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Abstract

Terrestrial catchments adjacent to the Great Barrier Reef have undergone extensive anthropogenic modification over the last 150 years, including substantial land clearing and land use change. From 1996 to 2006, rates of land clearing in Queensland were among the highest in the world. More than 60% of this clearing occurred within the Brigalow Belt bioregion, which includes 98% of the Fitzroy Basin and 46% of the Burdekin Basin, both of which drain directly into the Great Barrier Reef lagoon. This land clearing and land use change has led to increased pollutant loads of nutrients, sediment and pesticides entering the Great Barrier Reef, which adversely impact the survival of this precious ecosystem. Agricultural land use is currently the largest contributor to pollutant loads.

The effects of land clearing and land use change on runoff in the Brigalow Belt bioregion are well documented. Long-term research has shown clearing of virgin brigalow scrub for cropping or grazed pasture has doubled runoff irrespective of land use. Peak runoff rates doubled when land was cleared for cropping and increased by 50% when cleared for grazed pasture. The short-term effects of land clearing and land use change on land resources such as soil fertility were also documented, but the long-term implications were not.

It was unclear how these changes in hydrology and soil fertility as a result of land clearing and land use change impacted water quality. Contemporary water quality investigations seeking to address this question are confounded by multiple issues. For example, climatic variability in central Queensland is large, so long-term monitoring is essential to develop true systems understanding. Short-term, three-to-five-year monitoring programs often fail to capture extremes in climate, so findings may not translate temporally. Broad-scale land clearing in the Brigalow Belt bioregion of central Queensland commenced in the 1960s and was generally considered to have ceased in 2006. As such, contemporary water quality data sets, while reflective of current catchment condition, likely

provide little insight into the magnitude of change in water quality immediately post clearing due to multi-decadal lags between clearing and monitoring. Larger catchment scale water quality studies can be further confounded by mixed land use within a catchment and mixed land management within a single land use. Both scenarios make it difficult to separate land use effects on water quality from land management effects on water quality, with one likely to mask the effects of the other.

When broad-scale land clearing in the Brigalow Belt bioregion of central Queensland commenced in the 1960s, changes in hydrology and soil fertility were anticipated. In order to determine the effects of this land clearing and land use change on hydrology, soil fertility and productivity, the Brigalow Catchment Study was initiated in 1965. The subsequent data collected from this long-term paired, calibrated catchment study provided an opportunity to determine the impacts of land clearing and land use change on water quality. The use of long-term data from paired catchments of a single land use, that have been monitored for hydrological and soil fertility change since prior to clearing, resolves many of the confounding factors common to contemporary water quality studies.

This study of the effects of land clearing and land use change on water quality had four objectives as follows:

1) To determine the impact of changing land use from virgin brigalow scrub into a crop or pasture system on runoff water quality;
2) To evaluate whether clearing of brigalow scrub for cropping or grazing would alter the dynamics of soil organic carbon, nitrogen, phosphorus, sulfur and potassium over time;
3) To determine the impact on water quality of managing grazing land by varying stocking rate; and

4) To determine the impact of managing grazing land with tebuthiuron, a herbicide used for broad-scale woody weed control in grazing systems, on water quality.

All four of these objectives were priority knowledge gaps of the Reef 2050 Water Quality Improvement Plan 2017-2022, the 2017 Scientific Consensus Statement and their predecessors. Long-term water quality modelling indicated that changing land use from virgin brigalow scrub to cropping or grazing increased loads of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen. The well-managed (unfertilised) pasture system had less nitrogen in runoff compared to runoff from virgin brigalow scrub. In years when runoff occurred from the agricultural catchments, but no runoff occurred from the virgin brigalow scrub, water quality loads were entirely anthropogenic and totally attributable to land use change.

These changes in water quality were modelled by extrapolating data collected at least 17 years after land clearing and land use change. During this 17-year period, significant nutrient fluxes occurred within the surface 0.1 m of the soil profile associated with clearing, burning and subsequent agricultural production. These fluxes, in particular the nine-fold increase in ammonium-nitrogen, the eight-fold increase in nitrate-nitrogen and the two to three-fold increase in bicarbonate- and acid-extractable phosphorus immediately after clearing likely resulted in extremes in water quality loads and pollutant concentrations compared to that observed in later years.

The effect of managing grazing land by varying stocking rate was greater than that of changing land use from virgin brigalow scrub to conservatively grazed pasture. Heavy grazing of improved pasture more than tripled runoff, peak runoff rate and total suspended solids loss compared to conservatively grazed pasture. Loads of total suspended solids, nitrogen and phosphorus in runoff were also greater from heavy than conservative grazing.

The effect of land management on water quality was most easily determined where the input to the system was entirely anthropogenic, such as broad-scale application of herbicide. Unlike nutrients, with no confounding natural input, herbicide loss in runoff was entirely contingent on herbicide use. Tebuthiuron loss in runoff was primarily in the dissolved phase with no correlation to total suspended solids. Concentrations of tebuthiuron in runoff declined exponentially with time, cumulative rainfall and cumulative runoff.

The new knowledge of the effects of land clearing, land use change and land management on soil fertility and runoff water quality generated in addressing the four objectives of this thesis has been extended, both spatially and temporally, by its inclusion in models for Great Barrier Reef catchments. This modelling estimates the effects of land management on water quality from catchments such as the Fitzroy Basin. Specifically, the research presented in this thesis has underpinned the design, calibration and validation of models at both the paddock and catchment scales as part of the Reef 2050 Water Quality Improvement Plan 2017-2022. This new body of knowledge has also been used to guide the development of regulations for protection of the Great Barrier Reef. These regulations were the focus of a 2020 senate inquiry, during which new knowledge from this thesis was presented in both written submissions and given as evidence.

Statement of originality

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself

Craig Thornton

June 2022

Acknowledgements

This thesis contains over 20 years of data that I have personally collected from the Brigalow Catchment Study. That sounds impressive until you consider what has been done by the multitude of people that have worked with me on the study during that time and in the more than three decades preceding me. A standard acknowledgement for the Brigalow Catchment Study is as follows

Many staff have contributed to the design and execution of the Brigalow Catchment Study. We thank H Pauli, J Rosser, A Webb, P Lawrence, R Bryant, A Dowling, H Hunter, N Cocaris, J Kalnins, R Scarborough, R Pushmann, R Gillespie, D Sinclair, B Kitchen, A Key, P Hansen, G Thomas, E Anderson, P Back, D Miles, W Burrows, M Nasser, A Lloyd, A Barnes, M Jeffery, T James, N Purvis-Smith, B Radford, B Cowie, D Reid and A Elledge, staff of the Department of Environment and Science Chemistry Centre and staff of the former Department of Primary Industries Brigalow Research Station.

To this list I would like to add co-workers, co-authors and other ardent Brigalow Catchment Study supporters who have helped me make what we colloquially refer to as Brigalow what it is today. This includes but is not limited to D Allen, B Bosomworth, R Dalal, D Freebairn , K Roots, M Silburn, S Wallace, B Yu, and staff of the Department of Environment and Science Library Services. My gratitude extends to those who went before me with the vision and persistence to establish the study; to those that held my hand at the beginning; to those that encouraged me to grow and take ownership; and to those who have worked shoulder to shoulder with me, both in the field and in the office, as I've found writing is often harder than monitoring.

I extend my apologies to family and friends who have had to endure my unending enthusiasm for Brigalow!

Acknowledgement of papers included in this thesis

Included in this thesis are published papers in *Chapters 3, 4, 5 and 6* which were co-authored with other researchers. My contribution to each co-authored paper is outlined at the front of the relevant chapter. The bibliographic details for these papers including all authors, are:

Chapter 3:

Copyright status: Elsevier permit the insertion of the post-print version of an article in an author's thesis for publication on Griffith Research Online.

Elledge A, Thornton C (2017) Effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland to a crop or pasture system on sediment, nitrogen and phosphorus in runoff over 25 years in subtropical Australia. *Agriculture, Ecosystems & Environment* **239**, 119-131.

Chapter 4:

Copyright status: Open Access.

Thornton CM, Shrestha K (2021) The Brigalow Catchment Study: V. Clearing and burning brigalow (*Acacia harpophylla*) in Queensland, Australia, temporarily increases surface soil fertility prior to nutrient decline under cropping or grazing. *Soil Research* **59**, 146-169.

Chapter 5:

Copyright status: Elsevier permit the insertion of the post-print version of an article in an author's thesis for publication on Griffith Research Online.

Thornton CM, Elledge AE (2021) Heavy grazing of buffel grass pasture in the Brigalow Belt bioregion of Queensland, Australia, more than tripled runoff and exports of total suspended solids compared to conservative grazing. *Marine Pollution Bulletin* **171**, 112704.

Chapter 6:

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Thornton CM, Elledge AE (2016) Tebuthiuron movement via leaching and runoff from grazed Vertisol and Alfisol soils in the Brigalow Belt bioregion of central Queensland, Australia. *Journal of Agricultural and Food Chemistry* **64**, 3949-3959. Copyright 2016 American Chemical Society.

Appropriate acknowledgements of those who contributed to the research but did not qualify as authors are included in each paper. Each paper is presented as published in Appendices 1 to 4.

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Craig Thornton

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Chapter 1 - Introduction

Terrestrial catchments adjacent to the Great Barrier Reef have undergone extensive anthropogenic modification over the last 150 years, including land development for urban, mining and agricultural purposes (Department of the Premier and Cabinet 2009). These land use changes have led to increased pollutant loads of nutrients, sediment and pesticides entering the Great Barrier Reef, which adversely impact the survival of this precious ecosystem, with subsequent degradation to ecosystem services and dependent economic industries (Department of the Premier and Cabinet 2009). Agricultural land uses are currently the largest contributor to pollutant loads entering the Great Barrier Reef (Department of the Premier and Cabinet 2009). The primary agricultural land uses of the 42 Mha of land within the thirty-five major catchments of the Great Barrier Reef are grazing and cropping, which account for 73% (27 Mha) and 4% (1 Mha) of the catchment area, respectively (The State of Queensland 2022).

In 2009, the Australian and Queensland Governments enacted the Reef Water Quality Protection Plan to reduce the risk of declining water quality entering the Great Barrier Reef. The primary pollutants of concern to the Great Barrier Reef, and hence the focus of the plan, were suspended sediments, nutrients (particularly dissolved inorganic nitrogen, dissolved inorganic phosphorus, particulate nitrogen and particulate phosphorus) and pesticides (particularly the Photosystem II Inhibiting herbicides (PSII herbicides) diuron, hexazinone, atrazine, ametryn and tebuthiuron) (Waterhouse *et al.* 2012). The relative risk of these pollutants was quantified by Waterhouse *et al*. (2012), who identified dissolved inorganic nitrogen losses from sugarcane in the Wet Tropics, Burdekin and Mackay Whitsunday regions as the highest priority for pollutant reduction; followed by erosion management in the grazing industry in both the Fitzroy and Burdekin basins as the equal second highest management priority for pollutant reduction.

The largest bioregion in the Great Barrier Reef catchment is the Brigalow Belt. This bioregion covers an area of approximately 36.7 Mha, from Townsville in north Queensland to Dubbo in central-western New South Wales (Cowie *et al.* 2007; Thornton *et al.* 2007). This overlays 24 Mha or 56% of the Great Barrier Reef catchment area. Substantial areas of both the Fitzroy and Burdekin basins are contained within the bioregion. It overlays about 14 Mha or 98% of the Fitzroy Basin and 5 Mha or 46% of the Burdekin Basin. The dominant land use in the bioregion is agriculture, which accounts for greater than 90% of the area (Bastin and the ACRIS Management Committee 2008). Since European settlement, 58% of this bioregion has been cleared. In 1962, the Land Development Fitzroy Basin Scheme commenced, resulting in the Government-sponsored clearing of 4.5 Mha for cropping and grazing. This clearing represents 21% of all clearing in the bioregion and 32% of the Fitzroy Basin (Thornton *et al.* 2007). Broad-scale land clearing continued in the basin until 2006 (McGrath 2007). In the preceding decade, rates of land clearing in Queensland were among the highest in the world, with estimates of between 425,000 ha and 446,000 ha cleared per year (Wilson *et al.* 2002; Lindenmayer and Burgman 2005; Reside *et al.* 2017). More than 60% of this clearing, or about 261,000 ha/yr, was undertaken in the Brigalow Belt bioregion (Wilson *et al.* 2002; Cogger *et al.* 2003). It is estimated that up to 93% of brigalow (*Acacia harphophylla*) scrub vegetation has been cleared since European settlement (Butler and Fairfax 2003; Cogger *et al.* 2003; Tulloch *et al.* 2016).

The surface water hydrology of the bioregion is relatively well understood. More than 50 years of monitoring rainfall and runoff at the long-term Brigalow Catchment Study in the Fitzroy Basin has quantified pre-European catchment hydrology and changes in hydrology when the native brigalow landscape was cleared for long-term cropping or grazing (Thornton *et al.* 2007; Silburn *et al.* 2009; Thornton and Yu 2016). The Brigalow Catchment Study is a paired calibrated catchment study which commenced in 1965 to determine the impact of land clearing and land use change as a result of the Land Development Fitzroy Basin Scheme on hydrology, soil fertility and water quality (Cowie *et al.*

2007; Thornton and Elledge 2022). The study has demonstrated that clearing brigalow for cropping or grazing on improved pasture in small catchments of 12 to 17 ha has doubled runoff, and increased peak runoff rate by about 100% and 50% under cropping and grazing, respectively (Thornton *et al.* 2007; Thornton and Yu 2016). No analysis of long-term soil fertility or water quality data sets from the study had been undertaken. Indeed, despite the intrinsic link between hydrology and water quality, and the clear focus on water quality research in Great Barrier Reef catchments, little research on the effect of land use change on water quality has been undertaken in this bioregion. This is further confounded by the difficulty of separating the impacts of climate variability from the anthropogenic impacts of changing land use from native vegetation to agriculture, and from the effects of land management on water quality.

The relative risk assessment clearly states that the knowledge gaps in our understanding of runoff water quality from agricultural systems are losses of total suspended solids from grazing systems, dissolved inorganic nitrogen losses from cropping systems, and PSII herbicide losses from both cropping and grazing systems (Waterhouse *et al.* 2012). An estimate of pre-European water quality is also essential to quantify anthropogenic change to the water quality of these systems. Filling these knowledge gaps was the key aim of this thesis. The long-term Brigalow Catchment Study, representative of the 36.7 Mha Brigalow Belt bioregion, was the primary research site for this thesis. The thesis consists of seven chapters. Chapter 1 explains why runoff water quality is a concern for the Great Barrier Reef and states the knowledge gaps that the thesis addresses. Chapter 2 presents a literature review of the link between deforestation and changes in water quantity and quality. These changes have been demonstrated globally using the paired catchment study methodology, the evolution of which is traced from the earliest recorded observations of rivers through to contemporary studies. The key learnings about the effects of deforestation on hydrology and water quality from these paired catchment studies are then noted, with specific focus on the current state of knowledge

of hydrology, and the loss of sediment, nitrogen and phosphorus in runoff from Australian studies. Chapters 3 to 6 are published journal papers addressing the four identified knowledge gaps.

Chapter 3 addresses objective one, presenting runoff water quality from both cropping and grazing systems, and the anthropogenic changes in water quality loads associated with land use change from virgin brigalow scrub to cropping or grazing. Modelling of the long-term hydrology and water quality data from the Brigalow Catchment Study has shown that an unfertilised cropping system exports higher loads of total suspended solids, nitrogen and phosphorus (total and dissolved) compared to a conservatively grazed pasture. Furthermore, grazed pasture exports higher loads of total suspended solids and phosphorus compared to brigalow scrub, but less total and dissolved inorganic nitrogen. One explanation for the variation in the magnitude and direction of pollutant differences between treatments is dilution. That is, increased runoff from either above average rainfall or a treatment effect, such as grazing pressure or a bare fallow, results in the dilution of pollutants in runoff which leads to lower event mean concentrations. This highlights the importance of reporting runoff data, as high loads are not necessarily related to high event mean concentrations.

Chapter 4 addresses objective two, presenting changes in soil fertility when changing land use from brigalow scrub to either an unfertilised cropping system or a conservatively grazed pasture. The effective depth of interaction for rainfall, runoff and soil is 0.1 to 4.0 cm (Sharpley 1985) , so the cumulative loss of sediment and nutrients in runoff and the subsequent decline in surface soil fertility over time are interrelated. In Chapter 3 it was hypothesised that pollutant loads in runoff from cropping and grazing systems declined with time since land use change and land development due to soil fertility decline in the effective depth of interaction, which is the zone where soil and runoff interact. The first step in testing this hypothesis was to determine what changes in surface soil fertility had occurred when brigalow scrub was cleared and developed for cropping or grazing.

Substantial increases in mineral nitrogen and both total and available phosphorus were found in surface soil due to ash deposition from clearing and burning native vegetation. However, total and available nitrogen and phosphorus under both agricultural systems declined over the subsequent 32 years since land use change. This sudden release of nutrients followed by long-term decline in surface soil fertility supports the hypothesis presented in Chapter 3, that current loads of nitrogen and phosphorus in runoff from cropping or conservatively grazed pasture are substantially lower than those that would have occurred in runoff within one to two years following land clearing and land use change. This highlights the importance of not just monitoring runoff pollutants, but also the fertility of the soil surface to improve understanding of agricultural land management impacts on water quality.

Chapter 5 addresses objective three, presenting grazing land management effects on runoff water quality. After four below-average rainfall years from 2015 to 2018, heavy grazing resulted in 3.6 times more total runoff and 3.3 times greater average peak runoff rate compared to conservative grazing. No runoff occurred from brigalow scrub in two of the four years, which means that no runoff would have occurred from the conservatively grazed pasture had it remained uncleared. Mean annual loads of total suspended solids, nitrogen and phosphorus (total and dissolved) in runoff were greater from the two grass pastures than from brigalow scrub, while loads from heavy grazing were greater than from conservative grazing. In contrast, event mean concentrations were lower from heavy than conservative grazing due to the dilution effect of increased runoff. In the two years with no runoff from brigalow scrub, total runoff and pollutant loads from conservatively grazed pasture were an absolute anthropogenic increase attributable to land use change.

Chapter 6 addresses objective four, focusing on the behaviour of the PSII herbicide tebuthiuron in soil and runoff. Of the five PSII herbicides noted in the Reef 2050 Water Quality Improvement Plan

2017-2022 (The State of Queensland 2018), tebuthiuron was the only one registered for use in grazing, and hence was used extensively in the Brigalow Belt bioregion. The half-life of tebuthiuron in soil averaged 100 days. Concentrations of tebuthiuron in runoff declined exponentially with time, rainfall and runoff since application. The majority of tebuthiuron was lost in the dissolved phase, rather than being transported adsorbed to suspended sediments.

Chapter 7 concludes the thesis by highlighting the new knowledge about losses of total suspended solids from grazing systems; dissolved inorganic nitrogen losses from cropping systems; and PSII herbicide losses from both cropping and grazing systems presented in Chapters 3 to 6. It also illustrates some of the tangible real-world impacts that have arisen from this thesis, including how it has facilitated knowledge exchange and contributed to the uptake of scientific knowledge into decision-making processes, which are measures of success in contemporary science (Evans and Cvitanovic 2018). Examples include demonstrating how the thesis contributed to the design, calibration and validation of the model framework that underpins the Reef 2050 Water Quality Improvement Plan 2017-2022 (The State of Queensland 2018); how the thesis contributed to government policy to reduce nutrient and sediment pollution across Great Barrier Reef catchments; and how knowledge from this thesis was provided as evidence to 2020 Senate Inquiry 'Identification of leading practices in ensuring evidence-based regulation of farm practices that impact water quality outcomes in the Great Barrier Reef' (Commonwealth of Australia 2020). Chapter 7 also provides recommendations for future research that could overcome some of the limitations of this thesis. For example, extending some of the analyses undertaken in Chapters 3 to 6 to include unpublished historical data would likely give a better estimate of the magnitude of sediment and nutrients lost in runoff immediately after land clearing, which is likely to be substantially greater than that measured decades after clearing occurred.

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Chapter 2 – Literature review

2.1 Introduction

The world's forests once covered 57% of the planets habitable land (Ritchie 2021). Over the last 10,000 years about one-third of this forest cover has been lost, with 50% of the loss occurring since 1900 (Ritchie 2021). The majority of this deforestation is attributed to land clearing for agriculture. Land clearing and land use change typically decrease water quality as a result of increased non-point source pollution (Lal 1996; Wilson 2015; Chen *et al.* 2020). This is concerning given the high level of threat to water security faced by 80% of the world's population and the moderate to high threat to 65% of global river discharge and the aquatic habitat it supports (Vörösmarty *et al.* 2010).

Since European settlement in Australia in 1788, more than 40% of Australia's forests and woodlands have been cleared (Bradshaw 2012). Within Queensland, more than 60% of forests have been cleared with the majority of land clearing occurring post-1960 (Seabrook *et al.* 2006; McAlpine *et al.* 2009; Bradshaw 2012; Lewis *et al.* 2021). From 1981 to 2000, Queensland was considered a global deforestation hotspot, and some consider it is likely to remain so (Lepers *et al.* 2005; Reside *et al.* 2017). Land clearing in Queensland has focused heavily on the Brigalow Belt bioregion, which experienced some of the highest rates of land clearing in the world, with up to 93% of vegetation communities dominated by brigalow (*Acacia harpophylla*) cleared for agriculture since European settlement (Butler and Fairfax 2003; Cogger *et al.* 2003; Tulloch *et al.* 2016).

As with deforestation globally, land clearing in the Brigalow Belt bioregion of Queensland has decreased water quality (Possingham 2003; Hamman 2016; Reside *et al.* 2017; Lewis *et al.* 2021). The Brigalow Belt bioregion intersects with fifteen of the thirty-five Great Barrier Reef catchments, so declines in water quality associated with land clearing impact the health and resilience of the Great Barrier Reef. For example, the 2017 Scientific Consensus Statement stated that "key Great

Barrier Reef ecosystems continue to be in poor condition. This is largely due to the collective impact of land run-off associated with past and ongoing catchment development, coastal development activities, extreme weather events and climate change impacts" (Waterhouse *et al.* 2017, p. 7). This feedback mechanism has been noted globally with 25% of coral reefs threatened by poor water quality as a result of land use change (Burke *et al.* 2011).

The Australian literature currently provides an incomplete story on the impacts of land development and land use change on sediment and nutrients in runoff. For example, clearing virgin brigalow forest for agriculture is known to increase runoff volume and peak runoff rate (Lawrence and Sinclair 1989; Lawrence *et al.* 1991; Siriwardena *et al.* 2006; Thornton *et al.* 2007; Peña-Arancibia *et al.* 2012; Thornton and Yu 2016; Cheng and Yu 2019), and it is well established that runoff volume and total sediment loads are higher from cropped than grazed systems (Sharpley and Smith 1994; Stevens *et al.* 2006; Silburn *et al.* 2007; Freebairn *et al.* 2009; Murphy *et al.* 2013). However, other studies in the Fitzroy Basin reported higher loads of total nitrogen and phosphorus from cropping than grazing but said nothing about dissolved species (Stevens *et al.* 2006); while Murphy *et al*. (2013) reported total and dissolved concentrations of nitrogen and phosphorus from cropping but did not consider grazing. Neither study presents any data on pre-European water quality. A lack of pre-European erosion data has confounded interpretation of anthropogenic erosion rates in studies such as Hancock *et al*. (2014) in south-eastern Australia, while Bui *et al*. (2011) conclude that anthropogenic change is not always the cause of high erosion rates and does not always accelerate erosion.

The difficulty in determining anthropogenic effects on water quality is also extensively documented in the international literature. For instance, a review of studies in North America found elevated in-stream concentrations of nitrogen and phosphorus adjacent to grazed pastures compared to streams adjacent to recreational areas with ungrazed pastures. However, counterintuitively, the

review also found streams in areas not impacted by either grazing or recreation with concentrations equal to that of streams adjacent to grazed pastures (Ostoja *et al.* 2014). Silveira *et al*. (2011) present a range of values for annual phosphorus runoff from grazed pastures in Florida, United States, highlighting the variability of the data and lamenting the major limitation in using estimates rather than actual measured data for specific sites. In the same region, Sigua *et al.* (2010) noted that anthropogenic nitrogen losses from grazed landscapes were not well understood.

A summary of the key water quality data sets from the Fitzroy Basin is presented below. To position this local knowledge of total suspended solids, total erosion, nitrogen and phosphorus within an Australian and international context, comparison is made with recent key reviews of water quality studies (Tables 2.1 to 2.4, respectively). Paired catchment studies are a key source of this data. The evolution of the paired catchment study method is reviewed in Chapter 2.2, while key findings on the effect of deforestation on hydrology as demonstrated by paired catchment studies are reviewed in Chapter 2.3. Key findings on sediment, nitrogen and phosphorus loss in runoff from the Australian data sets noted in Tables 2.1 to 2.4 are reviewed in Chapter 2.4 and 2.5, respectively. The understanding of how temporal changes in soil fertility affect runoff water quality are reviewed in Chapter 2.6, while the effects of grazing land management on water quality are reviewed in Chapter 2.7.

Table 2.1. Indicative annual load and event mean concentration of suspended sediment for native vegetation compared to the agricultural land uses of cropping and grazing in Australia, New Zealand, Africa and America.

Location	Land use	Load (kg/ha/yr)	EMC (mg/l)	Source
north-eastern Australia	native forest	280		Thornton and Elledge (2013)
South America	native forest	0.61		Nacinovic *et al.* (2014)
South America	restored native forest	25.01		Nacinovic *et al.* (2014)
South Africa	native savanna	3700		Baade *et al.* (2012)
north-eastern Australia	forest and grazing		9 – 50[a]	Howley *et al.* (2021)
north-eastern Australia	forest and grazing		41 – 426[b]	Howley *et al.* (2021)
north-eastern Australia	cropping	1200		Murphy *et al.* (2013)
north-eastern Australia	cropping	4010		Carroll *et al.* (1997)
north-eastern Australia	cropping	8480		Stevens *et al.* (2006)
north-eastern Australia	cropping		809	Thornton and Elledge (2013)
predominantly eastern Australia	cropping		2501 (162 – 5339[c])	Bartley *et al.* (2012)
Atlantic Coastal Plains United States	cropping	237 - 1823		Endale *et al.* (2014)
Pacific Northwest United States	cropping	0 - 11000		Williams *et al.* (2014)
Nigeria, west Africa	cropping		200 - 5600	Lal (1997)
northern Australia	grazing		100 - 300	Silburn *et al.* (2022)
north-eastern Australia	grazing		187	Thornton and Elledge (2013)
north-eastern Australia	grazing		500	Murphy *et al.* (2013)
north-eastern Australia	grazing	600 - 1500		Koci *et al.* (2020)
north-eastern Australia	grazing		15[a], 259[b]	Howley *et al.* (2021)
Nigeria, west Africa	grazing		40 - 1400	Lal (1997)
South Australia	horticulture	2.3 - 41		Cox *et al.* (2012)

[a]base flow, [b]event flow, [c]10th and 90th percentiles respectively.

Table 2.2. Indicative annual load of sediment yield for native vegetation compared to the agricultural land uses of cropping, grazing and horticulture in Australia, Africa and America.

Location	Land use	Load (kg/ha/yr)	Source
New Zealand	forest	103	Donovan (2022)
New Zealand	grassland	98	Donovan (2022)
New Zealand	cropping	11000	Donovan (2022)
southeast Australia	grazing	800 - 2900	Hancock *et al.* (2015)
Australia (continent)	mixed	4000	Bui *et al.* (2011)
South Africa	grazing	44.5 - 109.6	Foster *et al.* (2012)
New Zealand	grazing	830	Donovan (2022)

Table 2.3. Indicative annual load and event mean concentration of total nitrogen for native vegetation compared to the agricultural land uses of cropping, grazing and horticulture in Australia and America.

Location	Land use	Load (kg/ha/yr)	EMC (mg/l)	Source
north-eastern Australia	forest and grazing		0.21 – 0.34[a]	Howley *et al.* (2021)
north-eastern Australia	forest and grazing		0.43 – 1.4[b]	Howley *et al.* (2021)
predominantly eastern Australia	cropping		1.99 (0.71 - 3.38[c])	Bartley *et al.* (2012)
Pacific Northwest United States	cropping	0.1 - 3.03	1.2 to 19	Diaz *et al.* (2010)
midwestern United States	cropping	2.9		Vadas *et al.* (2015)
northern Australia	grazing	1 - 2		Silburn *et al.* (2022)
north-eastern Australia	grazing		2 (0.4 - 9.6)	Silburn *et al.* (2022)
north-eastern Australia	grazing	1.3 - 3		Koci *et al.* (2020)
north-eastern Australia	grazing		0.46[a], 1.02[b]	Howley *et al.* (2021)
western United States	grazing under forest		0.06	Roche *et al.* (2013)
South Australia	horticulture	0.09 - 33.1		Cox *et al.* (2012)

[a]base flow, [b]event flow, [c]10th and 90th percentiles respectively.

Table 2.4. Indicative annual load and event mean concentration of total phosphorus for native vegetation compared to the agricultural land uses of cropping, grazing and horticulture in Australia and America.

Location	Land use	Load (kg/ha/yr)	EMC (mg/l)	Source
north-eastern Australia	forest and grazing		0.03 – 0.05[a]	Howley *et al.* (2021)
north-eastern Australia	forest and grazing		0.05 – 0.39[b]	Howley *et al.* (2021)
predominantly eastern Australia	cropping		0.85 (0.1-1.65[c])	Bartley *et al.* (2012)
midwestern United States	cropping	0 - 0.2		Ginting *et al.* (2000)
midwestern United States	cropping	0.1 - 4.1		Thoma *et al.* (2005)
midwestern United States	cropping	0.55		Smith *et al.* (2015)
midwestern United States	cropping	1		Vadas *et al.* (2015)
north-eastern Australia	grazing		0.02[a], 0.17[b]	Howley *et al.* (2021)
north-eastern Australia	grazing	0.2 - 0.3	0.5 (0.4 - 1.5)	Silburn *et al.* (2022)
north-eastern Australia	grazing	0.3 – 0.5		Koci *et al.* (2020)
western United States	grazing under forest		0.02	Roche *et al.* (2013)
south-eastern United States	grazing		0.19 - 1.63	Silveira *et al.* (2011)
South Australia	horticulture	0.01 - 0.19		Cox *et al.* (2012)

[a]base flow, [b]event flow, [c]10th and 90th percentiles respectively.

2.2 Evolution of the paired catchment study methodology

Fresh water is essential for earths habitability and hence for human existence (Depetris 2021). It is of such importance that efforts to measure river heights can be traced back to the beginning of recorded history. For example, the height of the Nile River has been documented since c. 3000 BCE due to the impact of seasonal inundation or drought on crop production and future water scarcity (Bell 1975; Eltahir and Wang 1999; Depetris 2021). The philosophical and scientific understanding of river behaviour developed over the next 2,500 to 3,000 years. Key concepts in what is now known as hydrology emerged around the time of Christ. At that time, Heron of Alexandria proposed that river

discharge was a product of flow velocity and river height rather than just height alone, while Vitruvius proposed the precursor to the modern hydrological cycle by extending the work of Theophrastus (c. 372-287 BCE), who had built on the theory of Anaxagoras of Clazomenae (500-428 BCE) (Chow *et al.* 1988; Koutsoyiannis and Mamassis 2021). These concepts were determined in other parts of the world, and typically quantified by measurement, during the Renaissance by the likes of da Vinci (Chow *et al.* 1988; Koutsoyiannis and Mamassis 2021).

