent standard deviation.

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Tables

Table 1. Soil characteristics.

	Granite	Basalt	Sandstone
Topsoil depth sampled (cm)	20-30	10-50	15-20
Subsoil depth sampled (cm)	>100	-	50 – 100
Lithology	Eskdale granodiorite	Main Range volcanics	Gatton sandstone
Description	Proximal to Eskdale granodiorite – pink granite	Olivine Basalt	Feldspathic to lithic feldspathic sandstone with clay matrix
Soil type/Name	Solodic	Dermosol/Spellman	Loamy Solodic/Stockyard
Age	Early Triassic	Tertiary	Jurassic

Table 2. Dry soil nutrient composition.

Soil type and depth	Extractable nitrate (mg kg ⁻¹)	Total organic carbon (mg kg ⁻¹)	Total kjeldahl nitrogen (mg kg ⁻¹)	Total kjeldahl phosphorus (mg kg ⁻¹)
Granite subsoil (GS)	1.00	4600	400	500
Sandstone subsoil (SS)	1.00	11500	800	200
Granite topsoil (GT)	12.0	18700	1500	200
Sandstone topsoil (ST)	5.00	23800	1500	200
Basalt topsoil (BT)	11.0	23400	1600	700

Table 3. Effects of soil type and stage of flood process on the rate of release of dissolved nutrients from different soil type. Analysis of variance F statistics and significance levels (0.05 = *, 0.01 = **, 0.001 = ***) are given, including Tukey HSD post-hoc examinations. Factors include soil type (Soiltype) and Rate. Rate refers to three stages nutrient release during the flood process (freshwater (FW) quick release (0-1 h), saltwater (SW) quick release (0-1 h) and SW slow release (1-4 weeks or 2-4 weeks). GT = Granite Topsoil, GS = Granite Subsoil, BT = Basalt Topsoil, ST = Sandstone Topsoil, SS = Sandstone Subsoil.

Nutrient	Soil type	Rate (FW quick release, SW quick release, SW slow release)	Soil type* Rate interaction	Ranking of release rate (highest to lowest)	Rate Tukey HSD	Ranking of soil types (highest to lowest release rates)	Soil type Tukey HSD
NH_4^+	$F = 13.83$ ***	$F = 215.08$ ***	$F = 9.60$ ***	SW quick release	A	BT	A
						GT	AB
				FW quick release	B	SS	BC
						GS	C
				SW slow release	C	ST	C
NO_x	$F = 171.87$ ***	$F = 381.24$ ***	$F = 89.58$ ***	FW quick release	A	BT	A
						GT	B
				SW quick release	B	ST	C

				release		GS	D
				SW slow	C	SS	D
				release			
PO₄³⁻	<i>F</i> = 61.56	<i>F</i> = 31.33	<i>F</i> = 18.76	FW quick	A	BT	A
	***	***	***	release		GT	B
				SW quick	A	SS	B
				release		GS	B
				SW slow	B	ST	B
				release			
DON	<i>F</i> = 31.57	<i>F</i> = 233.72	<i>F</i> = 22.19	FW quick	A	BT	A
	***	***	***	release		GT	B
				SW quick	B	SS	B
				release		ST	BC
				SW slow	C	GS	C
				release			
DOP	<i>F</i> = 51.45	<i>F</i> = 39.40	<i>F</i> = 26.40	FW quick	A	BT	A
	***	***	***	release		ST	B
				SW quick	A	GT	B
				release		SS	B

				SW slow	B	GS	B
				release			
DOC	$F = 373.88$	-	-	FW quick release		BT	A
	***			data only		SS	B
						GT	C
						ST	C
						GS	D

Highlights

- Our study quantified the release of nutrients from soils as a result of flooding
- We showed that substantial nutrient loads are released from catchment sediments in both fresh and marine waters.
- Additionally, ammonium was released from transported and settled sediment within a marine system, while nitrite + nitrate and phosphate were retained by sediment

ACCEPTED MANUSCRIPT

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5