Between 1850 and 1900, with about half of the worlds current deforestation having already occurred, the study of rainfall and runoff evolved beyond that which occurred from the Classical period to the Renaissance into what is now known as the science of hydrology and the first catchment studies appeared (Andréassian 2004; Koutsoyiannis and Mamassis 2021; Ritchie 2021). Belgrand is typically credited with commencing the first ever catchment study in 1850. It was undertaken in France and ran for three years, monitoring three catchments differing in forest extent to determine the hydrological impacts of forests, which was a question that had polarised French citizens, scientists and government officials since the French Revolution in 1789 (Andréassian 2004). By the early 20th century catchment studies were commencing worldwide. The Sperbelgraben and Rappengraben experimental catchments were established in 1903 near Emmental, Switzerland, followed by the Ota study in Japan in 1908 and the Wagon Wheel Gap study in Colorado, United States, in 1910 (Bates 1921; Penman 1963; Hibbert 1967; Andréassian 2004; Neary 2016). The Wagon Wheel Gap study commenced a new era in catchment research, being the first of what is now known as paired catchment studies, which were specifically established to determine the effects of forests on streamflow (Bates 1921; Hibbert 1967). Prior to this, catchment studies simply attributed differences in hydrology between two or more adjacent catchments to their differing vegetation and/or land use. The key limitation of this approach was that there was no way to be certain that differences in streamflow between the two or more catchments were caused solely by

differences in forest cover or land use (Hibbert 1967). The paired catchment study approach overcame this limitation by comparing streamflow from two similar catchments during a period of calibration, and then treating one catchment while leaving the other untreated as a control to account for inherent differences in hydrology between the two catchments (Hibbert 1967; Bosch and Hewlett 1982; Cowie *et al.* 2007; Thornton *et al.* 2007).

The first paired catchment study in Australia was the Parwan Experimental Area in Victoria, which commenced in 1953. The Parwan study comprised six catchments of 1.6 ha each with land uses of native pasture, improved pasture and woodland (Wu *et al.* 1986; Nandakumar and Mein 1993; Hartland and Papworth 1995). Commencing soon thereafter in 1955 was the Corranderrk Experiment, also in Victoria. The Corranderrk study comprised three catchments of between 53 ha and 65 ha, initially vegetated with mountain ash prior to timber harvesting treatments in two of the three catchments (Langford and O'Shaughnessy 1980). Just as happened internationally, both of these studies were preceded by non-paired catchment studies such as that of Adamson (1976) who in 1951 investigated the effects of soil conservation practices using two adjacent 7 ha catchments at Wagga in New South Wales.

Understanding the relationship between forests and hydrology was also the driver that commenced Australia's longest-running paired catchment study. In the 1960s, during UNESCO's International Hydrological Decade, which initiated studies of worldwide hydrological problems including 'The Influence of Human Activity on Hydrological Regimes', the Land Development Fitzroy Basin Scheme commenced in Queensland (Cowie *et al.* 2007; Thornton *et al.* 2007). This government sponsored scheme cleared 4.5 Mha of the Brigalow Belt bioregion for agriculture. In order to quantify the impacts of this broad-scale land use change on hydrology, soil fertility and productivity, the Brigalow Catchment Study commenced in 1965 and continues as Australia's longest-running paired

catchment study (Cowie *et al.* 2007; Thornton *et al.* 2007; Thornton and Yu 2016). The Brigalow Catchment Study is a paired calibrated catchment study located in the Dawson sub-catchment of the Fitzroy Basin, central Queensland, Australia. This design seeks to avoid the limitations of paired site studies that sit apart from one another in the landscape and are confounded by inherent differences in soil, slope, vegetation and climatic sequences (Thornton and Elledge 2021). The study consists of three catchments (C1, C2 and C3) with three distinct experimental periods. Stage I was a calibration period where all catchments were virgin brigalow scrub. During Stage II, C2 and C3 were cleared via pulling of vegetation with bulldozer and chain and the fallen timber burnt *in situ*. Following clearing, C2 was developed for cropping and C3 was developed for improved pasture. C1 was retained as an uncleared control. Stage III allowed for land use comparison between the three catchments (Cowie *et al.* 2007; Thornton *et al.* 2007; Thornton and Yu 2016). As with many paired catchment studies internationally, despite being initially designed as a hydrological study to monitor runoff, the aims of the Brigalow Catchment Study have expanded over the past six decades to include water quality monitoring (McCulloch 2007; Neal and Clarke 2007; Neary 2012; Neary 2016; Guillén *et al.* 2021; Slingsby *et al.* 2021).

2.3 Deforestation and hydrological change

Since the commencement of paired catchment studies over 100 years ago, more than 200 of them have been conducted worldwide (Peel 2009). Given they were undertaken for the express purpose of determining the effects of forests on streamflow, a body of evidence about the relationship now exists. This body of evidence has been the subject of multiple reviews, many building on those that went before them. The topic usually commences with the review of Hibbert (1967), who reported 39 studies, predominantly in the United States. That review was updated by Bosch and Hewlett (1982) to a total of 94 studies. Peel (2009) notes the evolution of reviews from Bosch and Hewlett (1982) to Sahin and Hall (1996), Andréassian (2004) and then Brown *et al.* (2005), who also considered the

reviews of Hornbeck *et al.* (1993), Stednick (1996) and Vertessy (2000), for a total of 200 individual studies. This number is still an underestimate as this list of reviews and the studies contained within them is not exhaustive. For example, when Bren and McGuire (2007) undertook their enumeration of Australian paired catchment studies they noted 12 studies omitted from Brown *et al.* (2005). Hibbert (1967) presented three generalisations from the 39 studies reviewed. Firstly, reduction of forest cover increases water yield. Secondly, establishment of forest cover on sparsely vegetated land decreases water yield. Thirdly, response to treatment is highly variable and, for the most part, unpredictable. Bosch and Hewlett (1982) concluded that these generalisations were little altered by the addition of information from a further 55 studies, with the exception that Hibbert (1967) was perhaps too cautious with the third generalisation and the response was in fact predictable. Brown *et al.* (2005) noted that these reviews were dominated by studies in temperate climates and contrasted them with the review of Bruijnzeel (1989), which focused on studies in tropical climates. A key finding of Brown *et al.* (2005) was that differing catchment processes can cause similar changes in the mean annual water yield as a result of deforestation. Changes in water yield can result from changes in surface runoff, changes in baseflow, or changes in both baseflow and surface runoff. It was also noted that these processes have seasonal implications which are less well understood, as earlier reviews were typically focussed on average annual change. A key limitation identified by the review was the suitability of scaling results to larger catchments where the area subject to vegetation change is likely to be patchy and relatively small compared to the overall catchment size (Brown *et al.* 2005).

Within the Brigalow Belt bioregion of central Queensland there were quite practical reasons for the need to understand the effects of forest on streamflow. If the Land Development Fitzroy Basin Scheme was to result in successful agricultural enterprises, then water was essential. It was known that underground water was very deep and expensive to access, and that the scheme would be

almost entirely reliant on surface water of questionable reliability (Queensland Government 1967). A burning question in the 1960s was how to best design and fill a farm dam (Johnson 1968; Stringer 1976).

In the six decades since the commencement of the Land Development Fitzroy Basin Scheme, the hydrology of the Brigalow Belt bioregion and how it changed with land development has been extensively documented (Siriwardena *et al.* 2006; Thornton *et al.* 2007; Peña-Arancibia *et al.* 2012; Thornton and Yu 2016; Cheng and Yu 2019). At the small catchment scale, the Brigalow Catchment Study has unequivocally shown that clearing and developing native brigalow scrub vegetation for cropping or grazed pasture has doubled runoff (Thornton *et al.* 2007; Thornton and Yu 2016). In its pre-European state, virgin brigalow scrub yielded 5% of rainfall as runoff (Thornton *et al.* 2007). Once the brigalow scrub was cleared and developed for agriculture, the runoff component of the water balance doubled, irrespective of whether the catchment was developed for cropping or for grazed pasture (Thornton *et al.* 2007). Similarly, peak runoff rates increased by 96% when brigalow scrub was developed for cropping and 47% when developed for grazed pasture (Thornton and Yu 2016). These increases can also be exacerbated by poor land management. Overgrazing, resulting from failure to reduce stocking rate with reduced pasture productivity, more than tripled runoff and peak runoff rate compared with conservatively grazed pasture (Thornton and Elledge 2021; Thornton and Elledge 2022).

The ability to scale results from small studies to the basin scale has also been investigated, quantifying the concerns expressed by Brown *et al*. (2005). Fox example, the findings from the Brigalow Catchment Study, generated from catchments of 12 to 17 ha, were also detected at the sub-basin scale within the Fitzroy Basin. One sub-basin, the 1.644 Mha Comet River catchment, was heavily impacted by the Land Development Fitzroy Basin Scheme. From the mid-1960s to 1970,

forest cover in the catchment was reduced from about 83% to 38% which increased annual runoff by 40% (Siriwardena *et al.* 2006). This finding was supported by Cheng and Yu (2019), who investigated both the Comet River catchment and the neighbouring Upper Dawson River catchment, also a sub-basin of the Fitzroy Basin. The Upper Dawson River catchment is 1.558 Mha, a similar size to the Comet River catchment, and has a similar history of deforestation. From the mid-1960s to 2013, forest cover in the catchment was reduced from about 100% to 30%, with the peak occurrence of clearing occurring at a similar time as the Comet River catchment (Cheng and Yu 2019). Multiple lines of evidence unmistakably detected increased runoff as a result of land clearing, with the effects most pronounced in wetter years or for wetter catchments (Cheng and Yu 2019). Cheng and Yu (2019) also noted that the greater the extent of land clearing, the larger the effect on streamflow. Land clearing in the Brigalow Belt bioregion, exemplified by the Land Development Fitzroy Basin Scheme, has resulted in increased runoff basin wide, mirroring the observations of more than 200 paired catchment studies conducted over more than 100 years.

2.4 Total suspended solids in runoff

The literature shows little data on total suspended solids (TSS) in runoff from brigalow scrub. Three years of data from the Brigalow Catchment Study showed a TSS load of 280 kg/ha/yr (Thornton and Elledge 2013). Current average erosion rate for all of Australia is estimated at 4, 000 kg/ha/yr; up to 50 times higher than the pre-European erosion rate (Bui *et al.* 2011). In an international context, this is higher than the sediment yield of <1 kg/ha/yr from native forest plots and 25 kg/ha/yr from restored forest plots in mountainous regions of South America (Nacinovic *et al.* 2014); yet similar to the natural erosion rate of 3,700 kg/ha/yr from the savanna of Kruger National Park, South Africa (Baade *et al.* 2012).

A summary of suspended sediment discharge from dryland cropping in 21 Australian locations gave a mean concentration of 2,501 mg/L with 10th and 90th percentiles of 162 mg/L and 5,339 mg/L, respectively (Bartley *et al.* 2012). These values are broadly similar to sediment concentrations in runoff of 200 mg/L to 5,600 mg/L from small catchments of 2 ha to 4 ha under a variety of cropping systems in Nigeria, west Africa (Lal 1997). An event mean concentration (EMC) of 809 mg/L for TSS from cropping at the Brigalow Catchment Study is at the lower end of the range noted by Bartley *et al.* (2012) (Thornton and Elledge 2013).

A study of sediment in runoff from a zero-till dryland cropping system on Vertosols in the Fitzroy Basin, similar to the cropping system and soils of the Brigalow Catchment Study, reported an annual load of 1,200 kg/ha/yr (Murphy *et al.* 2013). This is low when contrasted to the 4,010 kg/ha/yr load from a similar cropping study on Vertosols in the Fitzroy Basin managed with conventional cultivation (Carroll *et al.* 1997). Furthermore, all of these loads are less than the 8,480 kg/ha/yr reported from cropping on shallow, more erodible sodic duplex soils on greater slopes in a nearby area of the Fitzroy Basin (Stevens *et al.* 2006). The range of observed loads is in line with studies in both the Atlantic Coastal Plains and the Pacific Northwest regions of the United States, where observed sediment loads varied between 237 kg/ha/yr to 1,823 kg/ha/yr and zero to 11,000 kg/ha/yr, respectively, depending on slope and cropping system (Endale *et al.* 2014; Williams *et al.* 2014).

A review of grazing studies throughout northern Australia found that sediment concentrations in runoff were typically in the range of 100 to 300 mg/L, but could be substantially lower for sites with high cover and low slope (Silburn *et al.* 2022). Analysis of three years of data from the Brigalow Catchment Study showed a total suspended solids EMC of 187 mg/L (Thornton and Elledge 2013), which is within the range noted by Silburn *et al*. (2022). A higher EMC of 500 mg/L from a grazed landscape in the Fitzroy Basin, similar to the Brigalow Catchment Study, was reported by Murphy *et*

al. (2013). The difference between studies is probably associated with pasture cover levels which were lower (minimum of 50%) in Murphy *et al.* (2013) compared with consistently higher levels (minimum of 80%) in Thornton and Elledge (2013). All of these concentrations lie within the range of 40 mg/L to 1,400 mg/L reported from small catchments of 2 ha to 4 ha under pasture in Nigeria, west Africa (Lal 1997).

2.5 Nitrogen and phosphorus in runoff

Literature on nutrient loads and concentrations from cropping systems is sparse compared with sediment loads. Of the 21 dryland cropping sites considered in Bartley *et al.* (2012), none were cited as measuring nutrient concentrations and being representative of more than 90% of the catchment land use. Comparisons are also confounded by the application of fertiliser which is prone to movement in runoff. For example, total nitrogen load and EMC from cropping at the Brigalow Catchment Study is less than that measured from other cropping studies in the Fitzroy Basin which had applied fertiliser (Stevens *et al.* 2006; Murphy *et al.* 2013; Thornton and Elledge 2013). However, they were slightly higher than the mean of 17 sites Australia wide (Bartley *et al.* 2012); some of which would be located on less fertile soils from which lower nutrient loads would be expected. Total phosphorus load and EMC from cropping at the Brigalow Catchment Study are also less than those measured for another study in the Fitzroy Basin (Stevens *et al.* 2006), but were equal to the mean of the 17 sites Australia wide (Bartley *et al.* 2012).

A number of studies include data on loads without concentrations, and/or concentrations without flow, limiting comparison between studies. For example, it is not possible to compare the above concentration data from cropping in the Fitzroy Basin to loads of total nitrogen (0.1 kg/ha/yr to 2.9 kg/ha/yr) and phosphorus (0 to 4.1 kg/ha/yr) in runoff from cropping systems in the highly productive corn belt of the midwestern United States (Diaz *et al.* 2010; Smith *et al.* 2015; Vadas *et al.* 2015).

As for cropping systems, data for nutrient runoff from grazing is sparse, particularly for nutrient species as opposed to total nitrogen and phosphorus (Silburn *et al.* 2022). Within Queensland, total nitrogen and phosphorus loads appear to be reasonably consistent around 2.0 mg/L (ranging from 0.4 mg/L to 9.6 mg/L) and 0.5 mg/L (0.4 m/L to 1.5 mg/L), respectively. However, lower total phosphorus concentrations (0.04 mg/L) were reported in areas of less sediment generation, such as low slopes (Silburn *et al.* 2022). These values are higher than the mean concentrations of 0.06 mg/L of total nitrogen and 0.02 mg/L of total phosphorus from 155 grazed forest sites in northern California, western United States (Roche *et al.* 2013). However, they are similar to the 0.19 mg/L to 1.63 mg/L range of total phosphorus concentrations from grazed pastures in Florida, south-eastern United States (Silveira *et al.* 2011).

Streams adjacent to grazing in the Northern Territory have similar loads for total nitrogen, but lower loads for total phosphorus. Mean annual loads were generally 1 to 2 kg/ha/yr for total nitrogen and 0.2 to 0.3 kg/ha/yr for total phosphorus, except where erosion rates were considerably lower or higher due to specific landscape processes, such as high cover or bare scalds (Silburn *et al.* 2022). Three years of data show total nitrogen load (0.6 kg/ha/yr to 2.4 kg/ha/yr) and EMC (2 mg/L to 2.6 mg/L) for grazing at the Brigalow Catchment Study are comparable to these values (Thornton and Elledge 2013). Load of total phosphorus (0.07 kg/ha to 0.57 kg/ha) is also comparable; however, EMC (0.23 mg/L to 0.3mg/L) was 40% lower, which was similar to that of other well managed grazed landscapes in the Fitzroy Basin (Murphy *et al.* 2013; Silburn *et al.* 2022).

2.6 Temporal changes in soil fertility affect runoff water quality

Soil fertility is a key determinant of runoff water quality. For example, global decline in soil fertility and pressures to increase crop and pasture yields have resulted in fertiliser application beyond optimum levels for plant production, resulting in nutrient accumulation in soil leading to substantial

loss in runoff (Bieroza *et al.* 2021; Haque 2021). Similarly, natural variation in soil fertility between undisturbed, forested catchments has been shown to influence water quality in the absence of anthropogenic activities (Joensuu *et al.* 2001; Mattsson *et al.* 2003; Finér *et al.* 2004). This suggests that determining anthropogenic changes in water quality requires an understanding of anthropogenic changes in soil fertility.

Globally, land clearing has been shown to increase certain aspects of soil fertility, such as phosphorus, sulfur and potassium, particularly where vegetation is burnt and returned to the soil as ash. These changes can be restricted to the surface soil and in some instances persist for only one to two years (Raison 1979; Ellis and Graley 1983; Kyuma *et al.* 1985; Carreira and Niell 1995; Castelli and Lazzari 2002; Brennan *et al.* 2004; Fraser and Scott 2011; Butler *et al.* 2017; MacDermott *et al.* 2017). However, other aspects of soil fertility, such as carbon and nitrogen, have been shown to decline with land clearing (May and Attiwill 2003; Oyedeji *et al.* 2016). Initial loss of fertility with land clearing is then exacerbated by land use change, such as dryland cropping without nutrient replacement, which commences a long-term decline in soil fertility (Bowman *et al.* 1990; Aguilera *et al.* 2018; Kooch *et al.* 2022). This occurs in even the most fertile Vertosol soils, including those of the most productive broadacre farming land in Australia (Dalal and Mayer 1986; Dalal 1997; Hayman and Alston 1999; Young *et al.* 2009). This suggests that the effects of anthropogenic change in soil fertility on water quality will be site specific both spatially and temporally.

The conceptual model of temporal change in soil fertility being reflected in water quality is supported by the literature. For example, Tanaka *et al.* (2021) reviewed the effects of land clearing and land use change in tropical regions on soil fertility and runoff water quality, concluding that changes in nutrient cycling, and hence soil fertility, had a direct impact on runoff water quality. This is illustrated by the clearing of tropical forest for crops or pastures on steep slopes in South America,

which decreased soil organic matter, nitrogen, phosphorus and potassium while increasing loads of suspended sediments lost in runoff (Plamondon *et al.* 1991). Wildfire, rather than fire associated with land clearing and land use change, has also been shown to impact runoff water quality. Post-fire runoff typically contains higher concentrations of suspended sediments and nutrients associated with both ash deposits and chemical changes in soil associated with heating (Smith *et al.* 2011; Cawson *et al.* 2012). Where wildfire impacts on runoff water quality have been negligible, inherently low landscape soil fertility has been suggested as the cause (Townsend and Douglas 2000). This further supports the conceptual model that anthropogenic changes in soil fertility on water quality will be site specific both spatially and temporally. Indeed a global review described the effects of fire on nutrient export in runoff as varied and nuanced, often with no clear environmental indicators (Klimas *et al.* 2020). Consequently, in order to determine historical changes in water quality in the Brigalow Belt bioregion, it will be essential to determine how soil fertility has fluctuated over time, especially in catchments subjected to broad-scale land clearing and land use change.

2.7 Grazing land management affects runoff water quality

Land clearing and land use change in the Brigalow Belt bioregion is a primary driver of water quality change. However, after this initial perturbation, land management is likely to be the biggest anthropogenic driver of water quality change. Grazing is the primary land use within the Great Barrier Reef catchment of the Brigalow Belt bioregion, so grazing land management is likely to be a primary driver of water quality change. Grazing land management typically affects water quality in two ways. The first are management actions that affect catchment hydrology and fertility which subsequently change water quality in the absence of external inputs. For example, increases in stocking rate led to decreases in ground cover, which in turn increase runoff, erosion and nutrient loss (Nelson *et al.* 1996; Murphy *et al.* 2008; Schwarte *et al.* 2011; Silburn *et al.* 2011). The second are management actions that affect water quality due to an entirely anthropogenic input to the

catchment. For example, the application of herbicides which are then lost in runoff (Waterhouse *et al.* 2012).

2.7.1 The effects of managing grazing land by varying stocking rate on water quality

In the absence of external inputs, managing grazing pressure by varying stocking rate is the most common grazing land management technique as it is the most powerful management tool available to the grazier (Lawrence and French 1992). Varying stocking rate is the core principle of all grazing management techniques (Costa *et al.* 2021) including set stocking (Watson 1964), variable stocking (Hunt 2008), rotational grazing (Porensky *et al.* 2021), and other adaptive management practices (DeLonge and Basche 2018). While varying stocking rate is usually undertaken for the purpose of matching animal intake to pasture production, it also has a direct effect on water quality. For example, it has been documented for over 100 years that heavy continuous grazing accelerates runoff and erosion (Hubbard *et al.* 2004). This is due to grazing decreasing ground cover and increasing compaction, which consequently decreases protection from raindrop impact, decreases aggregate stability and infiltration, while increasing runoff. These impacts were greater from heavy grazing than conservative or rotational grazing (Eldridge *et al.* 2016; Byrnes *et al.* 2018; Sirimarco *et al.* 2018; Xu *et al.* 2018; McDonald *et al.* 2019; Wang and Tang 2019; Lai and Kumar 2020). Thus, erosion and sediment transport are primarily associated with high-density stocking and/or poor forage stands on grazed landscapes (Hubbard *et al.* 2004). This suggests that the effects of grazing management on water quality will also be site specific both spatially and temporally.

2.7.2 The effects of managing grazing land with tebuthiuron herbicide on water quality

Grazing land management in the Brigalow Belt bioregion using broad-scale anthropogenic inputs is uncommon. Typically, inputs to most grazing lands in Queensland are minimal with virtually no use of fertilisers or irrigation (Department of Environment and Resource Management 2011). Where the

nutritional value of pastures is low it is typically more economical to provide nutritional supplements directly to cattle rather than via fertiliser application to pastures themselves (McIvor *et al.* 2011). One instance where broad-scale anthropogenic inputs are made to grazing systems in the Brigalow Belt bioregion is weed control with herbicide, in particular tebuthiuron. Tebuthiuron is a photosystem II herbicide that is registered internationally for use in grasslands and grazing systems in South Africa and the United States (United States Environmental Protection Agency 1994; du Toit and Sekwadi 2012), and in sugarcane in Brazil (Cerdeira *et al.* 2007; International Union of Pure and Applied Chemistry 2015). It is not approved or known to be used in European countries (International Union of Pure and Applied Chemistry 2015; European Commission 2016). Granular tebuthiuron has been registered in Australia since the 1980s and is used to control regrowth of brigalow (*Acacia harpophylla*), tea tree (*Melaleuca* spp.), and other problem woody weeds on grazing lands in Queensland (Dow AgroSciences 2013b; Dow AgroSciences 2013a; King *et al.* 2013).

The impacts of photosystem II herbicides, including tebuthiuron, on water quality are of particular concern in the Great Barrier Reef catchments of the Brigalow Belt bioregion due to their environmental effects upon reaching the marine environment. They are toxic to coral (Jones and Kerswell 2003), microalgae (Magnusson *et al.* 2010) and seagrass (Flores *et al.* 2013). Tebuthiuron from the grazing industry has been detected in Great Barrier Reef flood plumes from the Wet Tropics, Burdekin, Mackay-Whitsunday, and Fitzroy catchments. The greatest concentrations of tebuthiuron found in flood plumes were 0.014 µg/L from the Fitzroy Basin and 0.006 µg/L from the Burdekin Basin (Kennedy *et al.* 2012b), both of which intersect with the Brigalow Belt bioregion. Tebuthiuron is persistent and stable in both fresh and marine waters (Mercurio *et al.* 2015; Mahlalela *et al.* 2021), regularly exceeding various guideline values (Álvarez-Ruiz *et al.* 2021). For example, Kennedy *et al.* (2012a) reported tebuthiuron concentrations exceeding the Australian and New Zealand Environment and Conservation Council trigger value of 0.02 µg/L for 99% ecological

protection at sites 3 km to 11 km from the mouth of the Burdekin River and up to 240 km from the mouth of the Fitzroy River. King et al. (2017) proposed a concentration of 4.8 µg/L as a guideline value for 99% ecological protection in freshwater ecosystems.

Tebuthiuron is highly soluble with low soil adsorption, hence is at high risk of being lost in runoff and drainage (United States Environmental Protection Agency 1994; Matallo *et al.* 2005; Gama *et al.* 2017; Qian *et al.* 2017; Faria *et al.* 2018). There is some evidence that soil organic matter and clay content are related to tebuthiuron movement (Chang and Stritzke 1977; Bovey *et al.* 1978; Scifres 1980). However, both these parameters also govern infiltration, drainage and runoff, hence the hypothesis of tebuthiuron adsorption to explain differences in tebuthiuron movement in soils of varying clay content (Emmerich *et al.* 1984; Matallo *et al.* 2005) is likely a surrogate for soil profile hydrology, rather than actual adsorption to soil particles. Experiments to determine the environmental fate of tebuthiuron have typically been conducted in laboratory settings (Matallo *et al.* 2005), or in high rainfall sugarcane systems in China (Qian *et al.* 2017) and South America (Gama *et al.* 2017; Faria *et al.* 2018); neither of which reflect the semi-arid subtropical Brigalow Belt bioregion. Similarly, a literature review using “tebuthiuron” and “Australia” in 2015 found 13 journal papers. Six of these studies focused on freshwater and/or marine water quality at the reef catchment scale (Lewis *et al.* 2011; Kennedy *et al.* 2012a; Kennedy *et al.* 2012b; Kroon *et al.* 2012; Lewis *et al.* 2012; Smith *et al.* 2012); five studies determined the impacts and toxicity of herbicides to a range of organisms, including plants, fish, algal, coral, and seagrass (Lane *et al.* 1997; Jones and Kerswell 2003; van Dam *et al.* 2004; Bengtson Nash *et al.* 2005; Magnusson *et al.* 2010); one study assessed the role of herbicides on sustainability and water quality of forest ecosystems (Neary and Michael 1996); and another study considered the use of chemically reactive barriers for the treatment of runoff and drainage containing herbicides (Craig *et al.* 2015). Some of these studies focus on PSII herbicides as a group rather than quantifying the concentration and effects of

tebuthiuron as an individual herbicide. Most of the published literature, particularly relating to water quality, has monitored large areas containing multiple land uses with interpretation of tebuthiuron data from grazing inferred rather than measured directly. Furthermore, this literature review found no Australian data relevant to the movement of tebuthiuron in soil or in runoff from grazed pastures at the small catchment scale. This suggests a substantial knowledge gap regarding the effects of grazing land management with tebuthiuron on water quality in the Great Barrier Reef catchments of the Brigalow Belt bioregion.

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Chapter 3 – Effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland to a crop or pasture system on sediment, nitrogen and phosphorus in runoff over 25 years in subtropical Australia

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My contribution to the paper involved:

Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Writing, - Original Draft, Writing - Review & Editing.

(Signed) _____ (Date) 03/06/2022____

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3.1 Abstract

Native vegetation has been extensively cleared for agricultural systems worldwide, resulting in increased pollutant loads that often have adverse impacts downstream. This study uses 25 years of flow data and 10 years of sediment, nitrogen and phosphorus (total and dissolved) event mean concentrations from paired catchments to quantify the effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland in a semi-arid subtropical region of Australia into an unfertilised crop or conservatively grazed pasture system. Both the cropped and grazed catchments exported higher loads of sediment and phosphorus than the virgin brigalow catchment; however, the grazed catchment exported less total, oxidised and dissolved nitrogen than the virgin brigalow catchment. The cropped catchment exported higher loads of all water quality parameters compared to the grazed catchment. The simple hydrology and water quality model presented was effective for measuring the effect of land use change on runoff water quality. Variations in water quality between the three catchments are likely due to the presence of native legumes, ground cover, tillage practices and pasture rundown.

3.2 Introduction

Worldwide, the total area of forests in 2010 was estimated to be four Bha, or 31% of the total land area (Food and Agriculture Organization of the United Nations 2010). Deforestation is typically associated with natural causes, such as fire and drought, and change of land use to agriculture. However, rates of net gain and loss vary between country and agro-ecological zones (Food and Agriculture Organization of the United Nations 2010). For example, in Australia the Fitzroy Basin Land Development Scheme commenced in 1963 resulting in 4.5 Mha of virgin brigalow woodland being cleared for agriculture. This scheme continued through to the 1990s (Department of Lands 1968; Partridge *et al.* 1994), with broad-scale clearing in

Queensland only ceasing in 2006 (Thornton *et al.* 2012). In 2009, 74.8% (11.7 Mha) of the Fitzroy Basin was being used for agricultural purposes, with 71.5% grazed and 3.2% cropped (Australian Bureau of Statistics 2009).

Pollutant loads exported in runoff have increased from natural rates as a consequence of broad-scale clearing of native vegetation and subsequent change of land use to agriculture. For example, Kroon *et al*. (2012) estimated that since European settlement mean annual loads exported from the thirty-five catchments along the coast of Queensland, Australia, into the Great Barrier Reef have increased 5.5 times for total suspended sediment (17,000 kt/yr), 5.7 times for total nitrogen (80,000 t/yr) and 8.9 times for total phosphorus (16,000 t/y). Transport of sediment and nutrients from the landscape into the Great Barrier Reef causes increased eutrophication and turbidity (Hansen *et al.* 2002; Brodie *et al.* 2011), which can lead to crown-of-thorns starfish (*Acanthaster planci*) outbreaks and coral mortality (Brodie and Waterhouse 2012; De'ath *et al.* 2012). The impact of different agricultural activities on downstream water quality is an issue in common with other parts of Australia and the world (Dilshad *et al.* 1996; Lal 1996; Barlow *et al.* 2007; Vink *et al.* 2007; Jarvie *et al.* 2010; Brion *et al.* 2011; Bossa *et al.* 2012; Singh and Mishra 2014).

It is well documented that runoff volume and/or sediment load increase when native forest is cleared for agriculture (Siriwardena *et al.* 2006; Cowie *et al.* 2007; Thornton *et al.* 2007; Hunter and Walton 2008). Numerous studies have also demonstrated higher runoff volume and/or sediment loads from cropped than grazed areas (Stevens *et al.* 2006; Freebairn *et al.* 2009; Murphy *et al.* 2013; Wilson *et al.* 2014). However, studies that have reported nutrient loads from agricultural systems tend to focus on total loads rather than dissolved loads (O'Reagain *et al.* 2005; Stevens *et al.* 2006; Povilaitis *et al.* 2014; Wilson *et al.* 2014). Dissolved nutrients pose

a great risk to aquatic systems, as they are less likely to settle than nutrients bound to sediment (Silburn *et al.* 2007). For example, Devlin and Brodie (2005) mapped flood plumes from rivers exporting into the Great Barrier Reef over nine years and found that most suspended solids and associated particulate nutrients were deposited within 10 km of the river mouth while dissolved nutrients were transported with the plume 50 to 200 km from the river mouth.

Studies that have reported both total and dissolved nutrients are typically at the catchment scale (Packett *et al.* 2009; Joo *et al.* 2012; Li *et al.* 2014), but catchments often have multiple land uses within the monitored area so it is difficult to separate the impacts of each land use on water quality (Bartley *et al.* 2012; Li *et al.* 2014; Povilaitis *et al.* 2014). Bartley *et al*. (2012) reviewed 755 sediment, nitrogen and phosphorus data points from studies across Australia for use in catchment scale water quality models. They found that a catchment with less than 90% of a specific land use could have its water quality signature influenced by the other land uses, whereas a catchment dominated by a single land use (>90%) was a more appropriate representation of that specific land use. However, using data from sites with more than 90% of the area dominated by a single land use dramatically reduced the number of data points and also biased data towards smaller plot sizes for intensive land uses, such as sugarcane, which rarely cover large areas of a catchment (Bartley *et al.* 2012). Thus, there is currently a paucity of total and dissolved water quality data from areas greater than plot scale that are dominated by a single land use.

This study investigates the impact of changing land use from a virgin brigalow woodland into a crop or pasture system on runoff water quality. It models data based on a 17 year calibration period of three catchments in their virgin condition before changing the land use of two

catchments to agriculture, and subsequent monitoring of all three catchments to collect 25 years flow and 10 years water quality data. The model presented uses long-term event mean concentrations (EMCs) with a regression based flow model described by Thornton *et al*. (2007). This research is unique as it: 1) reports on total and dissolved nitrogen and phosphorus in addition to sediment; and 2) compares both cropped and grazed catchments with a virgin woodland control catchment. This study improves understanding on the impact of agriculture on runoff water quality relative to the pre-European landscape and provides a comparison of water quality from crop and pasture systems.

3.3 Methods

3.3.1 Site description

The Brigalow Catchment Study (24°48'S and 149°47'E) is a paired, calibrated catchment study located near Theodore in central Queensland, Australia (Figure 3.1). It was established in 1965 to quantify the impact of land development for agriculture on hydrology, productivity and resource condition (Cowie *et al.* 2007). The study site was selected to represent the Brigalow Belt Bioregion which covers an area approximately 36.7 Mha from Townsville in north Queensland to Dubbo in central-western New South Wales (Thornton *et al.* 2007). The site in its native state was dominated by brigalow (*Acacia harpophylla*) trees, either in a monoculture or in association with other species, such as belah (*Casuarina cristata*) and Dawson River blackbutt (*Eucalyptus cambageana*) (Johnson 2004). The extant uncleared vegetation at the Brigalow Catchment Study is classified as regional ecosystems 11.4.8, woodland to open forest dominated by *Eucalyptus cambageana* and *Acacia harpophylla*, and 11.4.9, open forest and occasionally woodland dominated by *Acacia harpophylla* (Queensland Government 2014). Slope of the land averages 2.5% (range from 1.8 to 3.5%) and soils are an association of black and grey Vertosols, black and grey Dermosols, and black and brown Sodosols. Vertosols and

Dermosols (clay soils) cover approximately 70% of Catchments 1 and 2, and 58% of Catchment 3; Sodosols cover the remaining area (Cowie *et al.* 2007). These soil types are representative of 67% of the Fitzroy Basin under grazing: 28% Vertosols, 28% Sodosols and 11.3% Dermosols (Roots 2016). The region has a semi-arid, subtropical climate and mean annual hydrological year (October 1965 to September 2014) rainfall at the site was 661 mm.

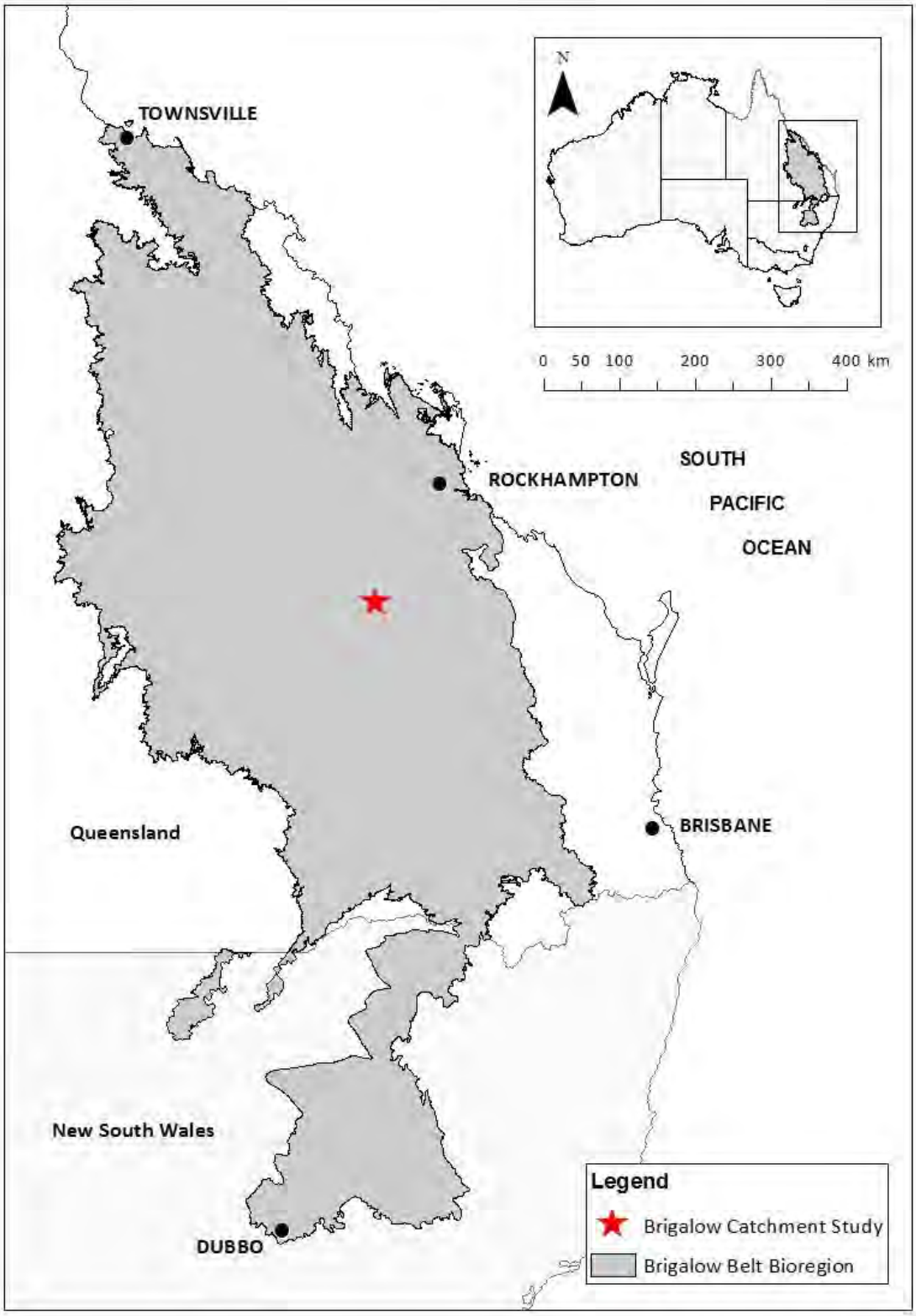

Figure 3.1. Location of the Brigalow Catchment Study within the Brigalow Belt Bioregion of central Queensland, Australia.

3.3.2 Calibration and development of catchments

Three contiguous catchments were monitored for rainfall and runoff from 1965 to 1982 (17 years). Each catchment was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 x 6.1 m concrete approach box. Water heights through the flumes were recorded using mechanical float recorders and converted to discharge using a rating table. Rainfall was recorded adjacent to each flume and at the top of the catchments using a tipping bucket rain gauge (Thornton *et al.* 2007). A runoff event was defined as commencing when stage height exceeded zero and finished when it returned to zero. These data were used to derive mathematical relationships to predict runoff from Catchment 2 (C2) and Catchment 3 (C3) given known runoff from Catchment 1 (C1) (Thornton *et al.* 2007). During this period, it was found that C2 and C3 in their uncleared state had 95% and 72% of the runoff from C1, respectively. Each catchment had its own intrinsic hydrological signature; for example, C3 had more runoff events but less total runoff volume on an annual basis compared to C1 and C2. Nonetheless, approximately 5% of the mean annual rainfall become runoff in all three catchments (Thornton *et al.* 2007).

Land development occurred between 1982 and 1983; that is, C1 remained virgin brigalow woodland to provide an uncleared control treatment, while C2 and C3 were cleared using a chain dragged between two dozers and the fallen timber burnt in-situ (Cowie *et al.* 2007). C2 was then developed for cropping with the construction of contour banks and grassed waterways, while C3 was developed for grazing by the planting of improved buffel grass pasture (Figure 3.2).

3.3.3 Land use comparisons

Rainfall and runoff were monitored from the virgin brigalow woodland (C1), cropped (C2) and grazed (C3) catchments from 1984 until 2010 (Thornton and Elledge 2013). This equates to 25 full hydrological years (October to September) monitoring and two incomplete hydrological years; July 1984 to September 1984, and October 2009 to January 2010. Over the 25 years, C2 had one sorghum crop followed by nine monoculture wheat crops, and then was opportunity cropped with sorghum (*Sorghum bicolor*), wheat (*Triticum spp.*), barley (*Hordeum vulgare*) or

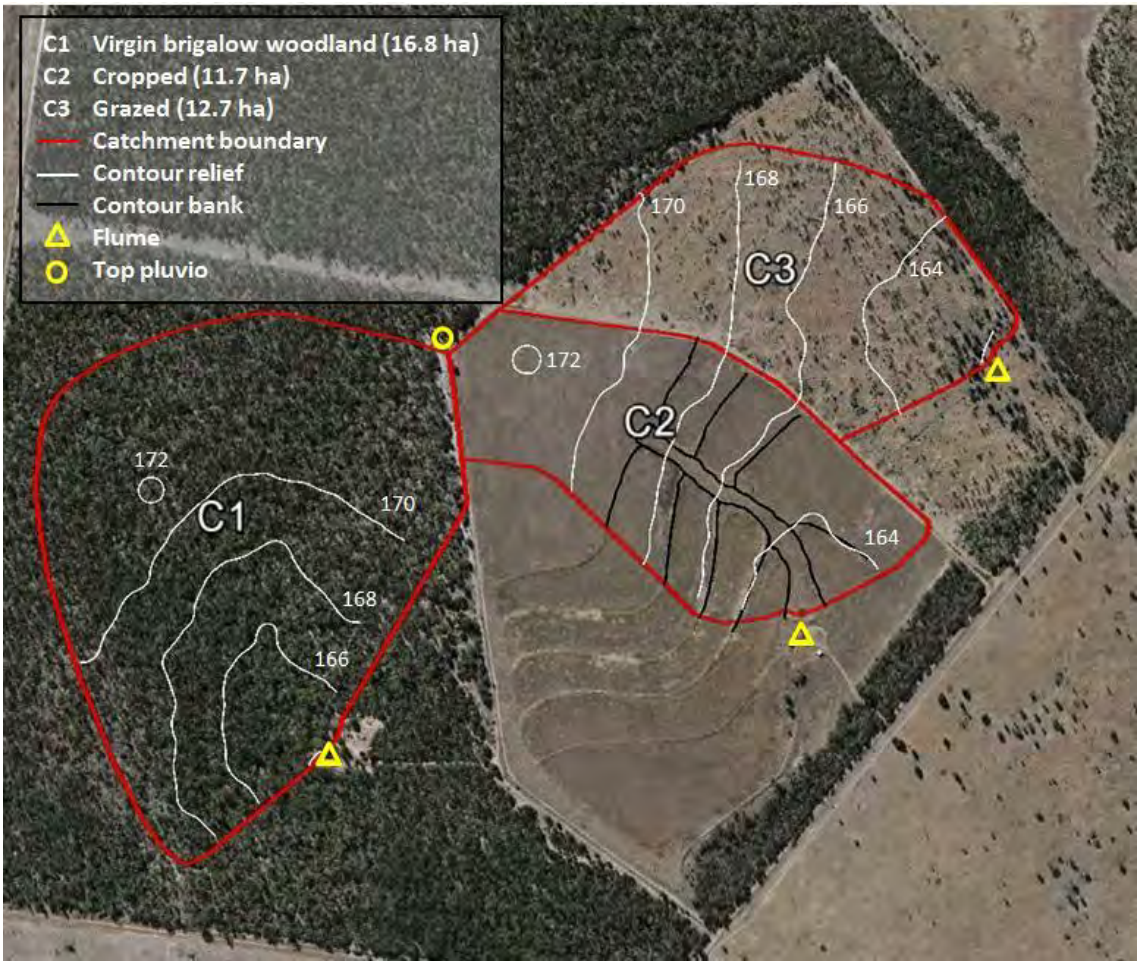

Figure 3.2. Aerial photo of the three catchments monitored at the Brigalow Catchment Study following land use change of two catchments from virgin brigalow woodland to crop and pasture systems.

chick peas (*Cicer arietinum*). Zero or reduced till fallows were introduced in 1990. There were no fertiliser inputs in the cropped catchment (Radford *et al.* 2007). C3 was grazed at industry recommended stocking rates with utilisation to result in no less than 1000 kg/ha of pasture available at any time. Conservative management of this catchment has resulted in groundcover averaging 91% since 2000 (earlier data not available), which is greater than paddocks of the same land type within a 50 km radius which averaged only 74% (Fitzroy Basin Association 2016). The foliage projective cover of tree regrowth in C3 has remained below 15% (Department of Science 2016). There was no fertiliser inputs or supplement feeding in the pasture catchment (Radford *et al.* 2007).

Discrete water quality samples were obtained using auto-samplers from 2000 to 2010. Auto-samplers were programmed to sample every 0.1 m change in absolute stage height. Runoff samples were analysed for seven parameters by Queensland Health Forensic and Scientific Services (https://www.health.qld.gov.au/qhcss/qhss/) (Table 3.1).

Event based water quality loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the loads over all the intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Where samples were only collected on the rising limb of the hydrograph, the event peak was considered to be the end of the sampling interval for the last discrete sample, and the mean concentration of the discrete samples was applied to flow from the event peak to the event end. Event based EMCs were calculated by dividing total event load by total event flow.

Table 3.1. Methods used by Queensland Health Forensic and Scientific Services for sediment, nitrogen and phosphorus analyses of water samples.

Parameter	Method
Total Suspended Solids	Method 18211 based on gravimetric quantification of solids in water.
Total Nitrogen	Method 13802 by simultaneous persulfate digestion. For the period 2000 to 2003, method 13804 based on simultaneous Kjeldahl digestion was reported and total nitrogen was manually calculated as total Kjeldahl nitrogen + oxidised nitrogen.
Oxidised Nitrogen	Method 13798 based on flow injection analysis of nitrogen as oxides.
Ammonium Nitrogen	Method 13796 based on flow injection analysis of nitrogen as ammonia.
Dissolved Inorganic Nitrogen	Manually calculated as oxidised nitrogen + ammonium nitrogen.
Total Phosphorus	Method 13800 by simultaneous persulfate or Kjeldahl digestion.
Dissolved Inorganic Phosphorus	Method 13799 by flow injection analysis; also known as orthophosphate.

Mean annual EMC was calculated by averaging the event based EMCs. These values were then averaged to determine the long-term EMC for each catchment. Where missing flow data occurred, estimations were obtained using the “HowLeaky?” modelling approach of Thornton *et al*. (2007). Where missing water quality data occurred, estimations were obtained by

multiplying the long-term EMC by the observed flow. Mean annual load was calculated by dividing the cumulative observed load for each catchment by the number of full hydrological years monitoring data (n=25). The effect of changing land use from virgin brigalow woodland to crop or pasture systems on sediment, nitrogen and phosphorus loads (kg/ha) on an event basis were calculated by:

$$\left(\frac{(Q_{Obs} \times EMC_{Current}) - (Q_{Est} \times EMC_{Brigalow})}{1{,}000{,}000}\right) \div Area$$

Model parameters were defined as follows:

Q_{Obs}	=	Observed discharge from the catchment under current land use (L/event)
$EMC_{Current}$	=	Observed long-term event mean concentration from the catchment under current land use (mg/L)
Q_{Est}	=	Estimated discharge from the catchment had it remained virgin brigalow woodland (L/event) (Thornton *et al.* 2007)
$EMC_{Brigalow}$	=	Observed long-term event mean concentration from the virgin brigalow catchment (mg/L)
Area	=	Catchment area (ha)

Observed load was calculated by multiplying the observed event flow from 1984 to 2010 by the long-term EMC (2000 to 2010) for the respective catchment. Predicted load was calculated by multiplying the estimated flow of C2 and C3 had they remained virgin brigalow woodland (using the relationship of flow between the catchments during the calibration phase from 1965 to 1982; for example, C2 in an uncleared state had 95% of the runoff from C1) by the EMC for the virgin brigalow catchment. Mean annual land use change effect was calculated by dividing the cumulative difference in observed and predicted loads by the number of full hydrological

years of monitoring data (n=25). The assumptions of this approach are that water quality from the three catchments in their virgin state would have been similar, and that the long-term EMC values for C1 apply to all catchments had they remained virgin brigalow woodland.

3.4 Results

3.4.1 Hydrology

Total annual rainfall exceeded the long-term mean annual rainfall of 661 mm for the Brigalow Catchment Study in 10 out of the 25 full hydrological years monitored (Figure 3.3). Observed mean annual runoff from the cropped and grazed catchments were 2.48 times (65.8 mm) and 1.97 times (52.2 mm) greater than observed runoff from the virgin brigalow woodland (26.5 mm), respectively. Similarly, observed runoff from the cropped catchment was 2.60 times greater than predicted runoff from this catchment had it remained uncleared (25.3 mm), and observed runoff from the grazed catchment was 2.74 times greater than predicted runoff from this catchment had it remained uncleared (19.0 mm). The rate of increase in cumulative runoff was greater in years with above average rainfall, particularly from 1987 to 1989 and 1996 to 1999 (Figure 3.4). Over the 25 year period, the virgin brigalow catchment discharged a total of 663 mm runoff over 45 days, the cropped catchment discharged a total of 1647 mm runoff over 99 days, and the grazed catchment discharged a total of 1304 mm runoff over 80 days.

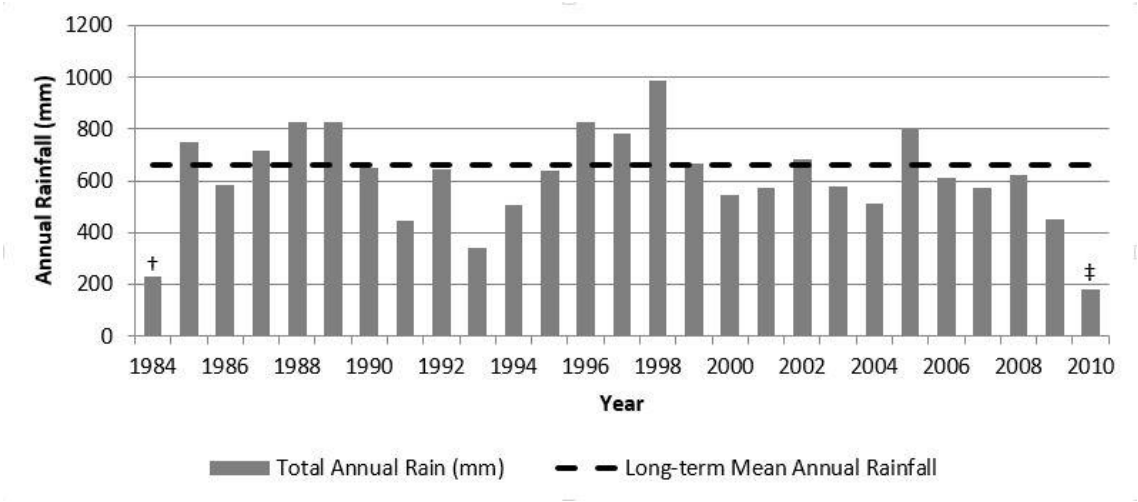

Figure 3.3. Total annual hydrological year rainfall (mm) for 1984 to 2010 relative to the long-term mean annual rainfall for the Brigalow Catchment Study. † Total rainfall only from 25/07/1984, as this relates to the first runoff event recorded at the Brigalow Catchment Study following land development. ‡ Total rainfall only to 19/01/2010, as event data after this date was excluded from the presented model due to a change in management practices.

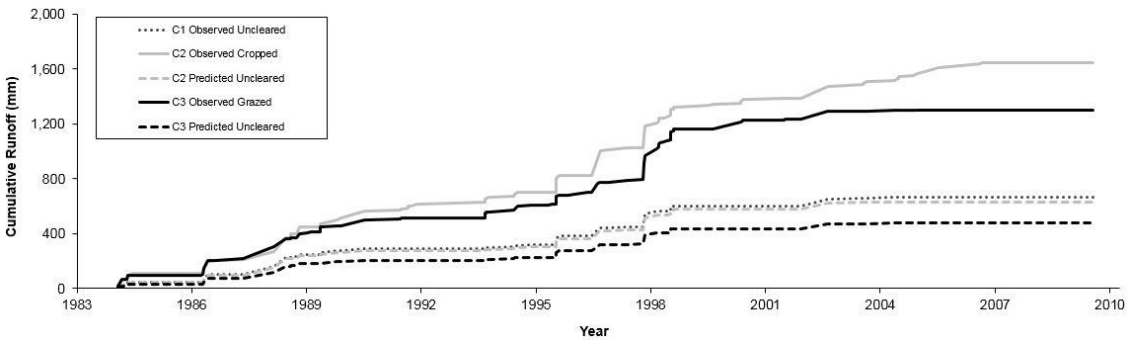

Figure 3.4. Cumulative runoff (mm) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted runoff for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

3.4.2 Event mean concentrations

Long-term EMCs for the three monitored catchments from 2000 to 2010 are presented in Table 3.2. Concentrations of total, oxidised and dissolved inorganic nitrogen from virgin brigalow woodland were 1.83, 2.89 and 2.78 times greater than concentrations from the cropped catchment and 4.53, 95.10 and 59.89 times greater than concentrations from the grazed catchment, respectively. In contrast, concentrations of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen from the cropped catchment were 2.60, 2.90, 3.00 and 1.73 times greater than concentrations from the virgin brigalow catchment and 3.49, 2.26, 1.57 and 2.67 times greater than concentrations from the grazed catchment, respectively.

Table 3.2. Long-term event mean concentrations (mg/L) of sediment, nitrogen and phosphorus for the virgin brigalow woodland, cropped and grazed pasture catchments over 10 years (2000 to 2010).

Parameter	**Event Mean Concentration (mg/L)**		
	Woodland (C1)	**Crop (C2)**	**Pasture (C3)**
Total Suspended Solids	307	798	229
Total Nitrogen	9.85	5.37	2.17
Oxidised Nitrogen	6.27	2.17	0.07
Ammonium Nitrogen	0.06	0.11	0.04
Dissolved Inorganic Nitrogen	6.32	2.27	0.11
Total Phosphorus	0.32	0.93	0.41
Dissolved Inorganic Phosphorus	0.12	0.35	0.22

Overall, the proportion of dissolved inorganic phosphorus that comprised total phosphorus was 37% from the virgin brigalow catchment, 38% from the cropped catchment and 55% from the grazed catchment. The proportion of ammonium nitrogen that comprised dissolved inorganic nitrogen was 1% from the virgin brigalow catchment, 5% from the cropped catchment and 38% from the grazed catchment.

3.4.3 Sediment, nitrogen and phosphorus loads

Cumulative loads of sediment, nitrogen and phosphorus are presented in Figures 3.5 to 3.11. Similar to runoff, the rate of increase in cumulative loads was greater in years with above average rainfall, particularly from 1987 to 1989 and 1996 to 1999.

The cropped catchment exported more sediment and nutrients (total and dissolved) than the grazed catchment over the 25 year period (Table 3.3). Changing land use from virgin brigalow woodland to either agricultural system increased loads of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen; the cropped catchment exported 6.45, 7.21, 7.45 and 4.29 times greater loads and the pasture catchment exported 1.46, 2.53, 3.75 and 1.27 times greater loads, respectively. In contrast, loads of oxidised and dissolved inorganic nitrogen were higher from virgin brigalow woodland than both agricultural systems; 1.16 and 1.12 times greater than loads from the cropped catchment and 48.34 and 30.44 times greater than loads from the grazed catchment, respectively. The virgin brigalow and cropped catchments exported 2.30 and 3.12 times greater total nitrogen than the pasture catchment, respectively.

Observed mean annual loads of total suspended solids, total phosphorus and dissolved inorganic phosphorus from the cropped catchment were 6.88, 7.70 and 7.95 times greater,

respectively, than predictions from this catchment had it remained uncleared (Table 3.3). Total and ammonium nitrogen were also 1.42 and 4.57 times greater than uncleared predictions, whereas uncleared predictions of oxidised and dissolved inorganic nitrogen were conversely 1.09 and 1.05 times greater than the observed means from this catchment under cropping, respectively. Observed mean annual loads of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen from the grazed catchment were 1.80, 3.11, 4.61 and 1.56 times greater, respectively, than predictions from this catchment had it remained uncleared (Table 3.3). In contrast, uncleared predictions of total, oxidised and dissolved inorganic nitrogen were 1.65, 39.36 and 24.79 times greater than the observed means from this catchment under grazing, respectively.

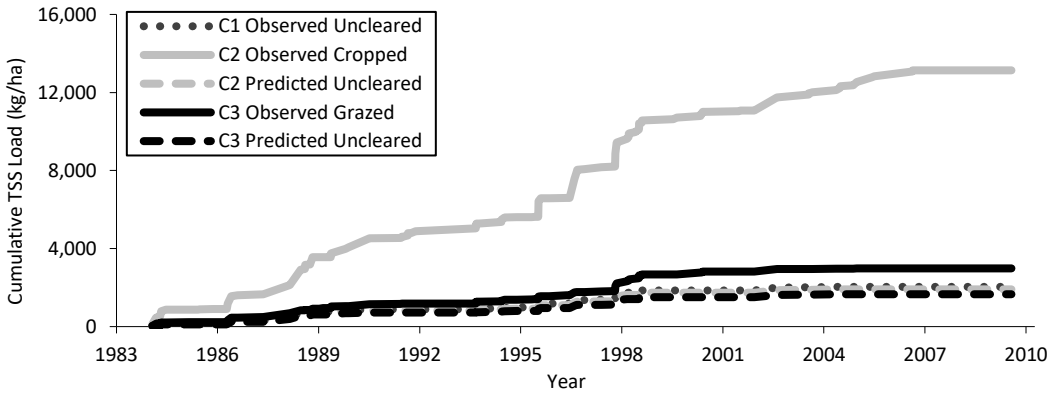

Figure 3.5. Cumulative load (kg/ha) of total suspended sediments (TSS) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

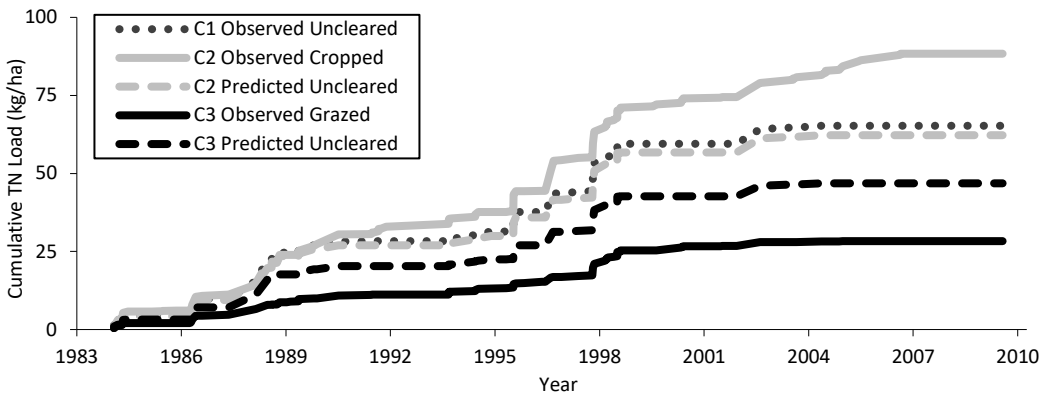

Figure 3.6. Cumulative load (kg/ha) of total nitrogen (TN) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

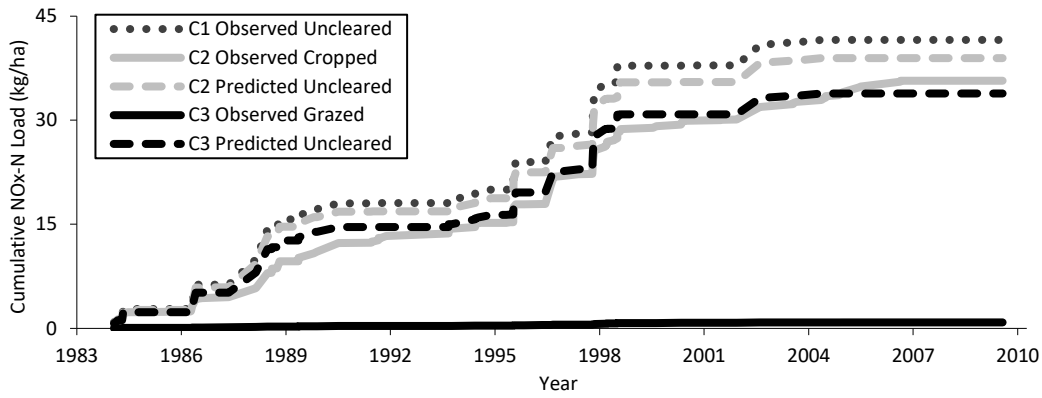

Figure 3.7. Cumulative load (kg/ha) of oxidised nitrogen (NOx-N) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

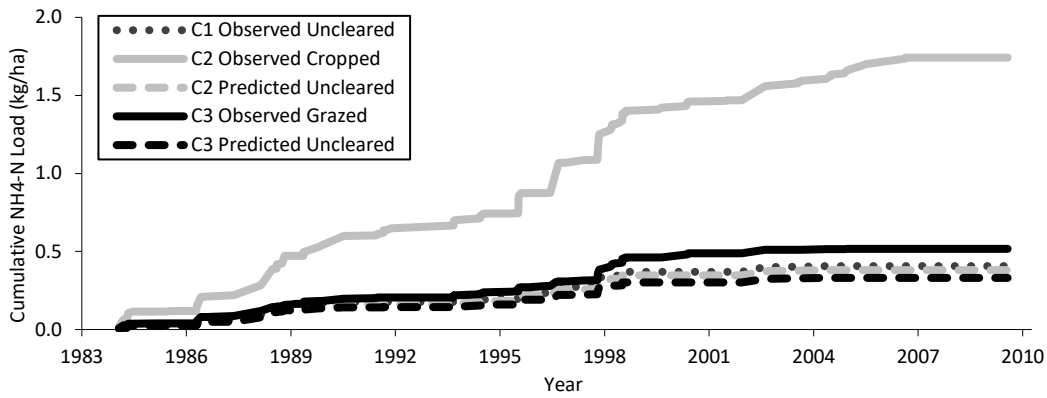

Figure 3.8. Cumulative load (kg/ha) of ammonium nitrogen (NH_4-N) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

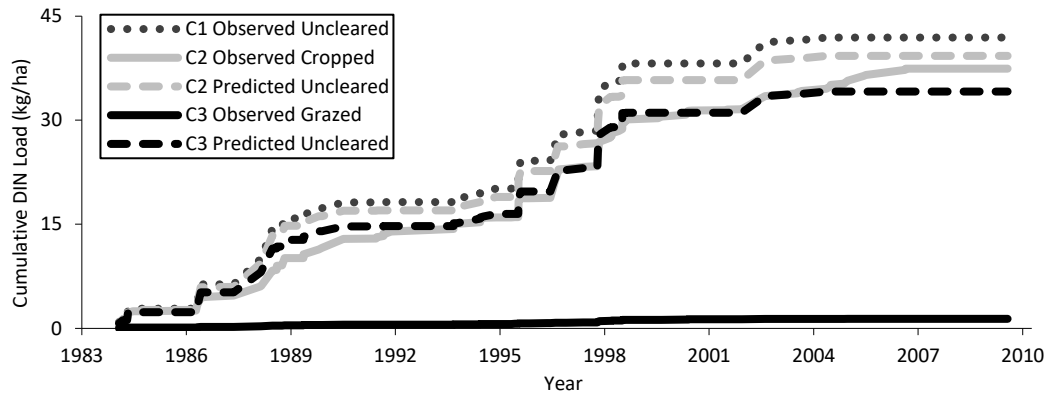

Figure 3.9. Cumulative load (kg/ha) of dissolved inorganic nitrogen (DIN) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

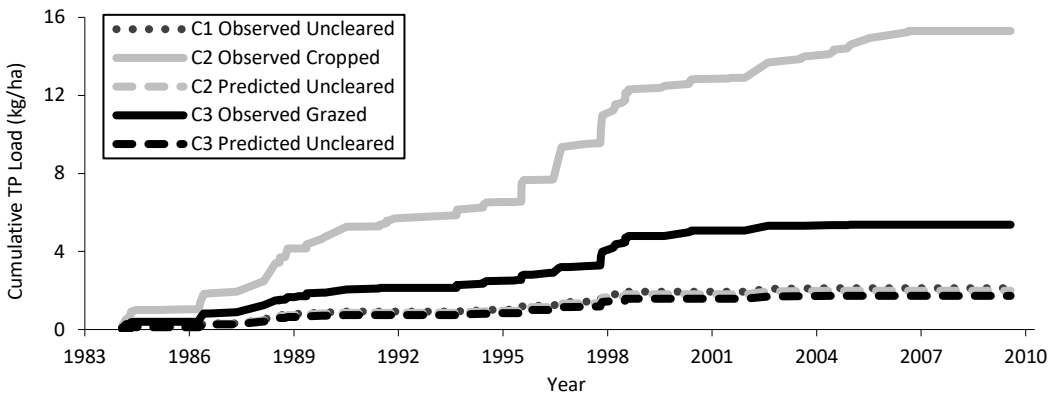

Figure 3.10. Cumulative load (kg/ha) of total phosphorus (TP) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

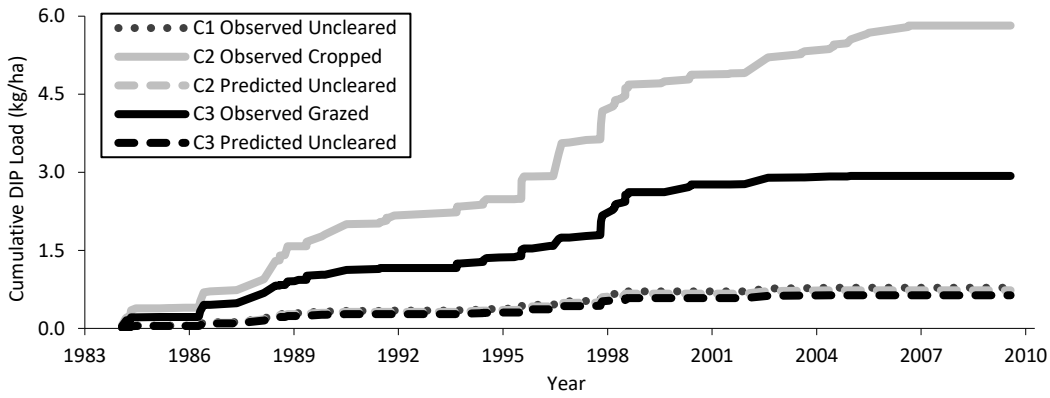

Figure 3.11. Cumulative load (kg/ha) of dissolved inorganic phosphorus (DIP) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

Table 3.3. Observed mean annual sediment, nitrogen and phosphorus loads (kg/ha/yr) from the virgin brigalow woodland, cropped and grazed pasture catchments over 25 years (1984 to 2010); and predicted mean annual loads from the cropped and grazed catchments had they remained virgin brigalow woodland.

Parameter	Load (kg/ha/yr)				
	Woodland (C1)	Crop (C2)	Pasture (C3)	C2 Predicted Uncleared	C3 Predicted Uncleared
Total Suspended Solids	81	525	119	76	66
Total Nitrogen	2.61	3.53	1.13	2.49	1.87
Oxidised Nitrogen	1.66	1.43	0.03	1.56	1.35
Ammonium Nitrogen	0.02	0.07	0.02	0.02	0.01
Dissolved Inorganic Nitrogen	1.68	1.50	0.06	1.57	1.37
Total Phosphorus	0.08	0.61	0.21	0.08	0.07
Dissolved Inorganic Phosphorus	0.03	0.23	0.12	0.03	0.03

3.4.4 Effect of land use change on water quality

Over the 25 year period, the mean annual effect of changing land use from virgin brigalow woodland to crop or pasture resulted in 449 kg/ha/yr and 53 kg/ha/yr more total suspended solids in runoff, respectively (Table 3.4). Similarly, more total phosphorus, dissolved inorganic phosphorus and ammonium nitrogen were exported from crop and pasture systems than virgin brigalow woodland. Crops exported total nitrogen at an average rate of 1.04 kg/ha/yr more than if the catchment had remained uncleared, whereas pasture exported 0.74 kg/ha/yr less than if the catchment had remained uncleared. Although the cropped catchment exported

more total nitrogen than its uncleared predictions, less oxidised and dissolved inorganic nitrogen were exported.

Table 3.4. Mean annual effect of changing land use from virgin brigalow woodland to crop and pasture systems on sediment, nitrogen and phosphorus loads (kg/ha/yr) over 25 hydrological years (1984 to 2010).

Parameter	Mean Annual Land Use Change Effect (kg/ha/yr)	
	Crop (C2)	Pasture (C3)
Total Suspended Solids	449	53
Total Nitrogen	1.04	-0.74
Oxidised Nitrogen	-0.13	-1.32
Ammonium Nitrogen	0.05	0.01
Dissolved Inorganic Nitrogen	-0.07	-1.31
Total Phosphorus	0.53	0.15
Dissolved Inorganic Phosphorus	0.20	0.09

3.5 Discussion

3.5.1 Event mean concentrations

The simple hydrology and water quality model presented was effective at quantifying the effect of changing land use from virgin brigalow woodland to crop and pasture systems; however, it is likely that the results are an underestimate of the true change. Although 25 years (1984 to 2010) of flow data was available for these three catchments, comprehensive water quality data had only been collected for the last 10 years of this period (2000 to 2010). If sediment and nutrient EMCs from the agricultural catchments immediately after land use change were higher to that observed later in the study, the model would underestimate

change. For example, wildfires in natural areas have been reported to increase sediment, nitrogen and phosphorus losses in runoff which typically remain high for about a year or until the soil stabilises and vegetation establishes (Ice *et al.* 2004; Smith *et al.* 2011; Stein *et al.* 2012). Historical cover data for the two agricultural catchments in this study indicate that plant cover was established by December 1983; C2 had 53% cover in June and 95% cover before the first crop was harvested in December, whereas C3 had 6.5% pasture cover in June and 96% cover by December. However, it is possible that the earlier runoff events may have had elevated sediment and nutrients in runoff as a residual impact of clearing and burning the catchments despite established cover.

Nonetheless, this study provides a rigorous estimate of sediment, nitrogen and phosphorus (total and dissolved) loads exported in runoff from these three catchments over 25 years. Bartley *et al*. (2012) reviewed sediment and nutrient concentration data from Australia suitable for catchment water quality models. Where upstream land use was dominated by more than 90% modified grazed pasture, they reported concentrations of 322 mg/L (10th and 90th percentiles 39 and 390 mg/L; n=9 sites) for total suspended solids, 3.04 mg/L (10th and 90th 1.65 and 4.92 mg/L; n=9 sites) for total nitrogen, and 0.73 mg/L (10th and 90th percentiles 0.17 and 2.17 mg/L; n=17 sites) for total phosphorus. EMCs from the grazed catchment in this study for total suspended solids (229 mg/L), total nitrogen (2.17 mg/L) and total phosphorus (0.41 mg/L) are within the range of values reported by Bartley *et al*. (2012).

There were no dryland crop sites in the review by Bartley *et al*. (2012) that were dominated (>90%) by a single upstream land use. However, plot and catchment scale data for sites with dryland crops as the main land use reported concentrations of 2501 mg/L (10th and 90th percentiles 162 and 5339 mg/L; n=21 sites) for total suspended solids, 1.99 mg/L (10th and 90th

0.71 and 3.38 mg/L; n=17 sites) for total nitrogen, and 0.85 mg/L (10th and 90th 0.096 and 1.65 mg/L; n=17 sites) for total phosphorus (Bartley *et al.* 2012). As for the grazed catchment, EMCs from the cropped catchment in this study were within the range of values reported by Bartley *et al*. (2012) for total suspended solids (798 mg/L) and total phosphorus (0.93 mg/L), but total nitrogen (5.37 mg/L) values from the cropped catchment in this study were higher despite no fertiliser applications. The lower total nitrogen values reported by Bartley *et al*. (2012) may be partly explained by: (1) diversity of study locations, including variations in the physical and chemical structure of soil; (2) data collection from different spatial scales (plot versus small, medium and large catchments); and (3) less than 90% of the upstream catchment areas were dominated by dryland crops, which due to a potential matrix of soil type, land use and ground cover provide a less accurate comparison than if data was collected from a single land use.

Soil characteristics and land use history are of particular interest when comparing runoff water quality studies, as physically more sediment and particulate nutrients are expected from sodic soils which readily erode (Gray and Murphy 2002) and chemically soil fertility declines over time. For example, total soil nitrogen (0 to 10 cm) has been shown to decline with an increase in cropping history ranging from 0 to 70 years (Dalal and Mayer 1986b; Dalal and Mayer 1986a). Following colonisation of Australia in 1788, clearing land for agriculture started in the southern states and slowly headed north to Queensland (Australian Government 2015). For example, 85% (407,840 ha) of cropping in Australia was conducted in the southern states of Victoria, South Australia and New South Wales in 1860 with only 0.3% (1,357 ha) occurring in Queensland (Australian Bureau of Statistics 2007). As a result, soils in the southern states where cropping has occurred for over 150 years are likely to be less fertile than in the Fitzroy Basin of Queensland where land development for cropping only commenced about 50 years ago. The shorter history of cropping at this study site in the Fitzroy Basin would also explain, at

least in part, the higher total nitrogen in runoff compared to other areas of Australia which were included in the Bartley *et al.* (2012) review.

In contrast to total nutrients, there are limited data available on dissolved concentrations of nitrogen and phosphorus in runoff from cropped and/or grazed areas. Murphy *et al*. (2013) reported 5.9 mg/L oxidised nitrogen and 0.017 mg/L dissolved phosphorus from a cropped area over one wet season; whereas concentrations over 10 years used in this study were 2.17 mg/L and 0.14 mg/L, respectively. The paucity of studies that have reported on dissolved nutrients from comparative single land use systems over enough wet seasons to account for annual variability makes interpretation difficult at present. However, the EMCs used in the model presented in this study are within the range of sediment and total nitrogen and phosphorus values reported from other cropped and grazed sites. This suggests that the results are comparable to other areas dominated by similar agricultural systems.

3.5.2 Effect of land use change on water quality

Differences in runoff volume between the catchments can be attributed to variable water use patterns of the different vegetation types; with ground cover, structural decline and surface roughness being secondary factors (Thornton *et al.* 2007). Clearing virgin brigalow woodland for agriculture is known to increase runoff volume (Siriwardena *et al.* 2006; Thornton *et al.* 2007), and it is well established that runoff volume and sediment loads are higher from cropped than grazed areas (Sharpley and Smith 1994; Stevens *et al.* 2006; Silburn *et al.* 2007; Freebairn *et al.* 2009; Murphy *et al.* 2013). Both these trends were observed in this study. However, Australian literature currently provides an incomplete story on the impacts of changing land use for these two agricultural systems on nutrients in runoff. For example, Stevens *et al*. (2006) reported higher loads of total nitrogen and phosphorus from cropped

than grazed areas but nothing on dissolved species, while Murphy *et al*. (2013) reported total and dissolved concentrations of nitrogen and phosphorus from cropped areas but nothing from grazed areas. This gap is also found in international studies; for example, in the southwestern United States of America, Sharpley and Smith (1994) reported higher loads of nitrogen and phosphorus (total and dissolved) following change of native grasslands to conventional tilled (fertilised) wheat but nothing from grazed areas. This highlights the uniqueness of this study's design which has collected long-term data on total and dissolved nutrients in runoff from both cropping and grazed areas concurrently with an uncleared control. In this study, more sediment and phosphorus (total and dissolved) were exported in runoff from both agricultural systems than virgin brigalow woodland. Changing land use to a pasture system also had less impact on runoff water quality than changing land use to a crop system for all sediment, nitrogen and phosphorus parameters reported.

The findings in this study also support other research which have reported a correlation between sediment and total phosphorus loss, and runoff and dissolved inorganic phosphorus loss (Sharpley and Smith 1990; Gillingham and Thorrold 2000; Hansen *et al.* 2002; Yuan *et al.* 2013). The considerably higher sediment loss from the cropped catchment is most likely the result of bare and/or low cover fallow management and tillage practices which are associated with erosion (Freebairn *et al.* 1993). Exports of sediment and total phosphorus increased at relatively proportional rates; however, the overall contribution of dissolved inorganic phosphorus to total phosphorus remained similar between the cropped catchment (38%) and its uncleared prediction (37%). This indicates that phosphorus from the cropped catchment was mainly exported in a particulate phase. Although this does not take into account the contribution of dissolved organic phosphorus which was not measured in this study, data from a nearby study has shown that dissolved organic phosphorus contributes only 3 to 5% of the

total phosphorus load (Rogusz *et al.* 2013). This supports phosphorus from the cropped catchment being mainly exported in a particulate phase.

In contrast, the lower loss of sediment from the virgin brigalow and grazed catchments can be attributed to the higher proportion of litter and pasture cover, respectively, which protects the soil surface from raindrop impact. High ground cover also helps maintain high infiltration rates, which reduces runoff and subsequently erosion (Freebairn and Wockner 1986; Silburn *et al.* 2011). Although conservative grazing of the unfertilised pasture resulted in only a 1.80 times increase in sediment compared to uncleared predictions for this catchment, total phosphorus increased 3.11 times and dissolved inorganic phosphorus 4.61 times. Furthermore, the overall contribution of dissolved inorganic phosphorus to total phosphorus increased from 37% for the uncleared prediction to 55% under grazing. The inclusion of dissolved organic phosphorus would increase the proportion of total phosphorus transported in the dissolved phase. The transport of phosphorus in mainly a dissolved phase is not surprising given the negative inverse relationship reported between dissolved phosphorus and sediment by Sharpley *et al.* (1981), and the management of this catchment to maintain high pasture cover and minimise erosion, which subsequently reduces particulate phosphorus loss (Sharpley *et al.* 1994).

The enrichment of dissolved phosphorus in runoff from the grazed catchment may also be explained by the presence of cattle, as grazing animals can return 60 to 99% of the nutrients they ingest back into the pasture system via dung and urine (Haynes and Williams 1993). Dung is the main form that phosphorus is excreted from animals, and it often has a higher inorganic content than the pasture ingested (Haynes and Williams 1993). For example, sheep dung has been shown to contain 80% inorganic phosphorus compared to only 64% from the pasture ingested (Haynes and Williams 1993). Australian data indicates that a 400 kg beef cattle steer

maintaining body weight will excrete 2.8 kg of faecal dry matter per day (Department of Agriculture and Fisheries 2011) which contains 2.1 g of phosphorus per kg of faecal dry matter (Jackson *et al.* 2012). Given the grazed catchment in this study is typically stocked at one 300 kg animal per 2.2 ha, approximately 0.71 kg/ha/yr of phosphorus is returned to the soil surface via dung.

Virgin brigalow woodland at this site is representative of the broader brigalow landscape in its pre-European condition, and the high nitrogen concentrations in runoff relative to the agricultural systems are likely due to the leguminous brigalow (*Acacia harpophylla*) tree which dominates the vegetation community. Although the concentration of total nitrogen in runoff from the virgin brigalow catchment was higher than the unfertilised cropped catchment, the mean annual load exported was less. This is a function of greater runoff volume and the number of days on which runoff occurred from the cropped catchment; that is, a total of 1647 mm was discharged over 99 days from the cropped catchment compared to only 663 mm discharged over 45 days from the virgin brigalow catchment over the 25 year period. This trend is similarly reported by Thornton *et al.* (2007) who found that in the same catchment 5.7% of rainfall become runoff in an uncleared state which increased to 11.0% under cropping.

In contrast to total nitrogen, oxidised and dissolved inorganic nitrogen both had higher concentrations and loads from virgin brigalow woodland compared to cropping. The contribution of particulate nitrogen to the total cumulative load of total nitrogen was 36% for virgin brigalow woodland and 58% for cropping; where particulate nitrogen was calculated as total nitrogen minus dissolved inorganic nitrogen. This indicates that total nitrogen load was dominated by a dissolved phase in the virgin brigalow woodland but a particulate phase in cropping. However, this does not take into account the contribution of dissolved organic

nitrogen which was not measured in this study. The literature shows that dissolved organic nitrogen load in runoff can equal dissolved inorganic nitrogen loads (Heathwaite and Johnes 1996; Martinelli *et al.* 2010; Rogusz *et al.* 2013), providing further evidence that the total nitrogen load from virgin brigalow woodland was dominated by a dissolved phase. It also suggests that total nitrogen load in cropping was likely to be equally comprised of both dissolved and particulate nitrogen if not dominated by a dissolved phase.

Although mean annual loads presented in this study are based on calculations using the 10 years of available EMC data, it is expected that total nitrogen concentrations in runoff would decline from the cropped catchment over the 25 years as nitrogen was removed from the system. Measurements of total soil nitrogen from 1981 to 2008 (the last sampling period before conversion of the cropped catchment into a ley pasture in 2010) shows that nutrient rundown occurred in the absence of fertiliser inputs and the export of nitrogen in grain and runoff. That is, concentrations of total soil nitrogen in the virgin brigalow catchment remained relatively stable (mean 0.176%) whereas concentrations in the cropped catchment declined from 0.197% in 1981 to 0.076% in 2008 (unpublished data). This result is expected given the previously reported declines in grain yield and grain nitrogen from the cropped catchment over 23 years (Radford *et al.* 2007).

Both agricultural systems had more ammonium nitrogen in runoff than the virgin brigalow woodland; 2% contribution to the total cumulative load of total nitrogen compared to less than 1%, respectively. However, the overall small contribution of ammonium to total nitrogen is most likely due to soil bacteria which rapidly convert ammonium into nitrate given ideal moisture and temperature conditions (Price 2006). Cumulative losses of ammonium in runoff from this study were more similar to sediment, and hence phosphorus, than other nitrogen

parameters. This trend has been reported in other studies and is attributed to the adsorption of ammonium onto sediment particles (Johnes and Burt 1991; Heathwaite and Johnes 1996). That is, ammonium (NH_4^+) is a positively charged cation which is attracted to the negatively charged surface of organic matter and clay particles, whereas nitrate (NO_3^-) is a negatively charged anion repelled by the soil and subsequently more readily lost via leaching and runoff.

The grazed catchment exported considerably less nitrogen than the virgin brigalow and cropped catchments. Loads of oxidised and dissolved inorganic nitrogen from pasture were almost negligible, and the higher total nitrogen loads can be attributed to particulate nitrogen. That is, dissolved inorganic nitrogen contributed only 5% to the total cumulative load of total nitrogen which indicates that particulate nitrogen strongly dominates transport from the grazed catchment. A dissolved organic nitrogen load equal to the dissolved inorganic nitrogen load would still result in particulate nitrogen strongly dominating transport from the grazed catchment. However, Radford *et al.* (2007) reported only 1.6 kg/ha/yr of nitrogen removal in cattle from the grazed catchment over 23 years compared to 36.1 kg/ha/yr nitrogen removal in grain from the cropped catchment. These observations imply that sown pasture in the grazed catchment is a sink for nitrogen. This is known as pasture rundown which occurs when mineral nitrogen becomes immobilised in soil organic matter and established grass plants, rather than a net loss from the system (Robertson *et al.* 1997; Lawrence *et al.* 2014). This is reflected in the soil mineral nitrogen data for the grazed catchment which remained relatively stable from 1983 to 2008 following an initial peak in 1982 due to clearing and burning of the catchment (unpublished data). Although rundown can lead to a decline in pasture productivity (Myers and Robbins 1991; Lawrence *et al.* 2014), the grazed catchment in this study has always been conservatively managed to maintain high pasture cover.

Lower nitrogen from the grazed catchment compared to the cropped catchment can also be attributed to the higher percentage of nitrogen removed by pasture (3.5%) compared to cereal grains (1.8%) (The State of Victoria 2015). As pasture tends to uptake more nitrate, a component of both oxidised and dissolved inorganic nitrogen, there is less available in the effective depth of interaction (0.1 to 4 cm) (Sharpley 1985) to be dissolved and transported with water in runoff or as leachate. Loads of nitrogen in runoff have also been shown to be lower from pasture cut to 155 mm above the ground than 47 mm (Mundy *et al.* 2003). This supports the use of management practices that promote higher pasture biomass to reduce runoff volume and hence improve water quality, such as wet season spelling and conservative stocking rates based on feed availability.

3.5.3 Effect of management practices

Management practices, such as fertiliser application and tillage method, are two factors that affect the quality of surface runoff from crop systems. Sharpley and Smith (1994) found that fertiliser applications on conventionally tilled wheat resulted in a 17-fold nitrogen and 30-fold phosphorus increase in runoff. Physical and chemical degradation of soils from cropped land is a slow process (Silburn *et al.* 2007), and based on more than 25 years of fertility rundown at this site, soil fertility and consequently nutrient loads in runoff are expected to be lower than fertilised crops. For example, Murphy *et al*. (2013) reported 7-8 kg/ha oxidised nitrogen (approximately 20% of the total nitrogen applied at planting) in runoff from a fertilised crop, whereas this study in a similar area of central Queensland, Australia, reported 1.43 kg/ha oxidised nitrogen from an unfertilised crop.

Conventional tillage practices are reported to have higher runoff volume and/or erosion loss than no-till crop systems (Connolly *et al.* 1997; Ehigiator and Anyata 2011; DeLaune and Sij

2012). No-till practices have higher stubble cover which reduces overland flow velocity and the ability of water to detach and transport sediment (Rose and Freebairn 1985). Cover levels above 30% have been suggested as critical for erosion control in crop systems (Connolly *et al.* 1997). Thus, management practices that retain cover and reduce runoff are also useful for reducing loads of sediment and some nutrients (McIvor *et al.* 1995; Hansen *et al.* 2002; Bartley *et al.* 2014a). For example, Sharpley and Smith (1994) found that changing a crop system from conventional to no-till reduced soil loss 18-fold, nitrogen loss four-fold and phosphorus loss three-fold, but an increase in bioavailable phosphorus was observed. Similarly, DeLaune and Sij (2012) reported a five-fold reduction in soil loss from no-till compared to conventional tilled systems. These authors also observed a trend of lower total phosphorus, dissolved phosphorus and ammonia nitrogen but higher nitrate nitrogen from no-till systems, although differences were not statistically different ($P<0.05$) (DeLaune and Sij 2012). Minimum tillage was introduced to the cropped catchment at the Brigalow Catchment Study in 1992 with intermittent use of conventional tillage practices in 1994, 1997 and 2007. Small increases in cumulative runoff and loads of sediment and nutrients can be seen around the periods when conventional tillage had been reintroduced; however, hydrology appears to be a stronger influence with the two main periods of an increased rate in cumulative loads (1991 to 1994 and 1996 to 1999) coinciding with periods of above average rainfall over multiple years. This supports the recommendation that management practices that reduce runoff also reduce sediment and nutrient loads.

Runoff water quality from pasture systems is similarly affected by cover. Silburn *et al.* (2011) suggested that more than 50% ground cover should be maintained in grazed areas to reduce excessive runoff and soil loss. This recommendation was based on a seven year study in a semi-arid area of Queensland which exported 30 to 50% of rainfall as runoff when cover was

less than 20%, but averaged only 5.9% when cover was greater than 50%. The trend of reduced runoff, and hence reduced sediment and nutrients exported in runoff, from grazed land with higher ground cover is supported by numerous authors (Nelson *et al.* 1996; Murphy *et al.* 2008; Schwarte *et al.* 2011). Bare areas (scalds) have a low tolerance to soil erosion due to low total water-holding capacity which results in lower infiltration and hence increased runoff compared to areas with greater cover (Silburn *et al.* 2011). However, management practices such as reduced stocking rates and rotational wet season resting have been shown to increase ground cover (Bartley *et al.* 2010; Bartley *et al.* 2014b). The pasture system at the Brigalow Catchment Study is conservatively grazed and aims to maintain at least 80% cover and less than 30% pasture utilisation, which is considered a well-managed system. Hence, the loads of sediment, nitrogen and phosphorus exported from this site may be lower than other areas which have higher stocking rates and greater pasture utilisation.

3.6 Conclusions

The simple hydrology and water quality model presented was based on a 17 year calibration period of the Brigalow Catchment Study in its native condition, and 25 years flow and 10 years water quality monitoring following land use change to agriculture. The model indicated that changing land use from virgin brigalow woodland to a well-managed (unfertilised) pasture system decreased nitrogen in runoff compared to runoff from virgin brigalow woodland which dominated the landscape during pre-European times; however, both crop and pasture systems increased loads of sediment and phosphorus. Overall, crops posed a greater risk to downstream water quality, and subsequently the end of catchment marine system, than pasture.

3.7 References

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Chapter 4 – The Brigalow Catchment Study: V. Clearing and burning brigalow (*Acacia harpophylla*) in Queensland, Australia, temporarily increases surface soil fertility prior to nutrient decline under cropping or grazing

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My contribution to the paper involved:

Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Writing, - Original Draft, Writing - Review & Editing.

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4.1 Abstract

In the Brigalow Belt bioregion of Australia, clearing of brigalow (*Acacia harpophylla*) scrub vegetation for agriculture has altered nutrient cycling over millions of hectares. In order to quantify the effect of this vegetation clearing and land use change on soil fertility, the Brigalow Catchment Study commenced in 1965. Initial clearing and burning of brigalow scrub resulted in a temporary increase of mineral nitrogen, total and available phosphorus, total and exchangeable potassium and total sulfur in the surface soil (0 to 0.1 m) as a result of soil heating and the ash bed effect. Soil pH also increased, but did not peak immediately after burning. Soil fertility declined significantly over the subsequent 32 years. Under cropping, organic carbon declined by 46%, total nitrogen by 55%, total phosphorus by 29%, bicarbonate-extractable phosphorus by 54%, acid-extractable phosphorus by 59%, total sulfur by 49%, total potassium by 9% and exchangeable potassium by 63% from post-burn, pre-cropping concentrations. Fertility also declined under grazing but in a different pattern to that observed under cropping. Organic carbon showed clear fluctuation but it was not until the natural variation in soil fertility over time was separated from the anthropogenic effects of land use change that a significant decline was observed. Total nitrogen declined by 22%. Total phosphorus declined by 14%, equating to only half of the decline under cropping. Bicarbonate-extractable phosphorus declined by 64% and acid-extractable phosphorus by 66%; both greater than the decline observed under cropping. Total sulfur declined by 23%; less than half of the decline under cropping. A similar decline in total potassium was observed under both land uses with a 10% decline under grazing. Exchangeable potassium declined by 59%. The primary mechanism of nutrient loss depended on the specific land use and nutrient in question.

4.2 Introduction

Soil fertility decline, soil structural decline and erosion are all considered to be consequences of changing land use from virgin forest to cropping and grazing. Traditionally, nutrient cycling in

undisturbed virgin ecological systems was considered a steady-state closed system, where soil nutrients are consumed by the growing plants and then released back to the soil via leaf litter, wood debris and roots (Moody 1998). In contrast, cropping and grazing systems disturb this cycle by removing nutrients in harvested products and animals (Radford *et al.* 2007); via increased surface runoff (Thornton *et al.* 2007; Elledge and Thornton 2017); via increased leaching (Silburn *et al.* 2009); and via increased gaseous losses from soil and animals (Huth *et al.* 2010; Dalal *et al.* 2013). Disturbance of nutrient cycles and increased losses of soil nutrients affect the viability and sustainability of farming systems. Increased nutrient loads lost to the environment impacts ecosystem health, resulting in substantial investment in harm minimisation and remediation programs worldwide (Carroll *et al.* 2012). Contemporary nutrient cycling research suggests that disturbance and nutrient loss on a local scale have ramifications on a global scale. This is demonstrated by feedback mechanisms between increasing temperature, increasing atmospheric carbon dioxide and nitrogen concentrations, and fluxes of soil organic matter as a result of concomitant change in soil carbon and nitrogen concentrations (Crowther *et al.* 2016; Tipping *et al.* 2017; Schulte-Uebbing and de Vries 2018).

In the Brigalow Belt bioregion of Australia, clearing of brigalow (*Acacia harpophylla*) scrub and land use change has substantially altered nutrient cycling over a large area. The bioregion occupies 36.7 million hectares of Queensland and New South Wales, stretching from Dubbo in the south to Townsville in the north of Australia. Since European settlement, 58% of this bioregion has been cleared. The bioregion contains Queensland's largest catchment, the Fitzroy Basin, which drains directly into the Great Barrier Reef lagoon. In 1962, the Brigalow Land Development Fitzroy Basin Scheme commenced, resulting in the Government-sponsored clearing of 4.5 million hectares for cropping and grazing. This clearing represents 21% of all clearing in the bioregion and 32% of the Fitzroy Basin area (Thornton *et al.* 2007). Broad-scale land clearing continued in the basin until 2006

(McGrath 2007). In the preceding decade, rates of land clearing in Queensland were among the highest in the world with estimates of between 425,000 ha and 446,000 ha cleared per year (Wilson *et al.* 2002; Lindenmayer and Burgman 2005; Reside *et al.* 2017). More than 60% of this clearing, or about 261,000 ha/yr, was undertaken in the Brigalow Belt (Wilson *et al.* 2002; Cogger *et al.* 2003). It is estimated that up to 93% of brigalow scrub has been cleared since European settlement (Butler and Fairfax 2003; Cogger *et al.* 2003; Tulloch *et al.* 2016).

In order to quantify the effect of this scale of vegetation clearing and land use change on soil fertility, the Brigalow Catchment Study (BCS) commenced in 1965. The objective of this study was to evaluate whether clearing of brigalow scrub for cropping or grazing would alter the dynamics of soil organic carbon, nitrogen, phosphorus, sulfur and potassium over time. It was hypothesised that land development for cropping would lead to a significant decline in soil fertility while less or no change was expected with land development for grazing. It was also expected that the trends noted by Radford *et al.* (2007), i.e. unchanged concentrations of soil organic carbon and total nitrogen under brigalow scrub and grazing land uses but significant decline under cropping, would continue; however, the planting of legume ley pasture may enhance nutrient status in soil under the cropping land use.

As resourcing pressures limit the commencement and continuation of long-term studies there is an increasing trend towards modelling. This study facilitates modelling by numerically describing the starting condition of the landscape and mathematically defining fertility trends over time. Discussion on the mechanisms of change further informs process based models, assisting in moving forward from traditional empirical black box models. The BCS continues today having adapted to answer new research questions, and having answered questions unanticipated at its inception more than five decades ago.

4.3 Materials and methods

The BCS is described in detail by Cowie *et al.* (2007); changes in runoff volume and peak runoff rate are given in Thornton *et al.* (2007) and Thornton and Yu (2016); agronomic and soil fertility results are given in Radford *et al.* (2007); the deep drainage component of the water balance is given in Silburn *et al.* (2009); and changes in water quality are given in Thornton and Elledge (2016) and Elledge and Thornton (2017).

4.3.1 Site location and climate

The study site is located at 24.81°S, 149.80°E at an altitude of 151 m above sea level, located within the Dawson sub-catchment of the Fitzroy Basin, central Queensland, Australia. A locality map is presented in Cowie *et al.* (2007). The region has a semi-arid, subtropical climate. Summers are wet, with 70% of the annual average (1964 to 2014) hydrological year (October to September) rainfall of 661 mm falling between October and March, while winter rainfall is low (Figure 4.1). Average monthly temperature ranges from a minimum of 6.3°C in July to a maximum of 33.8°C in January (Figure 4.1).

4.3.2 Experimental design

The BCS is a paired, calibrated catchment study consisting of three small catchments, C1, C2 and C3, ranging from 11.7 to 16.8 ha in size. Within each catchment, three permanent monitoring sites were established to monitor soil fertility. A map showing the location of the monitoring sites within the catchments is presented in Cowie *et al.* (2007). Establishment of the 20 m by 20 m sites was done using double stratification. Initial stratification was based on soil type and slope position with a monitoring site allocated to both an upper and lower-slope position on Vertosols, and the third on a Sodosol irrespective of slope position. Secondary stratification was by way of 10 sub-units, each 4 m by 10 m, within each monitoring site.

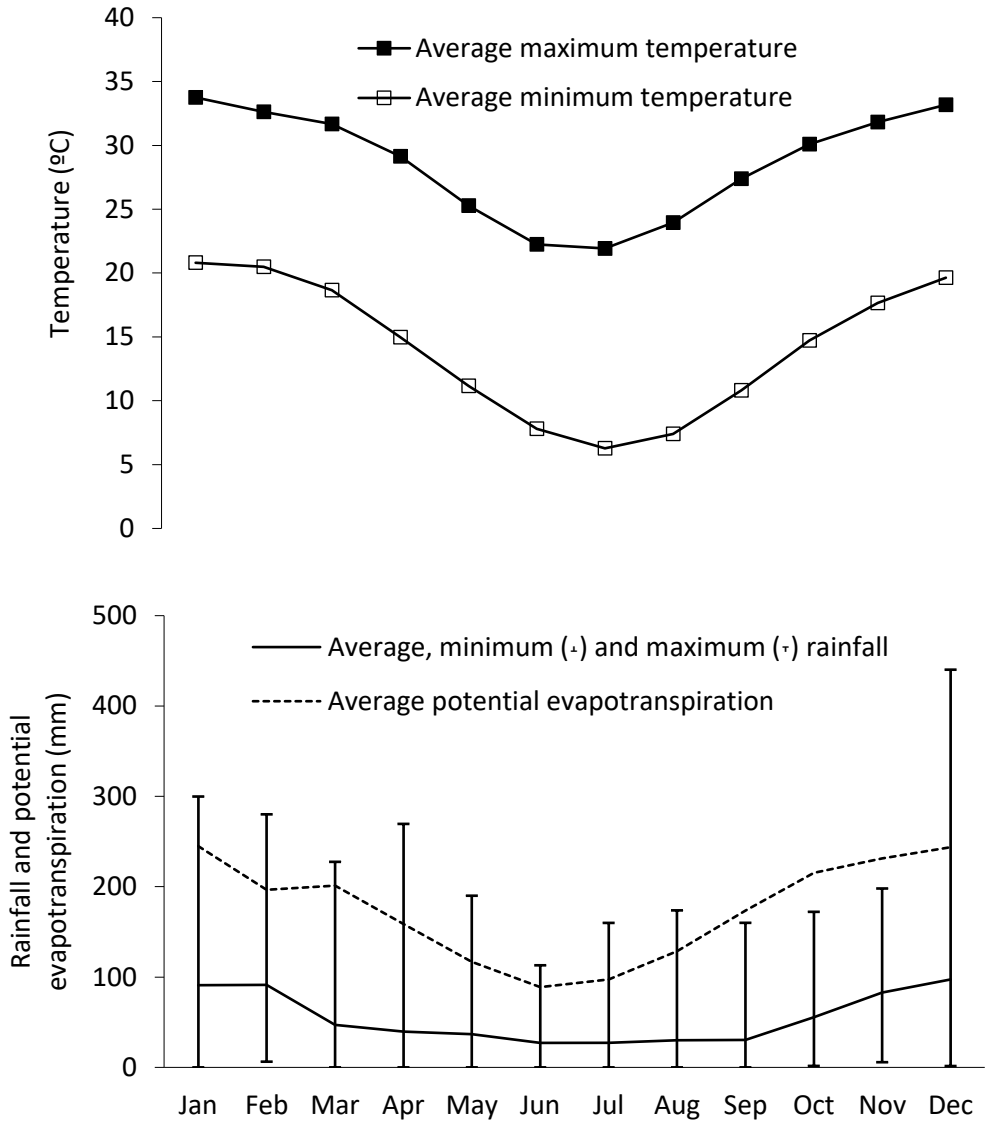

Figure 4.1. Average monthly temperature, rainfall and potential evapotranspiration for the Brigalow Catchment Study site from 1964 to 2014.

4.3.3 Soil types

Soil types were typically characterised by fine-textured dark cracking clays (Black and Grey Vertosols), non-cracking clays (Black and Grey Dermosols) and thin layered dark and brown sodic soils (Black and Brown Sodosols) (Isbell 1996; Cowie *et al.* 2007). Approximately 70% of C1 and C2 and 58% of C3 were comprised of Vertosols and Dermosols (clay soils); the remaining area in each

catchment was occupied by Sodosols. The plant-available water holding capacity of these soils ranged from 130 to 200 mm in the surface 1.4 m of the soil profile (Cowie *et al.* 2007). Average slope of the catchments is 2.5%. The catchments consisted of good quality agricultural land, all equally suitable for cropping or grazing (Cowie *et al.* 2007). The physiochemical characteristics of an upper-slope Vertosol, and a Sodosol, both within C1, are given in Table 4.1 (adapted from Cowie *et al.* (2007)). These sites were sampled in 1981 with sampling and sample handling procedures described in subsequent sections. Values for pH, EC and Cl were determined using 1:5 suspensions in water (Hunter and Cowie 1989). Total carbon, total nitrogen and total organic carbon were determined by Dumas high-temperature combustion as described in methods 6B2a, 7A5 and 6B5, respectively, in Rayment and Lyons (2011). Walkley and Black organic carbon was determined according to method 6A1 in Rayment and Higginson (1992). Nitrate-nitrogen was determined by the potassium chloride extraction method described in method 7C2 in Rayment and Higginson (1992). Cation exchange capacity and exchangeable cations were determined by extraction with alcoholic one molar ammonium chloride at pH 8.5 as described in method 15C1 in Rayment and Higginson (1992). Clay content was determined by drink mixer physical dispersion (Bouyoucos 1951) followed by fine-fraction determination by hydrometer (Thorburn and Shaw 1987; Hunter and Cowie 1989).

4.3.4 Vegetation

Vegetation was typical of the Brigalow Belt bioregion, dominated by brigalow (*Acacia harpophylla)*, as described in detail by Cowie *et al.* (2007). In their native “brigalow” state, the catchments were composed of three major vegetation communities, identified by their most common canopy species; brigalow (*Acacia harpophylla*), brigalow–belah (*Casuarina cristata*) and brigalow–Dawson Gum (*Eucalyptus cambageana*). Understoreys of all major communities were characterised by *Geijera* sp. either exclusively, or in association with *Eremophila* sp. or *Myoporum* sp.

Table 4.1. Average pre-clearing (1981) soil physiochemical characteristics for a Vertosol and a Sodosol within catchment 1 (adapted from Cowie *et al.* (2007)).

Depth (m)	pH	EC (dS/m)	Cl (µg/g)	TC (%)	TN (%)	TOC* (%)	NO3-N (KCL) (µg/g)	CEC	Exchangable Ca++	Mg++	Na+	K+	Clay (%)
									(cmol/kg)				
							Vertosol soil						
0.0-0.1	6.56	0.16	75	2.01	0.16	1.58	2.7	34	11.8	11.1	1.4	0.41	36
0.1-0.2	7.54	0.48	450	1.37	0.11	1.34	1.2	36	11.5	14.6	3.2	0.23	40
0.2-0.3	8.14	0.68	730	0.69	0.06	0.66	0.5	35	10.0	15.4	4.1	0.16	44
0.5-0.6	5.70	0.77	1040				0.2	32	5.9	14.6	4.6	0.21	45
0.8-0.9	4.76	0.83	1145				0.2	32	4.1	13.7	4.9	0.12	46
1.1-1.2	4.64	0.83	1170				0.2	34	3.4	13.4	5.4	0.12	46
1.4-1.5	4.52	0.92	1320				0.1	38	3.4	15.0	6.6	0.16	50
1.7-1.8	4.48	0.98	1385				0.1	39	3.3	15.7	6.9	0.27	54
							Sodosol soil						
0.0-0.1	6.80	0.10	20	2.43	0.17	2.33	4	21	9.5	4.1	0.3	0.51	18
0.1-0.2	7.16	0.17	130	0.87	0.07	0.84	1.1	25	6.4	9.2	2.3	0.18	31
0.2-0.3	7.52	0.22	220	0.79	0.06	0.78	0.5	23	5.6	9.3	2.9	0.12	28
0.5-0.6	8.83	0.40	400				0.2	24	6.3	9.9	4.7	0.15	
0.8-0.9	9.20	0.47	470				0.2	16	2.8	6.8	4.1	0.13	

* Walkley and Black OC (0 to 0.1 m)

4.3.5 Site history and management

The study has had four experimental stages (Table 4.2). Stage I, the calibration phase, monitored rainfall and runoff from the catchments, allowing an empirical hydrological calibration between

catchments to be developed. The permanent monitoring sites were established in each catchment during this stage. Baseline measurements of soil fertility were taken in 1981 (Cowie *et al.* 2007; Radford *et al.* 2007)).

Table 4.2. The land use history of the three catchments of the Brigalow Catchment Study.

Catchment	Area (ha)	Land use by experimental stage			
		Stage I (Jan 1965 to Mar 1982)	Stage II (Mar 1982 to Sep 1984)	Stage III (Sep 1984 to Jan 2010)	Stage IV (Jan 2010 to Jun 2014)
C1	16.8	Brigalow scrub	Brigalow scrub	Brigalow scrub	Brigalow scrub
C2	11.7	Brigalow scrub	Development	Cropping	Ley pasture
C3	12.7	Brigalow scrub	Development	Grazing	Grazing

Stage II, the land development phase, commenced in March 1982 when vegetation in C2 and C3 were developed by clearing with traditional bulldozer and chain methods. Catchment 1 was retained as an uncleared, undisturbed control. In C2 and C3, the fallen timber was burnt *in situ* in October 1982. Following burning, residual unburnt timber in C2 was raked to the contour for secondary burning. Narrow-based contour banks were then constructed at 1.5 m vertical spacing. A grassed waterway was established to carry runoff water from the contour channels to the catchment outlet. In C3, residual unburnt timber was left in place, and in November 1982 the catchment was sown to buffel grass (*Cenchrus ciliaris* cv. Biloela). The second soil fertility assessment was undertaken in December 1982, soon after burning.

Stage III, the land use comparison phase, commenced in 1984. In C2, the first crop sown was sorghum (*Sorghum bicolor*) (September 1984), followed by annual wheat (*Triticum aestivum*) for

nine years. Fallows were initially managed using mechanical tillage (disc and chisel ploughs), which resulted in significant soil disturbance and low soil cover. In 1992, a minimum tillage philosophy was introduced and in 1995 opportunity cropping commenced with summer (sorghum) or winter (wheat, barley (*Hordeum vulgare*) and chickpea (*Cicer arietinum*)) crops sown when soil water content was adequate. No nutrient inputs were used. In C3, the buffel grass pasture established well with >5 plants/m^2 and 96% groundcover achieved before cattle grazing commenced in December 1983. Stocking rate was 0.3 to 0.7 head/ha (each stock typically 0.8 adult equivalent), adjusted to maintain pasture dry matter levels >1000 kg/ha without nutrient inputs, feed or nutrient supplementation. The catchment was continuously stocked until December 1996 at which point irregular pasture spelling commenced when pasture dry matter was likely to decline below 1000 kg/ha with further grazing.

Stage IV, the adaptive land management phase, commenced in 2010. To sustain productive agricultural systems representative of commercial enterprises in the Brigalow Belt bioregion, management strategies to maintain or enhance soil fertility were implemented. In C2, the legume butterfly pea (*Clitoria ternatea*) was planted as a ley pasture in January 2010. The butterfly pea was left ungrazed to establish and set seed until March 2011 when grazing commenced. In September 2011, cattle were removed from both C2 and C3 to allow spelling of the pastures over the 2011/12 and 2012/13 wet seasons. Grazing recommenced in December 2013 when the catchments were "crash grazed" with high stocking rates of 0.5 adult equivalents/ha in C2 and 1.4 adult equivalents/ha in C3 for 45 days to reduce rank pasture growth. Subsequently, grazing continued at conservative stocking rates of about 0.3 adult equivalents/ha with regular periods of pasture spelling.

4.3.6 Soil sampling

Soil water in the surface 0.1 m of the soil profile was determined gravimetrically according to the methods of Cowie *et al.* (2007).

Soil samples for fertility analysis were collected from the surface 0.1 m of the soil profile at each monitoring site using manual coring tubes of 0.05 m diameter. Samples were typically a composite of eight 0.05 m-diameter cores. The eight cores were comprised of two cores sampled adjacent to each of four fixed locations within each sub-unit. More intensive sampling was undertaken pre-clearing in 1981, and in 2008 and 2014. In these years samples were a composite of 20 cores, with five cores sampled adjacent to each of the four fixed locations. Soil samples were collected annually from pre-clearing in 1981, to 1987 and then in 1990, 1994, 1997, 2000, 2003, 2008 and 2014, with samples retained after analysis in a long-term storage archive.

4.3.7 Measurements of agricultural productivity, nutrient removal and nutrient inputs

In the cropped catchment, grain yield, nitrogen and phosphorus content were measured according to the methods of Radford *et al.* (2007). Grain sulfur content was estimated as grain nitrogen multiplied by 10% (Byers *et al.* 1987; Győri 2005). Grain potassium content was estimated as 0.46% of grain yield (Mengel and Kirby 1982).

In the grazed catchment, cattle live weight gain was measured according to the method of Radford *et al.* (2007). Nutrient export in of beef was estimated as live weight gain multiplied by 2.4% for nitrogen (Radford *et al.* 2007), 0.71% for phosphorus (Gibson *et al.* 2002), 0.16% for sulfur (Ad Hoc Committee on Air Emissions from Animal Feeding Operations 2003) and 0.2% for potassium (Whitehead 2000). Nitrogen volatilisation losses from cattle urine and faeces was estimated as nitrogen intake multiplied by 19.77% (Laubach *et al.* 2013). Nitrogen intake was estimated as dietary

biomass intake multiplied by dietary nitrogen content. Daily dietary biomass intake was estimated as fasted animal live weight at entry to the catchment multiplied by 2% per day of grazing (Minson and McDonald 1987). Dietary nitrogen content was determined using the FNIRS technique of Dixon and Coates (2010).

Estimates of nutrient input from rainfall were obtained using the data of Packett (2017) multiplied by the annual average rainfall of the BCS. An average of rainfall chemistry values for Rockhampton and Emerald (mean values) were used given both sites are a similar distance from the BCS.

4.3.8 Soil physical and chemical analyses

Soil bulk density was measured pre-clearing in 1981, then post-clearing in 1984, 1987, 1994, 1997, 2000 and 2014, using the soil samples collected for fertility analysis. The tip diameter of the coring tubes was measured in field with the external wall of the tube marked at 0.1 m to indicate the depth of sampling. Intact soil cores not contaminated by rocks or organic matter >2mm were dried at 40°C then weighed and sub-sampled, with the sub-samples then dried at 105°C to a constant weight. Bulk density was calculated from the total sample mass corrected to the equivalent mass of 105°C oven-dry soil, per volume of core sampled.

Chemical analyses were performed by the Queensland Government soil laboratory network. Prior to analyses, soil samples were dried at 40°C and ground to pass through a 2 mm sieve. Samples were then analysed for soil pH, organic carbon, total nitrogen, mineral nitrogen (ammonium-nitrogen (NH_4-N) and nitrate-nitrogen (NO_3-N)), total phosphorus, available phosphorus (bicarbonate-extractable phosphorus and acid-extractable phosphorus), total sulfur, total potassium and exchangeable potassium. Soil pH in a 1:5 soil/water suspension ($pH_{(w)}$) was determined according to the method of Tucker and Beatty (1974) from 1981 to 1983, in 1985, and from 1987 to 1997. In all

other years $pH_{(w)}$ was determined according to method 4A1 in Rayment and Higginson (1992). Soil pH in a 1:5 soil/calcium chloride suspension ($pH_{(Ca)}$) was determined according to the method of White (1969) from 1981 to 1983, in 1985, and in 1987. In all other years $pH_{(Ca)}$ was determined according to method 4B1 in Rayment and Higginson (1992). For laboratory convenience method 4B2 has been used interchangeably with 4A1, as there is no significant difference in the results obtained from either method (Rayment and Higginson 1992). Where pH values have been averaged, they are presented as a true average pH, not an arithmetic average (Rayment and Lyons 2011). Organic carbon (OC) was determined by the dichromate oxidation method of Walkley and Black (1934) followed by titration. Post 1997, the titrimetric component of the procedure was replaced with a colorimetric procedure (Sims and Haby 1971) as described in method 6A1 in Rayment and Higginson (1992); these methods are well correlated (R^2 = 0.96) (Cowie *et al.* 2002). Total nitrogen (TN) was determined by macro-Kjeldahl digestion (Bremner 1965). Mineral nitrogen was determined by the potassium chloride extraction method described in method 7C2 in Rayment and Higginson (1992). Results less than the practical quantitation level of 2 mg/kg were set to a value of 0.5 mg/kg. Total phosphorus (TP) was determined using the X-ray fluorescence (XRF) method described in method 9A1 in Rayment and Higginson (1992). Bicarbonate-extractable phosphorus (P(B)) was determined using a modification of the Colwell (1963) method described in method 9B2 in Rayment and Higginson (1992) while acid-extractable phosphorus (P(A)) was determined using a modification of the Kerr and von Stieglitz (1938) method described in method 9G2 in Rayment and Higginson (1992). Total sulfur (TS) and total potassium (TK) were determined using the X-ray fluorescence (XRF) method described in methods 10 A1 and 17A1 respectively, in Rayment and Higginson (1992). Exchangeable potassium (Exch. K) was determined by extraction with alcoholic one molar ammonium chloride at pH 8.5 as described in method 15C1 in Rayment and Higginson (1992).

The full suite of chemical analyses was typically performed soon after soil sampling. When this had not occurred, analyses were performed as required on the archived samples. Cowie *et al*. (2007) presented chemical data from C1 in 1981 for most of the analytes reported in this study. However, with the exception of mineral nitrogen and Exch. K, repeat analyses in this study did not reflect the previously reported values, which were typically lower despite having been conducted according to the same method and utilising best practice of the day. Where this occurred, the results of the repeat analysis have been accepted for use in this study.

The number of samples analysed varied between soil samplings (Table 4.3). At a minimum, a composite sample comprised of a subsample of each of the 10 sub-units in a monitoring site was generated for analysis. This composite sample was representative of at least 80 soil cores from within a monitoring site. Alternatively, a sample from each of the sub-units in a monitoring site was generated for analysis. This resulted in 10 samples, with each being representative of at least eight soil cores.

Table 4.3. The number of soil samples analysed per parameter, per catchment, per sampling event.

	Number of samples analysed per catchment											
Year	$pH_{(w)}$	$pH_{(Ca)}$	OC	TN	NH_4-N	NO_3-N	TP	P(B)	P(A)	TS	TK	Exch. K
1981	30	30	3	3	30	30	3	3	3	3	3	30
1982	30	30	3	3	30	30	3	3	3	3	3	30
1983	30	30	3	3	30	30	3	3	3	3	3	30
1984	3	3	30	30[A]	3	3	3	3	6	3	3	3
1985	30	30	3[B]	3	30	30	3	3	3	3	3	30
1986	3	3	30	3	3	3	3	3	6	3	3	3
1987	30	30	30	30	30[C]	30[C]	3	3	6	3	3	3
1990	3	3	30	3	30	30	3	3	6	3	3	3
1994	3	3	3	3	3	3	3	3	6	3	3	3
1997	30	3	30	3	30[D]	30[D]	3	3	6	3	3	3
2000	3	3	3	3	3	3	3	3	6	3	3	3
2003	3	3	3	3	3	3	3	3	6	3	3	3
2008	30	30	30	30	30	30	30	30	30	30	30	30
2014	30	30[E]	30	3	30	30	30	30	30	30	30	30

[A]C1 = 27

[B]C1 = 30

[C]C1 = 25, C3=17

[D]C2 = 29

[E]C1 = 29

4.3.9 Approaches for assessing fertility decline

4.3.9.1 Comparison of observed soil fertility data

The observed soil fertility of a catchment was calculated as the average of the analytical results for all composite samples from the three monitoring sites within the catchment at the time of sampling. Changes in soil fertility over time since burning were assessed using both linear, exponential, double exponential and quadratic regression analysis tools in the statistical software package Genstat (VSN International 2016).

4.3.9.2 Calibrating to account for natural fertility change

The paired catchment design of the experiment allowed for the natural variation in soil fertility over time to be separated from the anthropogenic effects of land use change. This was done by dividing the observed soil fertility of C2 and C3 by the observed soil fertility of the control catchment C1. Analysis of these ratios accounts for likely change in the soil fertility of C2 and C3 had they remained uncleared and provides a more accurate estimation of change rather than simply comparing the observed fertility over time to pre-clearing levels. As for the observed data, changes in soil fertility over time since burning were assessed using regression analysis.

4.4 Results

4.4.1 Grain and beef production and associated nutrient removal

Grain production in C2 yielded 49,460 kg/ha of grain over 30 years (Figure 4.2). This removed 958 kg/ha of nitrogen, 130 kg/ha of phosphorus, 96 kg/ha of sulfur and 228 kg/ha of potassium from the catchment. Removal of grain (P <0.001, R^2 = 99%) (Equation 1), nitrogen (P <0.001, R^2 = 99%) (Equation 2) and phosphorus (P <0.001, R^2 = 99%) (Equation 3) over time since the first crop was planted all showed exponential trends. Grazing of ley pasture in C2 at a stocking rate of 0.33 adult equivalent animals per hectare for 173 days produced 46 kg/ha of beef. This removed 1.1 kg/ha of

nitrogen, 0.3 kg/ha of phosphorus, 0.07 kg/ha of sulfur and 0.1 kg/ha of potassium from the catchment. This grazing period was 47 days longer than the average crop length from planting to harvest; however, nitrogen, phosphorus, sulfur and potassium removal in beef was only 3%, 6.5%, 2% and 1% respectively, of that removed in an average crop.

$$C2\ grain\ removal\ (kg/ha) = 223{,}373 - 220{,}280 \times (0.999^{x}) \quad (1)$$

$$C2\ nitrogen\ removal\ (kg/ha) = 1{,}521 - 1{,}460 \times (0.999^{x}) \quad (2)$$

$$C2\ phosphorus\ removal\ (kg/ha) = 1{,}044 - 1{,}035 \times (0.999^{x}) \quad (3)$$

Where ^{x} is years since the first crop was planted.

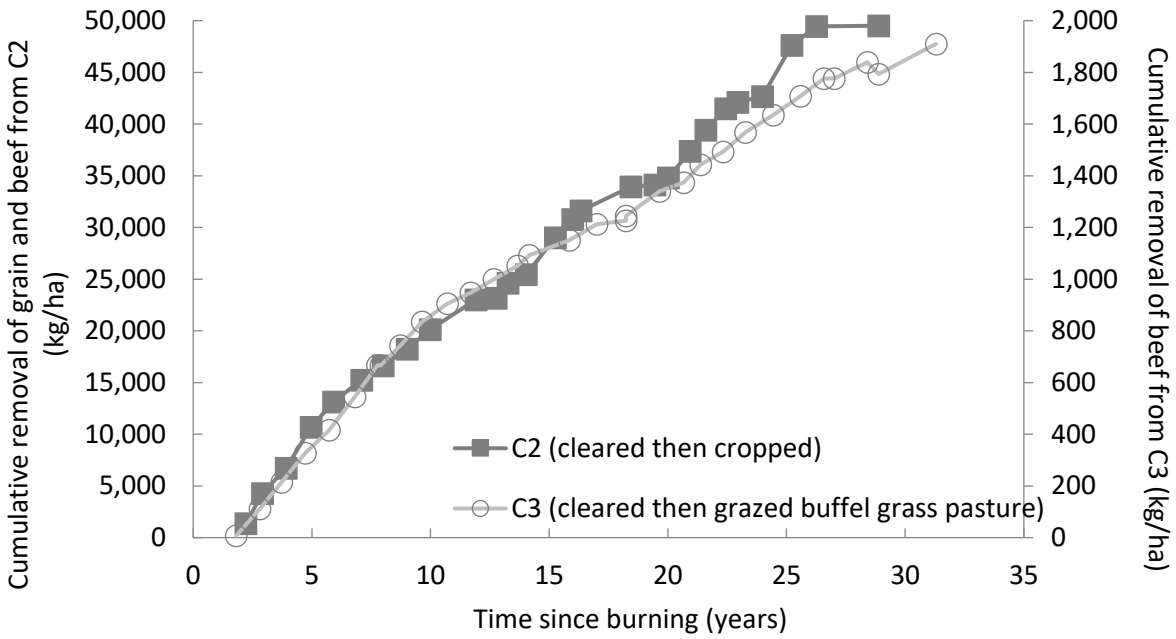

Figure 4.2. Cumulative yield of agricultural commodities removed from C2 and C3 since land use change.

Beef production in C3 yielded 1,910 kg/ha of beef over 31 years (Figure 4.2). This removed 46 kg/ha of nitrogen, 14 kg/ha of phosphorus, 3 kg/ha of sulfur and 4 kg/ha of potassium from the catchment. A further 71 kg/ha of nitrogen was removed via volatilisation from urine and faeces. Removal of beef

over time since grazing commenced showed an exponential trend (P <0.001, R^2 = 99%) (Equation 4) (Figure 4.2). As the nitrogen and phosphorus content of beef were estimated based on a percentage of live weight gain, the response curve for their removal from the catchment over time mirrored that of total beef removal.

$$C3\ beef\ removal\ (kg/ha) = 2{,}765 - 2{,}786 \times (0.999^x) \quad (4)$$

Where ^{x} is years since grazing commenced.

4.4.2 Trends in bulk density

Pre-clearing oven-dry bulk density for the three catchments in 1981 averaged 1.15 g/cm^3 (range 1.1 g/cm^3 to 1.22 g/cm^3). Over the following 32 years there was no significant linear or exponential change in bulk density in C1 (P = 0.498 and P = 0.773 respectively). Clearing and burning followed by 30 years of cropping resulted in a significant linear increase in bulk density (P = 0.062, R^2 = 44%). Fitting an exponential curve maintained the significance of the regression but improved the coefficient of determination (P = 0.06, R^2 = 63%). Ratios of C2/C1 bulk density showed no significant linear or exponential change (P = 0.136 and P = 0.292 respectively). Clearing and burning followed by 31 years of grazing resulted in a linear increase in bulk density (P = 0.097, R^2 = 35%); no significant exponential change was detected (P = 0.14). Ratios of C3/C1 bulk density mirrored both the linear and exponential results of the observed data (P = 0.053, R^2 = 47% and P = 0.132 respectively).

Observed bulk density in C2 and C3 post-clearing and burning was consistently higher than it was pre-clearing. Average bulk density post-clearing and burning was 116% of pre-clearing bulk density in C2 and 118% in C3. In the same period, bulk density in C1 declined to 98% of 1981 levels. Ratios of C2/C1 and C3/C1 bulk density were also higher post-clearing and burning, increasing to 119% and 120% of their respective pre-clearing ratios. As the average increase in bulk density in C2 and C3

equated to an additional 192 tonnes of soil in the surface 0.1 m of the soil profile, soil nutrient loss in kg/ha post-clearing and burning was calculated using the average bulk density of a catchment in that period, being 1.30 g/cm^3 in C2 and 1.34 g/cm^3 in C3.

In 1984 and 1987, soil water content was measured within two weeks of soil sampling occurring. In 1984, available soil water and bulk density at time of sampling was 5 mm and 1.18 g/cm^3 respectively in C1; 14 mm and 1.26 g/cm^3 in C2; and 17 mm and 1.30 g/cm^3 in C3. In 1987, available soil water and bulk density at time of sampling was 4 mm and 1.21 g/cm^3 respectively in C1; 23 mm and 1.21 g/cm^3 in C2; and 12 mm and 1.33 g/cm^3 in C3.

4.4.3 Trends in soil pH

Pre-clearing, $pH_{(w)}$ in the three catchments averaged 6.7 (range 6.6 to 6.9). From 1981 to 2014, $pH_{(w)}$ in C1 averaged 6.7 with no significant linear or exponential trend (P = 0.237 and P = 0.36 respectively) (Figure 4.3). Clearing and burning C2 and C3 in 1982 increased $pH_{(w)}$ in both catchments (Figure 4.3). Visually, $pH_{(w)}$ continued to increase until 5 years post-burning in C2 and 11 years post-burning in C3. However, $pH_{(w)}$ had peaked within 2 years of burning, with no significant linear change in either catchment from 1.92 to 11.3 years post-burning (P = 0.355 and P = 0.256 respectively). The maximum $pH_{(w)}$ in both C2 and C3 was 8. Thirty-two years after burning, $pH_{(w)}$ in C2 was 7.1 and $pH_{(w)}$ in C3 was 7.3, both greater than their pre-clearing $pH_{(w)}$ of 6.6 and 6.9, respectively. The exponential rise in $pH_{(w)}$ post-burning, followed by a long-term linear decline was significant in both C2 (P <0.001, R^2 = 79%) (Equation 1 in Table 4.4) and C3 (P <0.001, R^2 = 78%) when fitted with a double exponential curve (Equation 2 in Table 4.4).

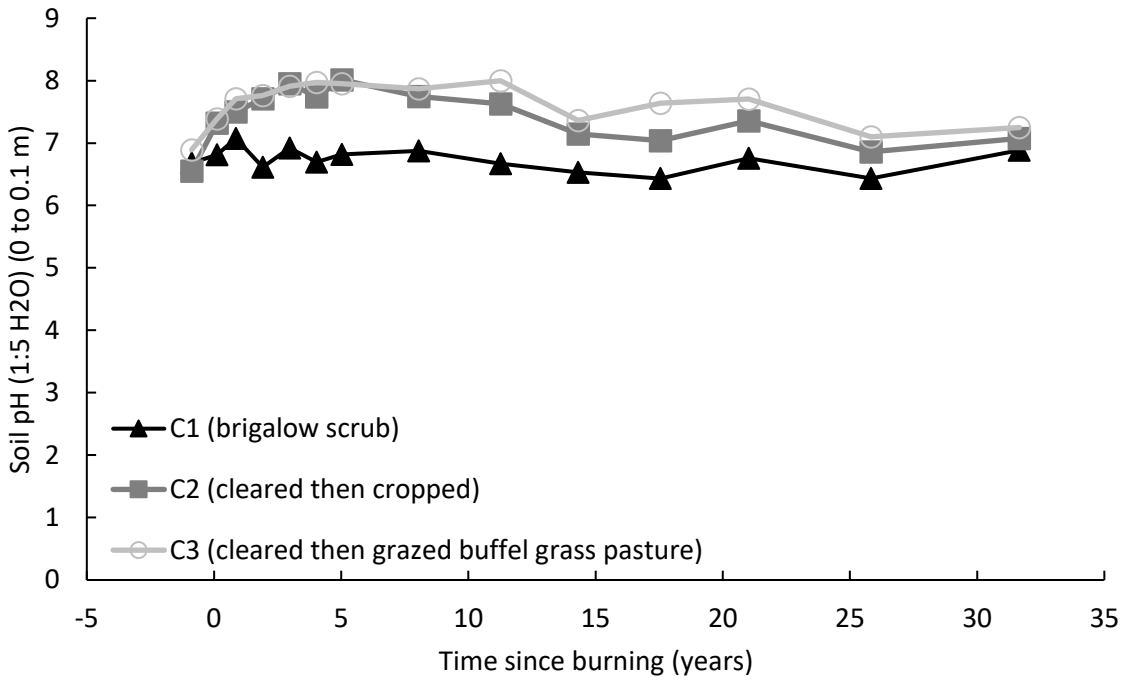

Figure 4.3. Soil pH (1:5 soil/water) (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

The behaviour of $pH_{(w)}$ in all catchments was mirrored by $pH_{(Ca)}$ (Figure 4.4). From 1981 to 2014, $pH_{(Ca)}$ in C1 averaged 5.9 with no significant linear or exponential trend (P = 0.357 and P = 0.069 respectively). The exponential rise in $pH_{(Ca)}$ post-burning, followed by a long-term linear decline was significant in both C2 (P <0.001, R^2 = 93%) (Equation 3 in Table 4.4) and C3 (P <0.001, R^2 = 72%) (Equation 4 in Table 4.4). Values of $pH_{(Ca)}$ were 0.3 to 1.3 pH units less than $pH_{(w)}$.

Table 4.4. Equations describing trends in soil fertility over time where *x* is years since burning.

Parameter	Catchment	Period	Trend equation	*P*	R^2	Equation number
$pH_{(w)}$	C1	1981 to 2014		NS		
	C2	1981 to 2014	$C2\ pH = 7.985 - 0.742 \times (0.459^x) - 0.03708x$	<0.001	0.79	1
	C3	1981 to 2014	$C3\ pH = 8.147 - 0.778 \times (0.565^x) - 0.03144x$	<0.001	0.78	2
$pH_{(Ca)}$	C1	1981 to 2014		NS		
	C2	1981 to 2014	$C2\ pH = 7.1952 - 0.706 \times (0.3357^x) - 0.04163x$	<0.001	0.93	3
	C3	1981 to 2014	$C3\ pH = 7.486 - 1.004 \times (0.538^x) - 0.0369x$	<0.001	0.72	4
Organic carbon	C1	1981 to 2014		NS		
	C2	1981 to 2014	$C2\ OC\ (\%) = 1.203 + 0.842 \times (0.823^x)$	<0.001	0.88	5
	C3	1981 to 2000	$C3\ OC\ (\%) = 1.53 + 0.207 \times (0.49^x)$	<0.001	0.79	6
Total nitrogen	C1	1981 to 2014		NS	0.39	
	C2	1981 to 2014	$C2\ TN\ (\%) = 0.0866 + 0.104 \times (0.84^x)$	<0.001	0.91	7
	C3	1981 to 2014	$C3\ TN\ (\%) = 0.12 + 0.028 \times (0.611^x)$	0.01	0.49	8
Total phosphorus	C1	1981 to 2014	$C1\ TP\ (\%) = 0.0265 + 0.0023 \times (1.035^x)$	<0.001	0.77	9
	C2	1982 to 2014	$C2\ TP\ (\%) = 0.0268 + 0.0097 \times (0.875^x)$	<0.001	0.91	10
	C3	1982 to 2014	$C3\ TP\ (\%) = 0.027 + 0.0053 \times (0.478^x)$	0.009	0.53	11
Bicarbonate-extractable phosphorus	C1	1981 to 2014		NS		
	C2	1982 to 2014	$C2\ P(B)\ (mg/kg) = 18.14 + 15.7 \times (0.852^x)$	<0.001	0.88	12
	C3	1982 to 2014	$C3\ P(B)\ (mg/kg) = 12.62 + 22.86 \times (0.744^x)$	<0.001	0.92	13
Acid-extractable phosphorus	C1	1981 to 2014		NS		
	C2	1982 to 2014	$C2\ P(A)\ (mg/kg) = 31.02 + 29.75 \times (0.849^x)$	<0.001	0.91	14
	C3	1982 to 2014	$C3\ P(A)\ (mg/kg) = 21.3 + 39.42 \times (0.818^x)$	<0.001	0.97	15
Total sulfur	C1	1981 to 2014	$C1\ TS\ (\%) = 0.0249 - 0.0043 \times (0.984^x)$	0.008	0.51	16
	C2	1982 to 2014	$C2\ TS\ (\%) = 0.0135 + 0.0095 \times (0.715^x)$	<0.001	0.9	17
	C3	1982 to 2014		NA		
Total potassium	C1	1981 to 2014		NS		
	C2	1982 to 2014	$C2\ TK\ (\%) = 0.457 + 0.039 \times (0.893^x)$	0.004	0.61	18
	C3	1982 to 2014	$C3\ TK\ (\%) = 0.239 + 0.027 \times (0.806^x)$	<0.001	0.94	19
Exchangeable potassium	C1	1981 to 2014	$C1\ Exch.K\ (\mathrm{cmol_c/kg}) = 0.4824 + (0.0367 + 0.00056x)/(1 - 0.07919x + 0.001865x\text{^}2\ )$	<0.001	0.94	20
	C2	1982 to 2014	$C2\ Exch.K\ (\mathrm{cmol_c/kg}) = 0.4081 + 0.3393 \times (0.7678^x)$	<0.001	0.8	21
	C3	1982 to 2014	$C3\ Exch.K\ (\mathrm{cmol_c/kg}) = 0.3178 + 0.3454 \times (0.8215^x)$	<0.001	0.89	22

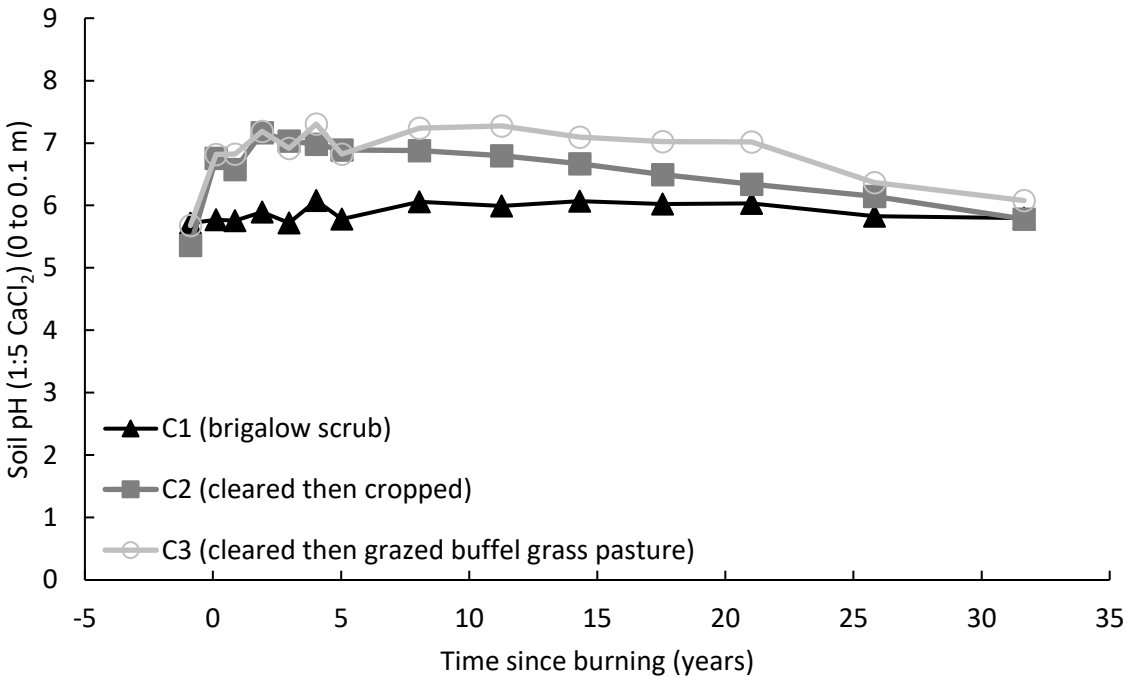

Figure 4.4. Soil pH (1:5 soil/calcium chloride) (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4 Trends in observed soil fertility data

4.4.4.1 Organic carbon

Pre-clearing, OC concentrations in the three catchments averaged 2.08% (range 1.93% to 2.25%). From 1981 to 2014, OC in C1 averaged 2.15% with no significant linear or exponential trend (P = 0.061 and P = 0.066 respectively) (Figure 4.5). Unlike C1, OC in C2 showed a significant exponential decline of 46% from 2.25% in 1981 to 1.21% in 2014 (P <0.001, R^2 = 88%) (Equation 5 in Table 4.4) (Figure 4.5). In C3, OC showed no significant linear or exponential trends from 1981 to 2014 (P = 0.293 and P = 0.343 respectively) (Figure 4.5). However, this analysis masks a significant exponential decline of 28% from 1.93% in 1981 to 1.39% in 2000 (P <0.001, R^2 = 79%) (Equation 6 in Table 4.4) (Figure 4.5) followed by an increase from 2000 to 2014.

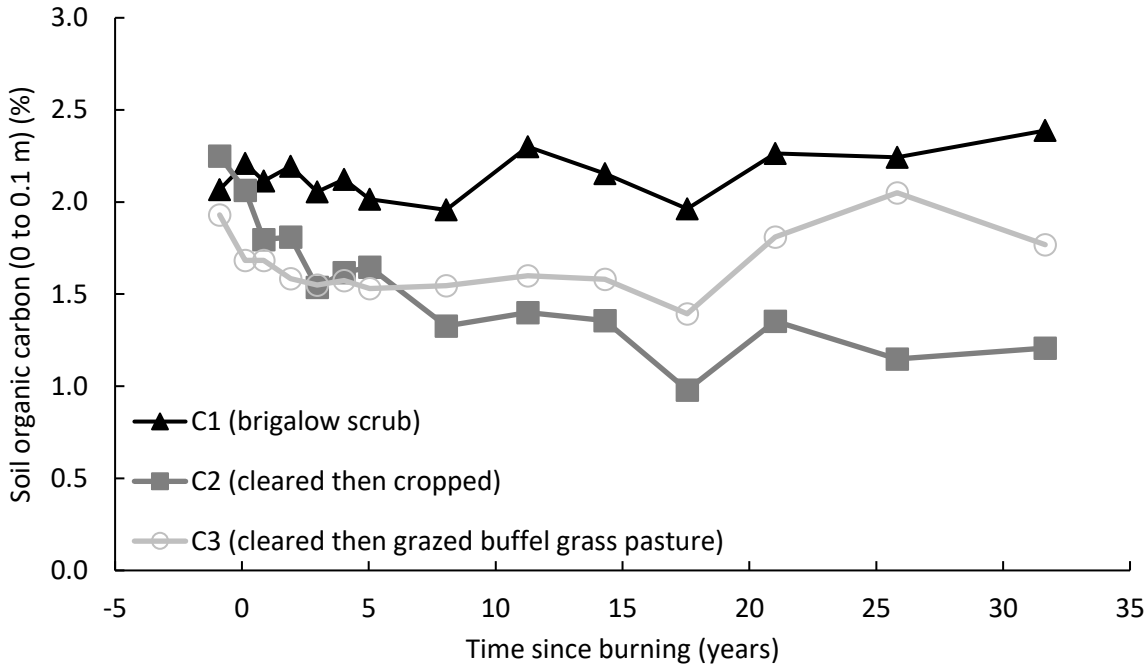

Figure 4.5. Soil organic carbon (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.2 Total nitrogen

Pre-clearing, TN concentrations in the three catchments averaged 0.18% (range 0.163% to 0.197%). From 1981 to 2014, TN in C1 averaged 0.175% with no significant linear or exponential trend (P = 0.191 and P = 0.161 respectively) (Figure 4.6). Unlike C1, TN in C2 showed a significant exponential decline of 55%, or 1,050 kg/ha, from 0.197% in 1981 to 0.088% in 2014 (P <0.001, R^2 = 91%) (Equation 7 in Table 4.4) (Figure 4.6). Similar to C2, C3 showed a significant exponential decline of 22%, or 143 kg/ha, from 0.163% in 1981 to 0.128% in 2014 (P = 0.01, R^2 = 49%) (Equation 8 in Table 4.4) (Figure 4.6).

These declines were exceeded when considering only the period from 1981 to 2008, prior to the commencement of the adaptive land management phase to enhance soil fertility. In this period, TN in C2 showed a significant exponential decline of 61%, or 1,201 kg/ha while TN in C3 showed a significant exponential decline of 24%, or 192 kg/ha. From 2010 to 2014, during the adaptive land

management phase, TN in C1 and C3 had similar increases of 2.4% and 2.9% respectively; however, TN in C2 increased by 15.3%, or 151 kg/ha.

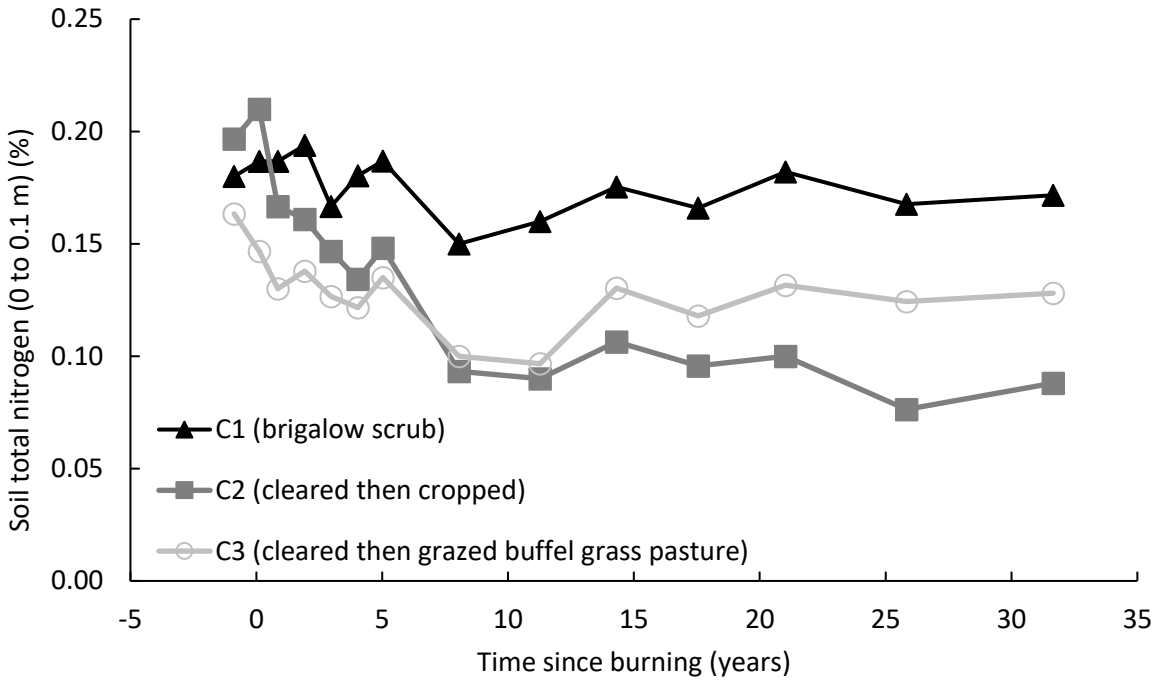

Figure 4.6. Soil total nitrogen (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.3 Mineral nitrogen

Pre-clearing, ammonium-nitrogen concentrations in the three catchments averaged 5.19 mg/kg (range 4.87 mg/kg to 5.5 mg/kg) and nitrate-nitrogen averaged 2.46 mg/kg (range 1.74 mg/kg to 3.4 mg/kg). Average mineral nitrogen, being the sum of ammonium- and nitrate-nitrogen, was 7.65 mg/kg (range 6.61 mg/kg to 8.58 mg/kg) (Figure 4.7 to Figure 4.9). In the first sampling post-burning, ammonium-nitrogen in C2 and C3 spiked to an average of 8.9 times their pre-clearing concentrations when adjusted for the natural increase in ammonium-nitrogen observed in C1 (Figure 4.7). This spike was short lived and by the following sampling, less than one year post-burning, ammonium-nitrogen concentrations in C2 and C3 declined back to that of C1. Ammonium-nitrogen concentrations

fluctuated at all subsequent samplings with C1 typically having highest concentrations and C2 and C3 having similar, lower concentrations.

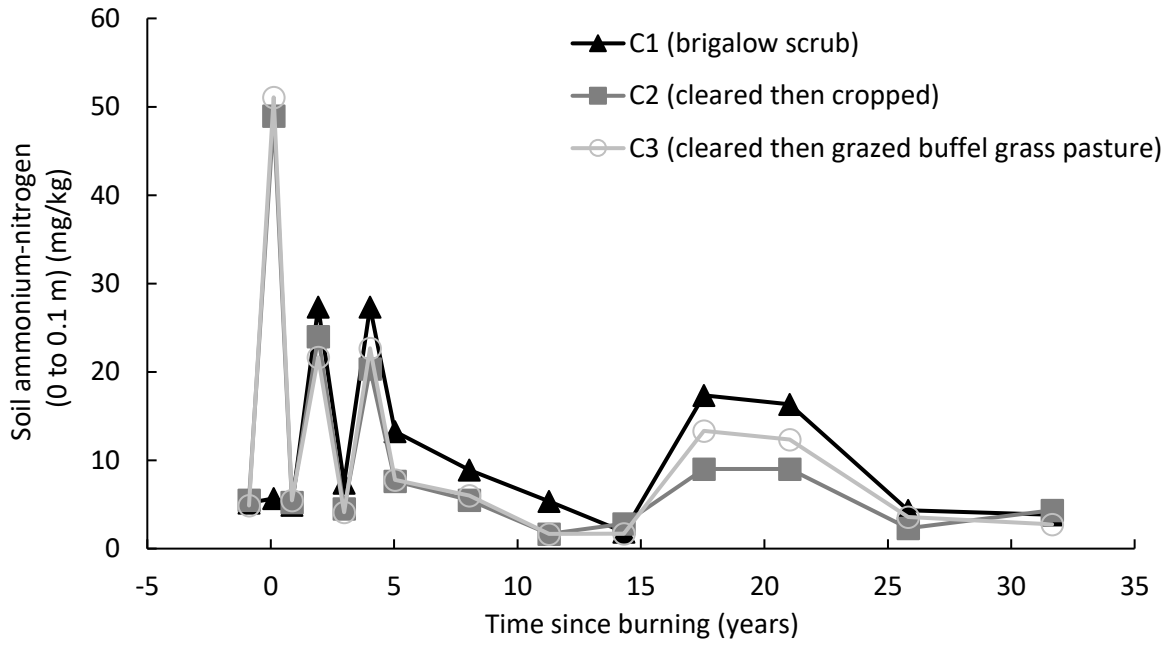

Figure 4.7. Soil ammonium-nitrogen (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

Nitrate-nitrogen in C2 and C3 had a similar spike post-clearing, increasing to an average of 7.5 times pre-clearing concentrations when adjusted for the natural decline in nitrate-nitrogen observed in C1 (Figure 4.8). The spike was observed after the ammonium-nitrogen spike had declined back to pre-clearing concentrations. Elevated nitrate-nitrogen concentrations were observed in C2 for at least eight years post-burning after which concentrations and fluctuations were similar to those observed in C1. Elevated nitrate-nitrogen concentrations in C3 declined within two years of burning and typically remained less than those observed in C1 with substantially less fluctuation.

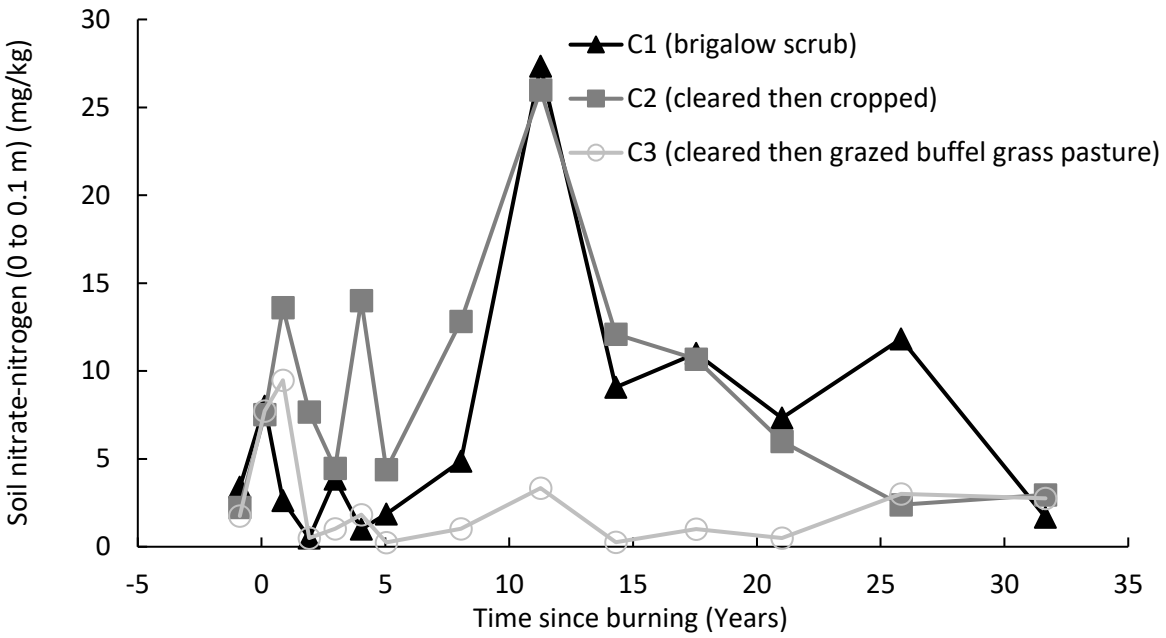

Figure 4.8. Soil nitrate-nitrogen (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

Total mineral nitrogen showed a post-burning spike in C2 and C3 of 5.1 times their pre-clearing mineral nitrogen when adjusted for the natural increase in mineral nitrogen observed in C1 (Figure 4.9). These increases declined substantially within one year post-burning and fluctuated similarly to mineral nitrogen concentrations in C1 up to five years post-burning. From this point mineral nitrogen in C1 and C2 had similar concentrations and fluctuations however concentrations in C3 were typically lower with less fluctuation.

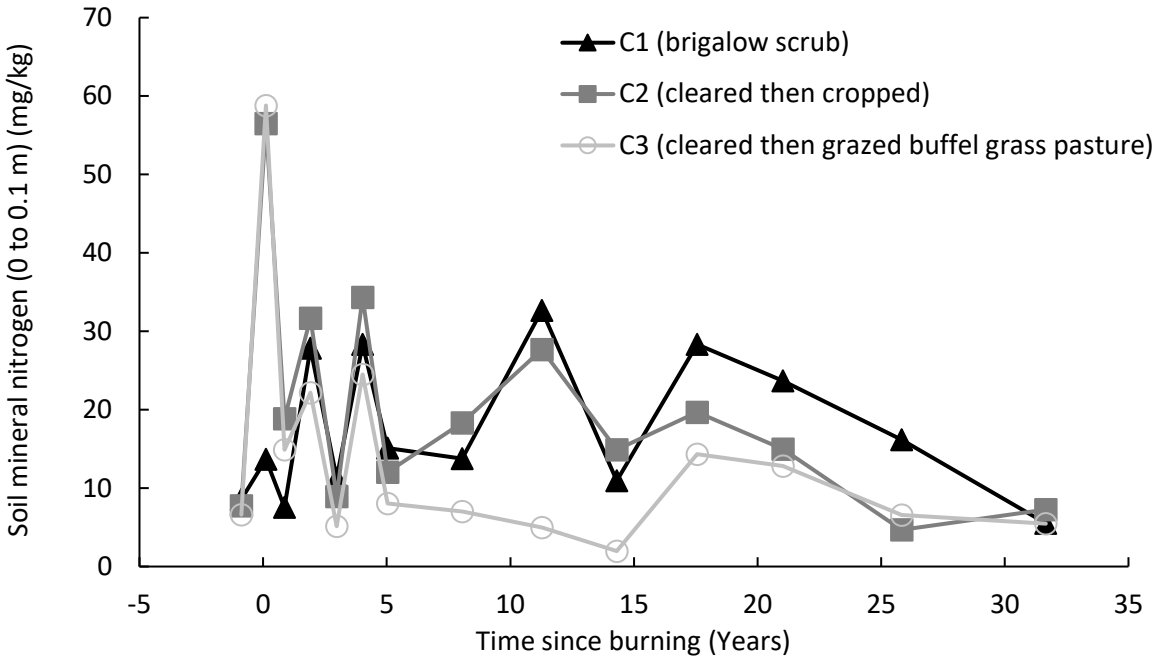

Figure 4.9. Soil mineral-nitrogen (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.4 Total phosphorus

Pre-clearing, TP concentrations in the three catchments averaged 0.031% (range 0.029% to 0.035%). In C1, TP showed a significant linear and exponential (Equation 9 in Table 4.4) increase of 14% from 0.029% in 1981 to 0.033% in 2014 (P <0.001, R^2 = 76% and P <0.001, R^2 = 77% respectively) (Figure 4.10). This increase was not constant over time with no significant linear or exponential trend occurring prior to 2003 (P = 0.082 and P = 0.15 respectively).

Clearing and burning C2 and C3 increased TP by an average of 4%. Post-burning, TP in C2 showed a significant exponential decline of 29%, or 131 kg/ha, from 0.036% in 1982 to 0.027% in 2014 (P <0.001, R^2 = 91%) (Equation 10 in Table 4.4) (Figure 4.10). Similarly, TP in C3 showed a significant exponential decline of 14%, or 59 kg/ha, from 0.032% in 1982 to 0.027% in 2014 (P = 0.009, R^2 = 53%) (Equation 11 in Table 4.4) (Figure 4.10). Visually, the decline in C3 was most prevalent from

1982 to 1997 followed by an increase from 2000 to 2014. This is supported by linear regression showing increasing *P*-values and decreasing R^2 with each successive sampling from 1997 onwards. Fitting an exponential curve showed similar results with R^2 declining from 81% at 2003 to 52% at 2008.

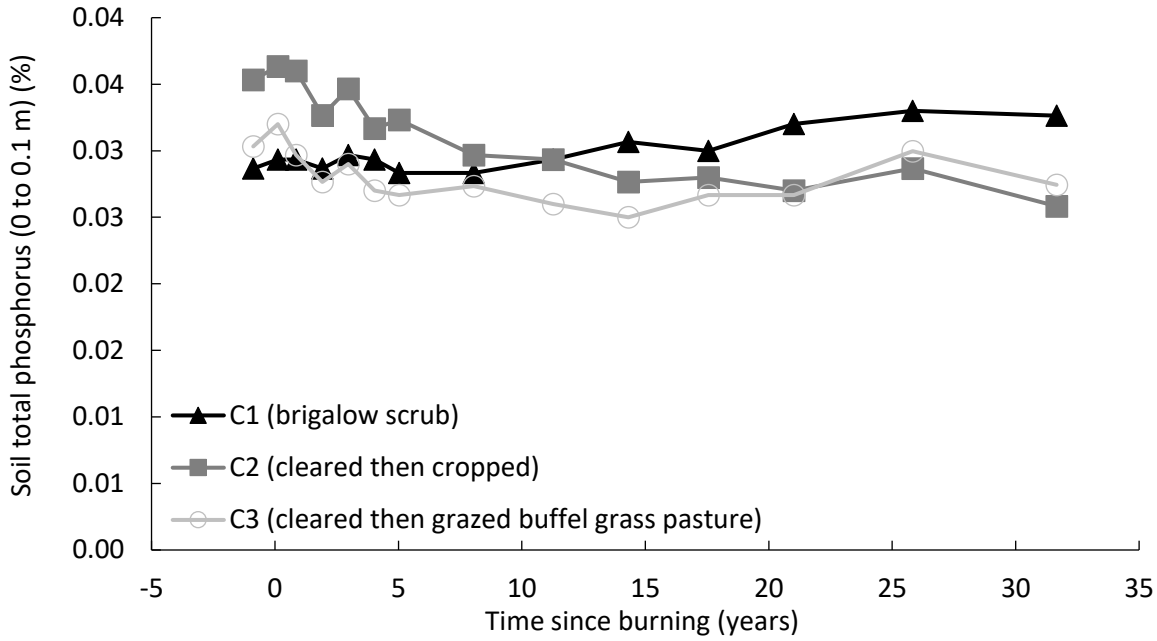

Figure 4.10. Soil total phosphorus (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.5 Bicarbonate-extractable phosphorus

Pre-clearing, P(B) concentrations in the three catchments averaged 13.67 mg/kg (range 13.3 mg/kg to 14 mg/kg). From 1981 to 2014, P(B) in C1 averaged 14.31 mg/kg and showed no significant linear or exponential trend ($P = 0.063$ and $P = 0.18$ respectively) (Figure 4.11). Clearing and burning C2 and C3 increased P(B) by an average of 2.5 times pre-clearing concentrations. After this initial increase a significant exponential decline occurred between 1982 and 2014 in both C2 ($P < 0.001$, $R^2 = 88\%$) (Equation 12 in Table 4.4) and C3 ($P < 0.001$, $R^2 = 92\%$) (Equation 13 in Table 4.4) (Figure 4.11). Thirty-

two years after the increase in P(B) concentrations as a result of burning, P(B) concentrations in C2 had declined to 15.9 mg/kg, equal to 114% of its pre-clearing concentration; P(B) concentrations in C3 had declined to 12.63 mg/kg, equal to 95% of its pre-clearing concentration. On a kg/ha basis, this was a decline of 18 kg/ha in C2 and 23 kg/ha in C3. During this 32-year period there was no significant correlation between P(B) and $pH_{(w)}$ in either C2 (P = 0.087) or C3 (P = 0.706).

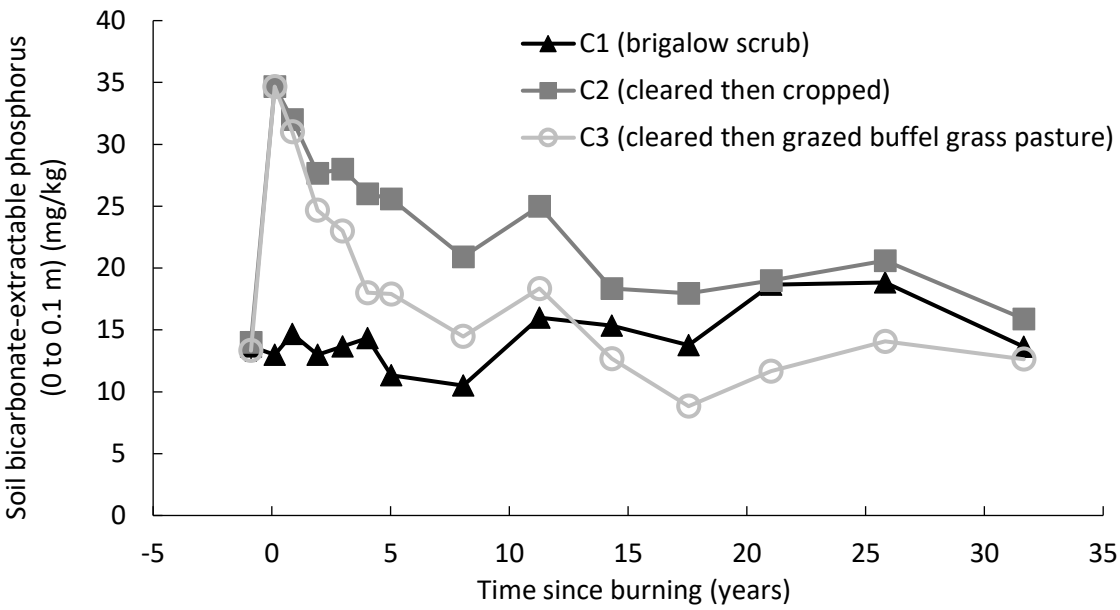

Figure 4.11. Soil bicarbonate-extractable phosphorus (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.6 Acid-extractable phosphorus

The behaviour of P(A) in all three catchments mirrored that of P(B). Pre-clearing, P(A) concentrations in the three catchments averaged 26 mg/kg (range 25 mg/kg to 26.3 mg/kg). From 1981 to 2014, C1 P(A) averaged 23.48 mg/kg and showed no significant linear or exponential trend (P = 0.063 and P = 0.18 respectively) (Figure 4.12). Clearing and burning C2 and C3 increased P(A) by an average of 2.2 times pre-clearing concentrations. After this initial increase a significant exponential decline occurred between 1982 and 2014 in both in C2 (P <0.001, R^2 = 91%) (Equation 14 in Table 4.4) and

C3 (P <0.001, R^2 = 97%) (Equation 15 in Table 4.4) (Figure 4.12). At 32 years post-burning, P(A) concentrations in C2 had declined to 24.63 mg/kg, equal to 94% of its pre-clearing concentration; P(A) concentrations in C3 had declined to 19.57 mg/kg, equal to 73% of its pre-clearing concentration. On a kg/ha basis, this was a decline of 36 kg/ha in C2 and 39 kg/ha in C3. During this 32-year period there was no significant correlation between P(A) and $pH_{(w)}$ in either C2 (P = 0.108) or C3 (P = 0.391).

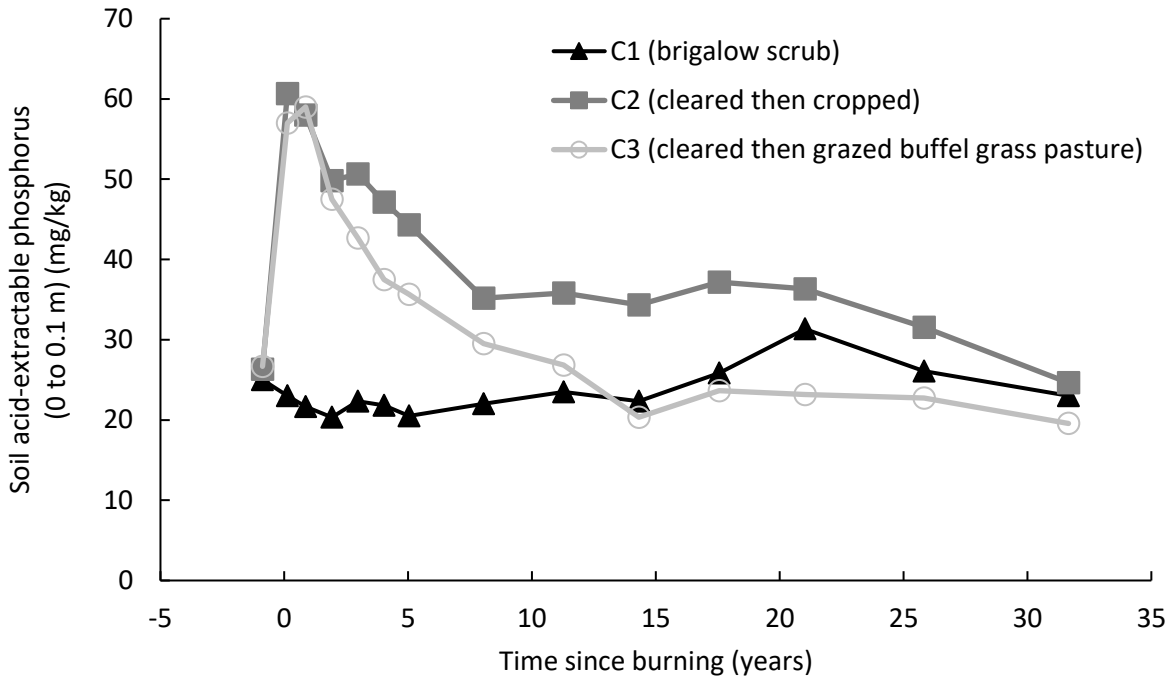

Figure 4.12. Soil acid-extractable phosphorus (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.7 Total sulfur

Pre-clearing, TS concentrations in the three catchments averaged 0.021% (range 0.02% to 0.023%). In C1, TS showed a significant linear and exponential (Equation 16 in Table 4.4) increase of 9% from 0.021% in 1981 to 0.022% in 2014 (P = 0.002, R^2 = 55% and P = 0.008, R^2 = 51% respectively) (Figure

4.13). As for TP, this increase was not constant over time with no significant linear trend occurring prior to 2000 (P = 0.058) or exponential trend prior to 2003 (P = 0.145).

Clearing and burning C2 and C3 increased TS by an average of 6%. Post-burning, TS in C2 showed a significant exponential decline of 49%, or 153 kg/ha, from 0.024% in 1982 to 0.012% in 2014 (P <0.001, R^2 = 90%) (Equation 17 in Table 4.4) (Figure 4.13). Data from C3 did not meet the assumptions for valid statistical testing so no statement of significance can be made about trends over the entire 32-year post-burning period. However, the calculated loss of TS was 23%, or 67 kg/ha, from 0.022% in 1982 to 0.017% in 2014. Visually, the increase in TS associated with clearing and burning declined rapidly from 1982 to 1984 followed by a gradual increase with a substantial spike in 2008 (Figure 4.13). The initial decline from 1982 to 1987 was exponential (P = 0.009, R^2 = 93%). An exponential curve could be fitted to the data up to 2003 (P = 0.001, R^2 = 80%); however, inclusion of the 2008 data resulted in a non-significant regression (P = 0.286*).* No significant linear trend occurred from 1984 to 2000 (P = 0.211); however, incremental inclusion of data from 2003 to 2014 showed significant increases in TS (P = 0.005 to 0.037, R^2 = 35% to 60%).

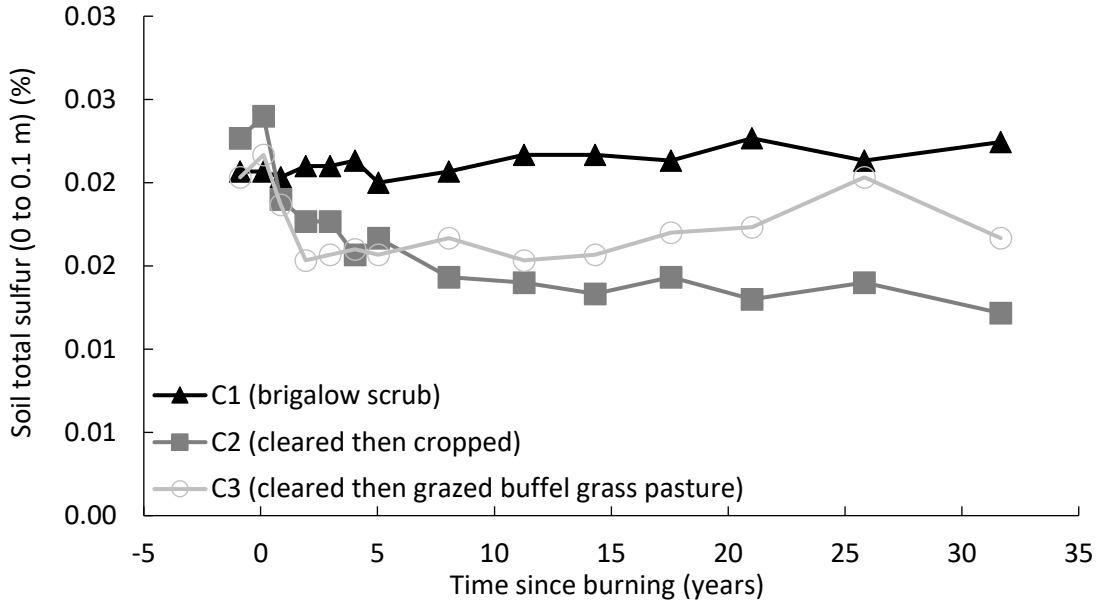

Figure 4.13. Soil total sulfur (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.8 Total potassium

Pre-clearing, TK concentrations in the three catchments averaged 0.483% (range 0.248% to 0.716%). In C1, TK averaged 0.716% and showed no significant linear or exponential trend from 1981 to 2014 (P = 0.084 and P = 0.119 respectively) (Figure 4.14).

Clearing and burning C2 and C3 increased TK by an average of 5%. Post-burning, TK in C2 showed a significant exponential decline of 9%, or 579 kg/ha, from 0.506% in 1982 to 0.461% in 2014 (P = 0.004, R^2 = 61%) (Equation 18 in Table 4.4). Post-burning, TK in C3 showed a significant exponential decline of 10%, or 364 kg/ha, from 0.264% in 1982 to 0.237% in 2014 (P <0.001, R^2 = 94%) (Equation 19 in Table 4.4) (Figure 4.14). At 32 years post-burning, TK concentrations in C2 had declined to 0.461%, equal to 95% of its pre-clearing concentration; TK concentrations in C3 had declined to 0.237%, equal to 96% of its pre-clearing concentration.

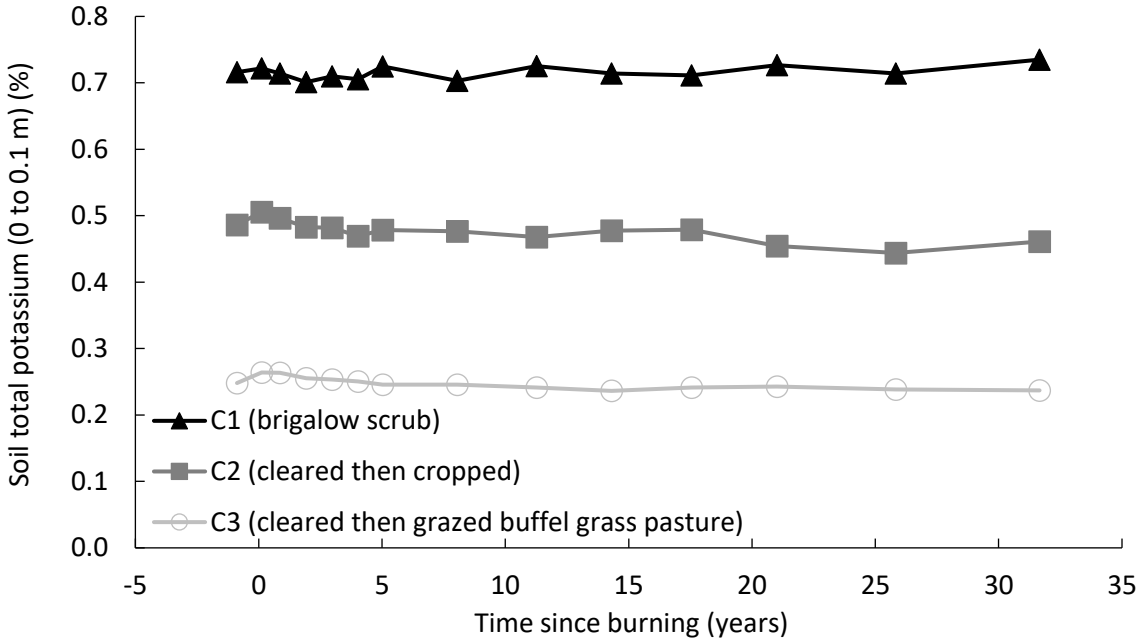

Figure 4.14. Soil total potassium (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

4.4.4.9 Exchangeable potassium

Pre-clearing, Exch. K concentrations in the three catchments averaged 0.46 $cmol_c$/kg (range 0.41 $cmol_c$/kg to 0.52 $cmol_c$/kg). From 1981 to 1990, Exch. K in C1 averaged 0.53 $cmol_c$/kg with no significant linear or exponential trend (P = 0.729 and P = 0.731 respectively) (Figure 4.15). From 1990 to 2003 Exch. K increased, peaking at 0.77 $cmol_c$/kg, before declining to 0.63 $cmol_c$/kg in 2014 (Figure 4.15). The Exch. K trend for the whole 32-year period was best described by a quadratic by quadratic curve (P <0.001, R^2 = 94%) (Equation 20 in Table 4.4).

Clearing and burning C2 and C3 increased Exch. K by an average of 1.7 times pre-clearing concentrations. After this initial increase a significant exponential decline occurred between 1982 and 2014 in both C2 (P <0.001, R^2 = 80%) (Equation 21 in Table 4.4) and C3 (P <0.001, R^2 = 89%) (Equation 22 in Table 4.4) (Figure 4.15). Thirty-two years after the increase in Exch. K concentrations

as a result of burning, Exch. K concentrations in C2 had declined to 0.29 $cmol_c$/kg, equal to 65% of its pre-clearing concentration; Exch. K concentrations in C3 had declined to 0.28 $cmol_c$/kg, equal to 70% of its pre-clearing concentration.

4.4.5 Trends after accounting for natural fertility change

4.4.5.1 Organic carbon

Similar to the observed C2 OC data, the C2/C1 OC ratio also showed a significant exponential decline from 1981 to 2014 (P <0.001, R^2 = 91%) (Equation 1 in Table 4.5). However the 54% decline in the ratio was greater than the 46% decline in the observed C2 OC data. In contrast to the observed C3 OC data, the C3/C1 OC ratio showed a significant exponential decline of 21% (P = 0.05, R^2 = 32%) from 1981 to 2014 (Equation 2 in Table 4.5). The exponential decline of 24% (P = 0.002, R^2 = 74%) in the C3/C1 OC ratio between 1981 and 2000 was similar to the observed data.

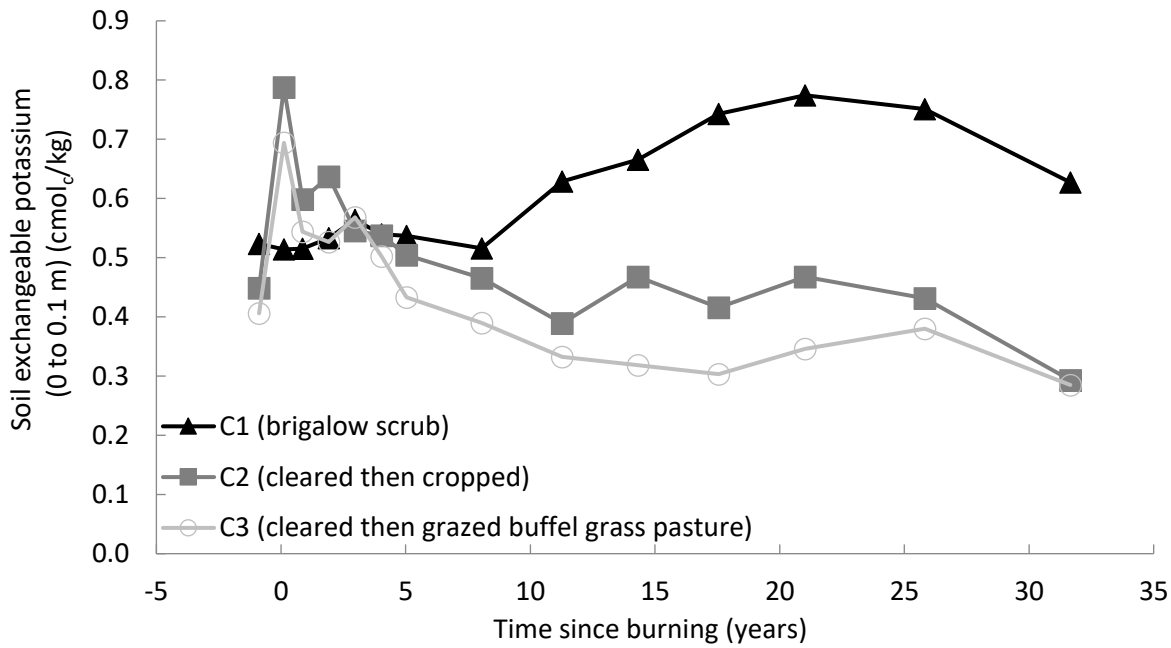

Figure 4.15. Soil exchangeable potassium (0 to 0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

Table 4.5. Equations describing the ratios of soil fertility over time in catchments two and three to the soil fertility in catchment 1, where *x* is years since burning.

Parameter	Ratio	Period	Trend equation	*P*	R^2	Equation number
Organic carbon	C2/C1	1981 to 2014	$C2/C1\ OC = 0.5251 + 0.4332 \times (0.8649^x)$	<0.001	0.91	1
	C3/C1	1981 to 2012	$C3/C1\ OC = 0.7613 + 0.02445 \times (0.1095^x)$	0.05	0.32	2
Total nitrogen	C2/C1	1981 to 2014	$C2/C1\ TN = 0.5059 + 0.5222 \times (0.8496^x)$	<0.001	0.93	3
	C3/C1	1981 to 2014	$C3/C1\ TN = 0.7071 + 0.0681 \times (0.290^x)$	0.004	0.57	4
Total phosphorus	C2/C1	1982 to 2014	$C2/C1\ TP = 0.7334 + 0.5014 \times (0.9406^x)$	<0.001	0.95	5
	C3/C1	1982 to 2014	$C3/C1\ TP = 0.8621 + 0.2019 \times (0.8091^x)$	<0.001	0.75	6
Bicarbonate-extractable phosphorus	C2/C1	1982 to 2014	$C2/C1\ P(B) = 0.913 + 1.556 \times (0.9216^x)$	<0.001	0.86	7
	C3/C1	1982 to 2014	$C3/C1\ P(B) = 0.768 + 1.746 \times (0.8197^x)$	<0.001	0.91	8
Acid-extractable phosphorus	C2/C1	1982 to 2014	$C2/C1\ P(A) = 1.0516 + 1.6841 \times (0.9018^x)$	<0.001	0.97	9
	C3/C1	1982 to 2014	$C3/C1\ P(A) = 0.7736 + 1.952 \times (0.8565^x)$	<0.001	0.97	10
Total sulfur	C2/C1	1982 to 2014	$C2/C1\ TS = 0.6177 + 0.4874 \times (0.756^x)$	<0.001	0.87	11
	C3/C1	1982 to 2014	$C3/C1\ TS = 0.7736 + 0.337 \times (0.245^x)$	0.009	0.53	12
Total potassium	C2/C1	1982 to 2014	$C2/C1\ TK = 0.58 + 0.112 \times (0.971^x)$	0.001	0.68	13
	C3/C1	1982 to 2014	$C3/C1\ TK = 0.32862 + 0.04139 \times (0.8752^x)$	<0.001	0.85	14
Exchangeable potassium	C2/C1	1982 to 2014	$C2/C1\ Exch.K = 0.539 + 0.8672 \times (0.8532^x)$	<0.001	0.91	15
	C3/C1	1982 to 2014	$C3/C1\ Exch.K = 0.4269 + 0.8494 \times (0.8556^x)$	<0.001	0.94	16

4.4.5.2 Total nitrogen

The C2/C1 TN ratio behaved similarly to the observed C2 TN data. The ratio showed a significant exponential decline of 53% from 1981 to 2014 (P <0.001, R^2 = 93%) (Equation 3 in Table 4.5). Prior to the commencement of the adaptive land management phase the ratio showed a significant exponential decline of 58 % from 1981 to 2014 (P <0.001, R^2 = 92%). From 2010 to 2014, during the adaptive land management phase, the ratio increased by 13%. The C3/C1 TN data also behaved similarly to the observed C3 TN data. The ratio showed a significant exponential decline of 18% from 1981 to 2014 (P = 0.004, R^2 = 57%) (Equation 4 in Table 4.5). From 2010 to 2014, during the adaptive land management phase, the ratio increased by 1%.

4.4.5.3 Total phosphorus

Compared to the observed TP data, both C2/C1 and C3/C1 TP ratios showed smaller increases with clearing and burning, averaging 2%, but greater declines over time. In C2, the C2/C1 TP ratio showed a significant exponential decline of 36% from 1982 to 2014 (P <0.001, R^2 = 95%) (Equation 5 in Table 4.5). In C3, the C3/C1 TP ratio showed a significant exponential decline of 23% from 1982 to 2014 (P <0.001, R^2 = 75%) (Equation 6 in Table 4.5).

4.4.5.4 Bicarbonate-extractable phosphorus

Compared to the observed P(B) data, both C2/C1 and C3/C1 P(B) ratios showed greater increases with clearing and burning, averaging 2.7 times the pre-clearing ratio, but similar declines over time from 1984 to 2014. The significant exponential decline in the C2/C1 ratio (P <0.001, R^2 = 86%) (Equation 7 in Table 4.5) to 114% of its pre-clearing ratio over 32 years post-burning, equalled the change in the observed data. The significant exponential decline in the C3/C1 ratio (P <0.001, R^2 = 91%) (Equation 8 in Table 4.5) to 95% of its pre-clearing ratio also equalled the change in the observed data.

4.4.5.5 Acid-extractable phosphorus

As for the P(B) ratios, both C2/C1 and C3/C1 P(A) ratios showed greater increases with clearing and burning compared to the observed P(A) data, averaging 2.4 times the pre-clearing ratio. However, over the 32 years post-burning, the P(A) ratios showed a smaller decline than the observed data. From 1982 to 2014, the C2/C1 P(A) ratio had a significant exponential decline (P <0.001, R^2 = 97%) (Equation 9 in Table 4.5) to 102% of its pre-clearing ratio while the C3/C1 P(A) ratio had a significant exponential decline (P <0.001, R^2 = 97%) (Equation 10 in Table 4.5) to 80% of its pre-clearing ratio.

4.4.5.6 Total sulfur

Clearing and burning C2 and C3 increased ratios of C2/C1 and C3/C1 TS by an average of 6%, equalling the average increase in the observed data. Post-burning, the C2/C1 TS ratio showed a significant exponential decline of 53% from 1982 to 2014 (P <0.001, R^2 = 87%) (Equation 11 in Table 4.5), similar to the observed data. In contrast to the observed C3 TS data, which did not meet the assumptions for valid statistical testing, the C3/C1 TS ratio could be fitted with a significant exponential decline curve (P = 0.009, R^2 = 53%) for the whole post-burning period (Equation 12 in Table 4.5). The decline in the C3/C1 TS ratio from 1982 to 2014 was 29%.

4.4.5.7 Total potassium

Clearing and burning C2 and C3 increased ratios of C2/C1 and C3/C1 TK by an average of 4%, similar to the observed data. Post-burning, the ratios for both catchments showed significant exponential declines, similar to the observed data. From 1982 to 2014 the C2/C1 TK ratio declined by 10% (P = 0.001, R^2 = 68%) (Equation 13 in Table 4.5) and the C3/C1 TK ratio declined by 12% (P <0.001, R^2 = 85%) (Equation 14 in Table 4.5).

4.4.5.8 Exchangeable potassium

Compared to the observed Exch. K data, both C2/C1 and C3/C1 Exch. K ratios showed greater increases with clearing and burning, averaging 1.8 times the pre-clearing ratio. The significant exponential decline in the C2/C1 ratio (P <0.001, R^2 = 91%) (Equation 15 in Table 4.5) to 55% of its pre-clearing ratio over 32 years post-burning, was greater than the decline in the observed data. The significant exponential decline in the C3/C1 ratio (P <0.001, R^2 = 94%) (Equation 16 in Table 4.5) to 59% of its pre-clearing ratio was also greater than the decline in the observed data.

4.4.6 Comparison of approaches for assessing fertility decline

All of the significant declines in observed soil fertility post-burning in both C2 and C3 (Table 4.4) were confirmed by the ratio analysis (Table 4.5). When the observed soil fertility data from C2 was adjusted for the natural variation in soil fertility in the control catchment, the R^2 of the exponential decline curves increased by an average of 3% with a maximum change of 12%. When this adjustment was made for C3, the R^2 of the exponential decline curves increased by an average of 9%; however, the maximum change was 42%. While observed C3 OC and TS data showed no significant change in the 32 years post-burning, adjusting for the natural variation in soil fertility in the control catchment revealed a significant decline, similar to C2.

4.4.7 Correlations between soil nitrogen and phosphorus decline and removal in produce

The sum of total nitrogen removed from C2 in grain between soil samplings showed an exponential correlation with soil TN (P = 0.061, R^2 = 54%) (Equation 5). The sum of total phosphorus removed showed an exponential correlation with TP (P = 0.014, R^2 = 75%) (Equation 6), P(A) (P = 0.01, R^2 = 78%) (Equation 7), and P(B) (P = 0.061, R^2 = 54%) (Equation 8).

$$C2\ TN\ (\%) = 0.0811 + 0.0993 \times (0.997^{\ total\ nitrogen\ removed\ in\ grain\ (kg/ha)}) \qquad (5)$$

$$C2\ TP\ (\%) = 0.02739 + 0.0085 \times (0.970^{\ total\ phosphorus\ removed\ in\ grain\ (kg/ha)}) \quad (6)$$

$$C2\ P(A)\ (mg/kg) = 34.26 + 37.1 \times (0.945^{\ total\ phosphorus\ removed\ in\ grain\ (kg/ha}) \quad (7)$$

$$C2\ P(B)\ (mg/kg) = 18.55 + 13.59 \times (0.971^{\ total\ phosphorus\ removed\ in\ grain\ (kg/ha)}) \quad (8)$$

The sum of total nitrogen and total phosphorus removed from C3 in beef showed no significant correlation with soil TN (P = 0.907) and soil TP (P = 0.702) respectively. The sum of total phosphorus removed showed an exponential correlation with P(A) (P <0.001, R^2 = 97%) (Equation 9), and P(B) (P = 0.002, R^2 = 75%) (Equation 10).

$$C3\ P(A)\ (mg/kg) = 19.83 + 27.63 \times (0.781^{\ total\ phosphorus\ removed\ in\ beef\ (kg/ha}) \quad (9)$$

$$C3\ P(B)\ (mg/kg) = 12.26 + 12.63 \times (0.709^{\ total\ phosphorus\ removed\ in\ beef\ (kg/ha)}) \quad (10)$$

4.5 Discussion

Nutrient cycling in natural ecosystems was traditionally considered a steady-state, closed system, with nutrients being taken up from the soil by plant roots and being recycled back to the soil through leaf and litter fall and root decay (Murty *et al.* 2002; Radford *et al.* 2007). Under this hypothesis it is expected that no change in soil fertility would occur under brigalow scrub. This was generally supported by the study data with no significant change in organic carbon, total nitrogen, bicarbonate- and acid-extractable phosphorus and total potassium. Radford *et al.*'s (2007) study of organic carbon and total nitrogen at this site from 1981 to 2003 also supports the hypothesis. However, as rainfall patterns fluctuate over time, extended wet periods are likely to result in increased nutrient uptake from deeper down the soil profile by the extending root systems of actively growing plants, followed by increased leaf and litter fall and root decay. This may lead to measurable nutrient redistribution at particular timescales within an otherwise steady-state ecosystem. This redistribution may account for the increases noted in total phosphorus and total

sulfur. Alternative mechanisms for redistribution include the ability of plants to move water through the soil profile via hydraulic lift and downward siphoning, allowing access to nutrients otherwise unavailable due to inadequate soil moisture (Sardans and Peñuelas 2014). Rainfall also provides nutrient inputs. The rainfall nutrient concentrations reported by Packett (2017) indicate that between 1981 and 2014, 60 kg/ha of dissolved nitrogen, 0.5 kg/ha of dissolved phosphorus (in the form of phosphate) and 1070 kg/ha of dissolved sulfur (in the form of sulfate) are estimated to have been supplied in rainfall. The magnitude of these inputs has increased over time as a result of anthropogenic activity which, for example, has increased atmospheric concentrations of carbon dioxide and nitrogen (Tipping *et al.* 2017; Schulte-Uebbing and de Vries 2018). These inputs are a counter to the natural loss of nutrients in runoff and may also explain fluctuations within what was traditionally considered a steady-state ecosystem. Feedback cycles between increasing deposition of carbon and nitrogen and increasing temperature may also contribute to fertility changes (Crowther *et al.* 2016; Tipping *et al.* 2017), which would affect all land uses, but would likely to be easiest to detect in virgin ecosystems where no other treatment effects are present.

Irrespective of the analysis methodology, two distinct trends in soil fertility were observed as a result of land development and land use change. The first trend was for clearing and burning to release a flush of nutrients which subsequently declined over time to near, or below, pre-clearing concentrations. The clearest display of this trend was in mineral nitrogen and available phosphorus, with smaller increases in total phosphorus, total sulfur and total potassium. The second trend was an ongoing decline in fertility commencing at clearing. This was observed in organic carbon and total nitrogen. Both of these trends reflect predictions that clearing brigalow followed by subsequent exploitative land use would result in declining nutrient availability and landscape productivity (Dowling *et al.* 1986).

4.5.1 The effect of land clearing and burning on soil bulk density

Worldwide, an increase in bulk density as a result of land development and long-term cropping or grazing is commonplace (Dalal and Mayer 1986a; Murty *et al.* 2002; Dalal *et al.* 2005). The primary mechanism for increase is physical compaction by machinery and animal hoof traffic, and the degradation of soil structure and loss of organic matter in tilled soil. Conceptually, land use change followed by more than 30 years of either cropping or grazing should have increased bulk density in both the cropped and grazed catchments of this study. Although the significance of trends identified via regression analysis varied, all comparisons of pre-clearing bulk density with long-term averages under cropping and grazing showed an increase with land development. In the same period, bulk density under brigalow remained constant. Changes in the ratios of bulk density between the developed catchments and the control catchment also suggested an increase with land development.

Determining change in bulk density was confounded due to it only being measured in seven of the fourteen sampling events. In addition to limited data, other confounding issues include differing soil water content between samplings and the corresponding shrinking and swelling characteristics of Vertosols; and, the ability of the chosen core diameter to obtain representative samples, particularly in heavily cracked dry soils, in wet soils prone to compaction or distortion and in soils prone to shattering (Berndt and Coughlan 1977; Coughlan *et al.* 1987; Al-Shammary *et al.* 2018).

Coughlan *et al.* (1987) stress the influence of soil water content on bulk density and note that the swelling of Vertosols with increasing soil water and the resultant reduction in bulk density complicates the comparison of measurements over time. On two occasions soil water was measured within two weeks of a soil sampling event that had measured bulk density. In both instances, soil water under cropping and grazing was substantially greater than under brigalow. However, despite

likely reductions in observed bulk density due to increased soil water storage, bulk densities of the agricultural catchments continued to be similar or higher than that of the brigalow catchment. This provides additional evidence that an increase in bulk density has occurred with land development and long-term cropping or grazing. Other than variations in soil water content, the primary limitation to measuring bulk density in this study is likely to be sampling error associated with loss of sample and inaccurate core trimming in friable soils or due to shattering of dry soil during coring.

4.5.2 The effect of land clearing and burning on soil pH

Globally, the burning of forests as a result of land use change and the burning of crop residues in agricultural systems both result in increased soil pH (Ellis and Graley 1983; Roder *et al.* 1993; Guinto *et al.* 2001; Herpin *et al.* 2002; Fraser and Scott 2011). The mechanism of this increase has been attributed to the deposition of ash which releases basic cations (Raison 1979; Guinto *et al.* 2001; Castelli and Lazzari 2002; Herpin *et al.* 2002). Upon wetting, these cations hydrolyse to form alkaline residues which convert to hydroxides or carbonates (Fraser and Scott 2011). Increases in soil pH as a result of burning have been shown to persist for decades (Herpin *et al.* 2002; Fraser and Scott 2011).

The increases in soil pH as a result of clearing and burning brigalow scrub in this study, the mechanism of increase, and the persistence of increased pH, clearly follow typical global responses. For example, Hunter and Cowie (1989) attributed the initial increase in soil pH at this site to soil heating and the release of basic cations as a result of organic matter combustion. Alkaline salts were then likely leached from strongly alkaline ash deposits, which had an average pH of 12.5 (Hunter and Cowie 1989), further raising soil pH. Thirty-two years after burning, soil pH in both agricultural catchments was greater than it was pre-clearing.

4.5.3 The effect of raised soil pH on nutrient availability

Changes in soil pH can have implications for nutrient availability. The preferred range of soil $pH_{(w)}$ for plant growth is 6 (slightly acid) to 8 (slightly or mildly alkaline), with nutrient availability optimised in the range 6 to 7 (Rayment and Lyons 2011). For example, maximum phosphorus availability is considered to occur near pH 6.5 (Penn and Camberato 2019). Pre-clearing, soil $pH_{(w)}$ in C1 and C2 was classified as neutral, while C3 was classified as slightly or mildly alkaline (Bruce and Rayment 1982; Rayment and Lyons 2011). As such, the pH of the surface soil in its pre-cleared state is unlikely to limit nutrient availability. The increases in soil pH as a result of clearing and burning at this site were not great enough to raise the soil pH classifications of the catchments, with C2 remaining neutral and C3 remaining slightly or mildly alkaline; both still within the preferred range for plant growth. Despite being above the optimum range for nutrient availability, average soil $pH_{(w)}$ in C2 and C3 post-clearing and burning was below the threshold of 7.9 where plant availability of nutrients such as phosphorus may be restricted (Rayment and Lyons 2011).

About 36% of Queensland soils have a neutral or alkaline surface pH. Within the Brigalow Belt bioregion these neutral or alkaline soils are dominated by black and grey Vertosols (Ahern *et al.* 1994). The Vertosols of the BCS are representative of these soils, with average soil $pH_{(w)}$ values within the range reported for other Vertosols developed for cropping and grazing within the bioregion (Dalal and Mayer 1986a; Allen *et al.* 2016).The limited field data in the literature suggest that the pH of these well-buffered Vertosols (Ahern *et al.* 1994; Page *et al.* 2018) is not easily changed, much less raised to a level likely to limit plant growth. For example, additions of gypsum to a moderately alkaline Vertosol had no significant effect on pH (Hulugalle *et al.* 2010). Similarly, the addition of biochar, a product of organic matter combustion, to a neutral Vertosol had no significant effect on pH or crop productivity (Macdonald *et al.* 2014). Land use change was reported to increase soil $pH_{(w)}$ and limit nutrient availability for plant growth on a grazed Vertosol (Sangha *et al.* 2005).

However, the natural variability in soil $pH_{(w)}$ reported for the three catchments in this study prior to clearing and burning equalled many of the increases in soil $pH_{(w)}$ that Sangha *et al.* (2005) attributed to land use change. This suggests that Sangha *et al.* (2005) found limited evidence of pH increase and resultant decline in nutrient availability.

Additionally, declines in available nutrients have been reported in the neutral or alkaline Vertosols of the Brigalow Belt bioregion in the absence of soil pH change. For example, significant declines in available phosphorus were observed over seven years of cropping with no significant change in pH (Standley *et al.* 1990). Similarly, significant declines in available phosphorus occurred in this study during a nine-year period with no significant change in soil pH. Over the entire experimental period, there was no significant correlation between soil $pH_{(w)}$ and bicarbonate-extractable or acid-extractable phosphorus under cropping or grazing. Subsoil acidity, and to a lesser extent alkalinity (Dang *et al.* 2006a; Dang *et al.* 2006b; Dang *et al.* 2008; Page *et al.* 2018), is a much greater concern to agricultural production on the neutral or alkaline Vertosols of the Brigalow Belt bioregion than any unlikely reduction in nutrient availability as a result of fire-induced increases in surface soil pH.

4.5.4 The effect of land clearing and burning on soil fertility

Increases in mineral nitrogen, total phosphorus, available phosphorus, total sulfur and total potassium as a result of burning vegetation on the soil surface, as observed in this study, are well documented in both the Australian and international literature (Ellis and Graley 1983; Kyuma *et al.* 1985; Carreira and Niell 1995; Castelli and Lazzari 2002; Brennan *et al.* 2004; Fraser and Scott 2011; Butler *et al.* 2017; MacDermott *et al.* 2017). The increase has been attributed to nutrient release from plant material and deposition in ash, and is often referred to as the ash bed effect (Raison 1979; Kyuma *et al.* 1985; Roder *et al.* 1993; Castelli and Lazzari 2002; Herpin *et al.* 2002; May and Attiwill 2003; Cowie *et al.* 2007). These increases are typically restricted to the surface few

centimetres of the soil profile and often persist for only one to two years (Raison 1979; Ellis and Graley 1983; Kyuma *et al.* 1985; Castelli and Lazzari 2002).

Decreases in soil organic carbon and total nitrogen as a result of burning are also well documented in Australian and international literature (May and Attiwill 2003; Oyedeji *et al.* 2016). However, some studies, including a meta-analysis, have shown no change in total nitrogen as a result of burning (Guinto *et al.* 2001; Wan *et al.* 2001). Initial soil nitrogen level, soil clay content and fire intensity can account for these contrasting observations. Firstly, low-fertility soils may have already lost their most fire-susceptible nitrogen fractions. Secondly, clay particles within soil assist in physically protecting organic matter from the effects of fire, therefore soils with varying clay content are likely to display different responses to burning (Guinto *et al.* 2001). Finally, low-intensity fires have been shown to increase total nitrogen whereas high-intensity fires decrease total nitrogen (Raison 1979). The fire intensity resulting from the burning of pulled brigalow scrub would be similar to that of slash fires and wildfires, providing intense heat for long periods (Johnson 1964). The loss of total nitrogen with burning observed in this study is consistent with that recorded from other sites subjected to high-intensity fires (Raison 1979).

4.5.5 The effect of land use change on soil organic carbon

The decline in organic carbon when brigalow scrub was developed for cropping supports the earlier findings of Radford *et al*. (2007) at this site, and mirrors the response of other pre-clearing Australian and international landscapes developed for, and managed as, long-term cropping (Murty *et al.* 2002; Collard and Zammit 2006). The decline is typically restricted to the surface soil layers no deeper than one metre (Dalal *et al.* 2005). The mechanism is usually attributed to the removal of nutrients in harvested grain, reduced carbon inputs, and the impacts of tillage on soil structure, chemical and

biological processes including shattering, redistribution, oxidation and decomposition (Murty *et al.* 2002).

The finding of no significant change in observed organic carbon when brigalow scrub was developed for grazing is in agreement with the findings of other studies conducted at this site (Radford *et al.* 2007; Dalal *et al.* 2011; Dalal *et al.* 2013). The international review of Murty *et al.* (2002) concluded that on average, the conversion of forest to uncultivated grazing does not lead to a loss of organic carbon; however, this does not hold for all specific sites. Within Australia, Harms *et al.* (2005) reported organic carbon losses from coarse-textured soils such as Kandosols as a result of changing land use from native vegetation to grazing, but found no change in Sodosols and Vertosols, which reflect the soil types of this study. However, while no decline in organic carbon was observed after clearing brigalow followed by grazing for 31 years, a significant decline was evident during the first 17 years of grazing, during the period of continuous stocking prior to irregular spelling. When the observed organic carbon data was adjusted for the natural variation in soil fertility in the control catchment, a statistically significant decline in the organic carbon ratios between the catchments was found for the entire study period. These alternative approaches suggest that a decline in organic carbon has occurred.

Change in organic carbon cycling under grazing at this site is apparent in the observation that organic carbon derived from the original brigalow vegetation comprised only 58% of measured organic carbon while buffel grass-derived organic carbon contributed the remaining 42% (Dalal *et al.* 2011). Without this replacement of carbon by buffel grass, a greater decline in total organic carbon would have occurred. For example, declines in soil organic carbon have been found at sites with low inputs of root biomass (Li *et al.* 2018), which is expected given root biomass is the main source of carbon input to soil organic carbon (Rasse *et al.* 2005). Indeed, long-term bare fallow sites with nil

inputs of organic matter have been found to lose between 21% and 65% of initial soil organic carbon over 36 years and 80 years, respectively (Barré *et al.* 2010). This may explain the observed increase in organic carbon after the commencement of irregular spelling in 1996, undertaken specifically for the purpose of allowing regeneration of the buffel grass pasture. If grazing management over the 32 years since development had resulted in continual overgrazing, it is likely that the ability of the buffel grass pasture to sequester carbon and buffer fertility decline would have been reduced or negated (Conant and Paustian 2002).

Buffel grass growth is also highly responsive to seasonal rainfall trends, hence variation in the observed organic carbon data could indicate changes in carbon inputs and nutrient redistribution within a steady-state ecosystem, as hypothesised could occur under brigalow scrub. The literature also shows that there is potential for increased organic carbon sequestration with low precipitation and decreased sequestration with high precipitation. McSherry and Ritchie (2013) attribute this to greater, more active microbial biomass carbon and more labile organic matter pools in wetter environments, which may increase carbon turnover under grazing. This suggests that carbon sequestration at the study site is likely to vary temporally due to the variable semi-arid climate, further explaining fluctuations in observed organic carbon.

4.5.6 The effect of land use change on soil total nitrogen

As for organic carbon, the decline in total nitrogen when brigalow scrub was developed for cropping supports the earlier findings of Radford *et al*. (2007) at this site. Significant loss of total nitrogen following the conversion of forest to cropping or multiple years of cultivated cropping alone was also found in other long-term studies (Dalal and Mayer 1986a; Dalal *et al.* 2005; Anaya and Huber-Sannwald 2015) and international reviews (Murty *et al.* 2002). Removal of nitrogen in grain has been identified as the primary mechanism of total nitrogen loss (Dalal and Mayer 1986b; Dalal *et al.* 2005)

and was shown by Radford *et al.* (2007) to account for 39% of the total nitrogen lost from the surface 0.3 m of the soil profile at this site between 1981 and 2003. In agreement with these findings, regression analysis showed nitrogen removed from the cropped catchment as grain accounted for 54% of the variation in total nitrogen from 1981 to 2014. On a kg/ha basis, nitrogen removed from the catchment in grain accounted for 80% of the total nitrogen lost from the surface 0.1 m of the soil profile prior to planting of the legume ley pasture. In contrast, the equivalent of 8% of soil total nitrogen decline was lost in runoff (Elledge and Thornton 2017).

The increase in total nitrogen from 2008 to 2014 may be attributed to nitrogen fixation by the butterfly pea legume ley pasture planted in 2010. The ley pasture was planted in order to arrest declining total nitrogen that was limiting the productivity of dryland farming in the catchment (Radford *et al.* 2007; Huth *et al.* 2010). The ability of butterfly pea to increase total nitrogen in a grazed ley pasture system is well documented in central Queensland (Collins and Grundy 2005). However, despite the addition of legumes into the cropping system, modelling suggests that fertility decline will continue to occur (Huth *et al.* 2010).

With no pasture legumes to maintain fertility, developing brigalow scrub for grazing resulted in ongoing total nitrogen decline from 1981 to 2014. This supports the findings of Dalal *et al.* (2013) who found significant decline in total nitrogen at this site 23 years after clearing brigalow scrub for grazing. However, both of these studies contrast with the findings of Radford *et al.* (2007). This is likely due to differences in sampling strategies, analytical methods, and the specific comparisons being made. This current study reports the longest period of record, used the most intensive sampling strategy, consistent analytical methodology and compared each catchment to its starting soil fertility, so should be considered the most robust. Globally, the conversion of forest to uncultivated grazing generally does not lead to a loss of total nitrogen, however this does not hold

for all specific sites (Murty *et al.* 2002). This is reflected in the contrasting conclusions of Australian studies. For example, a single paired site study by Dalal *et al. (2005)* found a decrease in total nitrogen when mulga forest were developed for grazed pasture with the majority of loss occurring from the surface 0.1 m of the soil profile. Removal of total nitrogen in beef accounted for less than half of this loss with additional potential losses via deep drainage. In contrast Harms *et al.* (2005) found no significant loss of total nitrogen across multiple paired sites encompassing the same soil and vegetation. Similar to Dalal *et al.* (2005), Pringle *et al.* (2016) found a 19% decline in total nitrogen where fire had been used to clear native vegetation for grazing across 11 locations in the Brigalow Belt bioregion. The similarity of the 11 locations with the monitoring sites of the Brigalow Catchment Study is undisputable, extending to having been historically subjected to the same land use change and similar subsequent management regime (Allen *et al.* 2016). This clearly demonstrates that the decline in total nitrogen observed when brigalow scrub was developed for grazing in this study is representative of decline processes under grazing in the wider Brigalow Belt bioregion. It is also likely representative of fertility decline across most of the extensively grazed landscapes of northern Australia, which can halve the productive capacity of the pasture (Peck *et al.* 2011). The incorporation of legumes, particularly leucaena, into grazing systems within the Brigalow Belt bioregion has been shown to increase both soil fertility and enterprise profitability (Bowen and Chudleigh 2017). However, broad-scale adoption within the grazing industry is still evolving (Burgis 2016).

In this study there was no significant correlation between the decline in total nitrogen and the amount of nitrogen removed in beef. However, removal of nitrogen in beef accounted for 32% of the total nitrogen lost from the surface 0.1 m of the soil profile. This is comparable to the equivalent of 25% of soil total nitrogen decline lost in runoff (Elledge and Thornton 2017). Losses of nitrogen through volatilisation from urine and faeces was estimated to remove 71 kg/ha of nitrogen, equivalent to 49% of total nitrogen loss. Annual buffel grass yields have been shown to be in the

order of 3, 000 kg/ha (Myers and Robbins 1991). Previous work at this site has shown the standing above ground biomass of buffel grass was 4, 601 kg/ha and contained the equivalent of 27.6 kg/ha of nitrogen, equivalent to 19% of total nitrogen loss (Thornton and Elledge 2013). Annual root growth biomass estimations at this site are similar to above ground biomass (Dalal *et al.* 2013) and are likely to have similar nitrogen contents (Robertson *et al.* 1993), potentially accounting for a similar proportion of total nitrogen loss. The work of Graham *et al.* (1985), on similar vegetation and soil associations elsewhere within the Fitzroy Basin, suggests that this is likely an underestimation having measured 207 kg/ha of nitrogen in buffel grass roots to 0.3 m. The combination of annual above- and below-ground plant growth and litter deposition over 32 years likely accounts for the majority of total nitrogen decline and immobilisation in plant biomass under grazing although substantial losses occur via removal in beef, volatilisation and runoff.

4.5.7 The effect of land use change on soil mineral nitrogen

The immediate, short-term increase in ammonium-nitrogen post-burning in C2 and C3, followed by a delayed, longer-lived increase in nitrate-nitrogen clearly demonstrates the generalised pattern of available nitrogen response to fire, as documented in the meta-analyses of Boerner *et al.* (2009) and Wan *et al.* (2001). The mechanism of increase is attributed to ammonium-nitrogen liberation from organic matter followed by its nitrification to nitrate-nitrogen. This is supported by previous work at this site attributing many of the changes in soil chemistry after burning to the effects of soil heating (Hunter and Cowie 1989). Subsequent declines over time were attributed to runoff losses, plant uptake and microbial immobilisation (Hunter and Cowie 1989).

The extended period of elevated nitrate-nitrogen under cropping is likely to reflect the stimulating influence of fallow tillage on nitrogen mineralisation as described by Dalal and Mayer (1986a). This is supported by the observed decline in mineral nitrogen around 15 years post-burning that

corresponds to a change in cropping management practices to minimum tillage and opportunity cropping. These practices reduce tillage and shorten fallows, leading to reduced mineralisation combined with increased nitrogen uptake due to increased cropping frequency. Declining total nitrogen is also likely to result in declining mineral nitrogen under continuous cropping. This is demonstrated elsewhere within the Dawson sub-catchment of the Fitzroy Basin where mineral nitrogen levels of Vertosols after more than 30 years of cropping were 82% lower than adjacent Vertosols still supporting native brigalow scrub (Shrestha *et al.* 2015).

The rapid decline of nitrate-nitrogen in C3 is likely due to uptake by the newly planted buffel grass pasture. Similar pastures in central Queensland have been shown to be highly productive in the first two years after planting due to high levels of available nitrogen, with productivity declining over time as available nitrogen declines and nitrogen immobilisation occurs (Myers and Robbins 1991). Decline and immobilisation in the grazed catchment at this site is demonstrated after the first two to three years in the ongoing low concentrations and minimal fluctuation of total and mineral nitrogen compared to that under cropping and brigalow. It is further demonstrated by the decline in pasture productivity and cattle live weight gain over time at this site as described by Radford *et al.* (2007).

4.5.8 The effect of land use change on soil total phosphorus

While the enrichment of surface soil with phosphorus as a result of burning was clear, in the absence of fertilisation, phosphorus depletion commenced immediately. Within four years, total phosphorus was depleted to near or below pre-clearing concentrations. Removal of phosphorus in grain was equivalent to 95% of total phosphorus lost under cropping; however, removal of phosphorus in beef was only equivalent to 22% of the loss of total phosphorus under grazing. Removal of total phosphorus in runoff was equivalent to 12% of the total decline under cropping and 11% of the total decline under grazing (Elledge and Thornton 2017). Extraction of phosphorus from the soil profile

below 0.1 m is clearly occurring under cropping given that total phosphorus removal in grain and runoff exceeded the measured total phosphorus decline in the top 0.1 m of the soil profile.

Other Queensland and international studies have also reported declines in total phosphorus under cropping (Bowman *et al.* 1990; Standley *et al.* 1990; Zhang *et al.* 2006; Song *et al.* 2011; Wang *et al.* 2012). Typically, the decline could be almost entirely accounted for in crop removal (Dalal 1997). However, changes in total phosphorus under grazing are typically less pronounced and the mechanism for change less obvious. Erosion and leaching losses are acknowledged to play some role in total phosphorus decline under grazing however they are unlikely to be a key decline mechanism, particularly in flat landscapes with high clay content soils such as Vertosols (Townsend *et al.* 2002). Internationally, the removal of phosphorus in beef was poorly correlated with total phosphorus decline and hence was unlikely to be a key decline mechanism (McGrath *et al.* 2001; Townsend *et al.* 2002). These observations lead Townsend *et al.* (2002) to conclude that the bulk of total phosphorus decline must be occurring by other mechanisms.

Previous work has shown the above ground biomass of buffel grass in the grazed catchment contained the equivalent of 5.8 kg/ha of phosphorus (Thornton and Elledge 2013). Assuming the soil contribution to phosphorus in above ground biomass is equal to one third of the phosphorus content of the biomass grown each season, this transfer over 32 years is equivalent to the amount of total phosphorus removed from the soil. The cycling of phosphorus from soil to plant to animal waste is also likely to account for some of the phosphorus lost given that phosphorus in dung can exceed that contained within both the above-ground plant and litter biomass (Dubeux Jr *et al.* 2007), and its deposition on the soil surface increases its susceptibility to loss in runoff (McGrath *et al.* 2001). The key mechanisms of decline in total phosphorus under grazing in this study is likely to be

redistribution into plant biomass and litter with additional smaller losses through runoff and removal in beef.

4.5.9 The effect of land use change on soil available phosphorus

Similar to total phosphorus, the enrichment of surface soil with available phosphorus as a result of burning was clear and in the absence of fertilisation, depletion commenced immediately. Under cropping, bicarbonate-extractable phosphorus was still above pre-clearing concentrations 32 years post-burning while acid-extractable phosphorus had declined below pre-clearing concentrations. Under grazing, both acid and bicarbonate-extractable phosphorus declined below pre-clearing concentrations within 14 years post-burning.

Other long-term Queensland studies conducted at Chinchilla and Mt. Murchison on Vertosols that originally supported brigalow vegetation associations, also found declines in available phosphorus as a result of cropping (Thomas *et al.* 1990; Dalal 1997). The declines were attributed to removal of phosphorus in grain, transformation within soil, and runoff and erosion processes. However, at Mt. Murchison, it was noted that phosphorus removal by the crop and stubble could not be accounted for simply in terms of acid- and bicarbonate-extractable phosphorus (Thomas *et al.* 1990). Greater retention of bicarbonate-extractable phosphorus in treatments with higher soil biomass and the replacement of depleted bicarbonate-extractable phosphorus with phosphorus from other pools (Standley *et al.* 1990) further indicates that land use change alters the speciation and cycling of phosphorus in soil. Similar declines in available phosphorus are noted internationally (Nancy Mungai *et al.* 2011; Song *et al.* 2011). They are also attributed to cultivation and erosion-induced declines in soil structure leading to reductions in soil organic matter, promoting microbial cycling of available phosphorus (Zhang *et al.* 2006). Harvest losses were also noted as a decline mechanism. In this study, phosphorus removal in grain was better correlated with total phosphorus than with either

measure of available phosphorus. As total phosphorus accounts for losses from the organic pool, this suggests that both the inorganic and organic phosphorus pools are depleted by grain removal. The key mechanism of decline in available phosphorus under cropping in this study is likely to be removal in grain combined with cycling into other phosphorus pools.

The levels of phosphorus enrichment and decline following land use change for grazing in this study exceed that reported by Sangha *et al.* (2005) for grazing systems developed on similar vegetation and soil associations elsewhere within the Fitzroy Basin. Their study found no difference in bicarbonate-extractable phosphorus under uncleared brigalow compared to sites cleared for grazing five, twelve and thirty-three years previously. This lack of difference in bicarbonate-extractable phosphorus is likely due to the space-for-time paired site approach, which fails to guarantee the same starting condition for each pair; the impacts of grazing on the uncleared control plots; and the bicarbonate-extractable phosphorus levels of their uncleared control being only 56% of the BCS brigalow scrub control in this study.

Internationally, changing land use from virgin forest to grazing has also resulted in an initial flush of available phosphorus followed by a decline (McGrath *et al.* 2001; Townsend *et al.* 2002). Pasture growth and above-ground biomass accounted for some of the decline; however, beef production was poorly correlated. While removal of phosphorus in beef showed no correlation with total phosphorus in this study, it explained 97% of the decline in acid-extractable phosphorus and 75% of the decline in bicarbonate-extractable phosphorus. This suggests that any loss of phosphorus from the organic pool is likely being replaced from the inorganic pool (Garcia-Montiel *et al.* 2000; McGrath *et al.* 2001; Townsend *et al.* 2002; Fonte *et al.* 2014). The key mechanism of decline in available phosphorus under grazing in this study is likely to be removal in beef combined with cycling

into other phosphorus pools. Additional losses are likely through the cycling of phosphorus from soil to plant to animal waste with smaller losses in runoff.

4.5.10 The effect of land use change on soil total sulfur

As for phosphorus, surface soil was enriched with sulfur as a result of burning and in the absence of fertilisation, depletion commenced immediately. Other studies, both in the Brigalow Belt bioregion and internationally, attribute sulfur decline under cropping to mineralisation associated with cultivation (Dalal and Mayer 1986a; Wang *et al.* 2006; Kopittke *et al.* 2016). Decline under grazing has also been attributed to accelerated mineralisation with additional declines as a result of reduced inputs of plant residues, particularly in arid, low-fertility landscapes, and losses in runoff and leaching (Steffens *et al.* 2008; Wiesmeier *et al.* 2009).

Sulfur is a constituent of organic matter and has similar responses under agriculture as nitrogen (Williams 1962; Kopittke *et al.* 2016). The rapid decline in sulfur within two years of burning mirrors that of total and mineral nitrogen, suggesting its removal from soil by actively growing crops and pasture in response to the ash bed effect. Leaching losses are also likely during this time given deep drainage through the soil profile increased from <1 mm/yr pre-clearing to 59 mm/yr under development for cropping and 32 mm/yr under development for grazing (Silburn *et al.* 2009). Some ongoing loss of easily leached sulfur fractions may have occurred under cropping where deep drainage averaged 19.8 mm/yr; however, leaching losses under grazing are unlikely with deep drainage returning to near pre-clearing rates of <1 mm/yr.

While some of the continued sulfur decline under cropping can certainly be attributed to mineralisation associated with tillage, estimates of grain sulfur content combined with measured yield data indicate that 63% of the lost sulfur can be accounted for in crop removal. In contrast,

estimates of the sulfur content of beef combined with measured live weight gain data indicate that only 5% of the lost sulfur can be accounted for in beef removal. This is supported by the observed sulfur data showing continued decline under cropping but little change under grazing after the initial decline in the ash bed effect. Thus removal of sulfur in agricultural products is a major pathway under cropping but is negligible under grazing.

4.5.11 The effect of land use change on soil total potassium

As for phosphorus and sulfur, surface soil was enriched with potassium as a result of burning, and in the absence of fertilisation, depletion commenced immediately. Both cropping and grazing land uses lost similar amounts of potassium over the 32 years post-burning. Potassium decline has been noted in cropping systems worldwide, particularly where crop residue removal was practiced in addition to grain removal (Chen *et al.* 2006; Karlen *et al.* 2013; Rezapour *et al.* 2013). Decline has also been noted under grazing systems, typically with erosion as the primary loss mechanism, while reafforestation of grazing lands has been shown to increase surface soil potassium (Sangha *et al.* 2005; Liu *et al.* 2010; Huth *et al.* 2012; Cheng *et al.* 2016).

While some potassium is removed in grain, potassium in crop residues greatly exceeds that removed in grain (Chen *et al.* 2006). This implies that removal of potassium in beef is greatly exceeded by the potassium retained in pasture and litter. Despite similar percentage declines in potassium under both cropping and grazing, potassium removal in grain accounted for 39% of the total decline under cropping while removal in beef accounted for only 1% of the decline under grazing. This suggests that removal of potassium in agricultural produce is not the primary loss mechanism.

Potassium is relatively immobile in soil and prone to surface stratification, but can be leached slowly and lost in runoff (Drew and Saker 1980; Bertol *et al.* 2007). The return of crop residues and buffel

grass litter to the soil surface promotes stratification in both the cropping and grazing systems of this study, leaving nutrients vulnerable to loss in runoff. Given that changing land use from brigalow scrub to cropping or grazing doubled runoff (Thornton *et al.* 2007), and similar potassium losses were found under both cropping and grazing, it is likely that loss in runoff is the primary loss mechanism at this site. Loss in runoff as a primary loss mechanism is supported by earlier analyses of study data and has been noted as a loss mechanism internationally (Hunter and Cowie 1989; Kayser and Isselstein 2005). Drainage is unlikely to be a primary loss mechanism given drainage under the two systems is two orders of magnitude apart and does not reflect the similar potassium losses from the surface soil of each system.

4.5.12 Natural fluctuations in soil exchangeable potassium

According to the criteria of Bruce and Rayment (1982), average exchangeable potassium concentrations in the catchments pre-clearing were medium. Fluctuations in exchangeable potassium concentrations in C1 are likely due to feedback mechanisms between variable climate cycles and biological processes, including uptake, recycling, maintenance of soil potassium pool equilibrium, and the respective lags of each process. Comparison of exchangeable potassium concentrations with a five-year moving average of annual rainfall (Thornton *et al.* 2007) shows a general trend of lower exchangeable potassium in above average rainfall periods and higher exchangeable potassium in below average rainfall periods. Increased plant growth during wet periods could result in greater exchangeable potassium uptake than in dry periods, resulting in lower measured soil exchangeable potassium. This process is responsible for the low-rainfall and drought-induced accumulation of nitrate (Liebig *et al.* 2014; Chen *et al.* 2015; Segoli *et al.* 2015) and is a likely driver of exchangeable potassium dynamics in this study. Increased return of potassium to the soil surface as a result of leaf drop (Tripler *et al.* 2006) in subsequent dry periods, combined with the requirement of the soil potassium pools to remain in equilibrium (Moody and Bell 2006), could then

result in higher measured soil exchangeable potassium. Fluctuations in exchangeable potassium concentrations have been noted in other long-term studies of native forest, which concluded that the changes are real, informative of natural processes, and should not be treated simply as statistical noise (Johnson *et al.* 2008).

4.5.13 The effect of land use change on soil exchangeable potassium

Post-burning, exchangeable potassium concentrations in C2 and C3 increased from medium to high. This increase may be attributed to soil biomass breakdown due to heating (Hunter and Cowie 1989), to exfoliation of mica from disturbed regolith (CSIRO 2006) or illite clay minerals in the soil profile exposing potassium in formerly contracted interlayers and to removal of organic coatings (Scott and Smith 1968; Smith and Scott 1974; Sharpley and Smith 1988). In the absence of fertilisation, depletion commenced immediately, similar to the behaviour of available phosphorus. After 32 years of cropping or grazing, the concentrations of exchangeable potassium that had increased from medium to high with burning, declined to low.

Declines in exchangeable potassium over time under cropping have been reported both elsewhere in Australia and internationally, and are typically attributed to plant uptake followed by removal in harvested grain and stubble (Cope 1981; Sharpley and Smith 1988; Bell *et al.* 1995; Litvinovich *et al.* 2006; Curtin *et al.* 2015). Declines in exchangeable potassium over time under grazing have also been reported both elsewhere in Australia and internationally, with the primary loss occurring during potassium cycling, particularly from urine patches, which account for about 80% of the potassium cycled through the animal (Cox 1973; Williams and Haynes 1990; Haynes and Williams 1992; Prober *et al.* 2002; Kayser and Isselstein 2005; Sangha *et al.* 2005). Preferential flow of water soluble urine potassium, which is deposited in concentrated patches, to beneath 0.1 m of the soil profile may also account for some of the measured decline in exchangeable potassium (Kayser and

Isselstein 2005). Leaching of exchangeable potassium, particularly urine potassium, is often cited as a loss mechanism (Kayser and Isselstein 2005). However, as for total potassium, the similar decline in exchangeable potassium under both cropping and grazing at this site, despite the drainage under the two systems being two orders of magnitude apart , indicate that drainage is unlikely to be a primary loss mechanism. In addition, the feedback mechanisms between variable climate cycles and biological processes that drive exchangeable potassium fluctuations in native forests will also influence dynamics in agricultural systems. This will occur in parallel to loss via removal in agricultural products and loss from cycling pathways specific to either cropping or grazing.

4.6 Conclusion

Development of brigalow scrub for cropping or grazing significantly altered soil nutrient balances. Initial clearing and burning resulted in a temporary increase, or flush, of mineral nitrogen, total and available phosphorus, total potassium and total sulfur in the surface soil (0 to 0.1 m) as a result of soil heating and the ash bed effect. Bulk density was consistently higher post-clearing and burning than it was pre-clearing. Soil pH also increased, but did not peak immediately after burning. Increases in soil pH were unlikely to limit nutrient availability and plant growth.

Over the 32 years since changing land use from brigalow scrub to cropping, surface soil fertility has declined significantly. Specifically, organic carbon has declined by 46%, total nitrogen by 55%, total phosphorus by 29%, bicarbonate-extractable phosphorus by 54%, acid-extractable phosphorus by 59%, total sulfur by 49%, total potassium by 9% and exchangeable potassium by 63% from post-burn, pre-cropping concentrations. This decline in fertility has limited crop yields and would have had an economic impact on a commercial cropping enterprise. However, the planting and maintenance of a butterfly pea legume ley pasture increased total nitrogen by 15% within five years, which was consistent with other studies in the region. Nutrient removal from the catchment as beef

following 173 days of grazing the ley pasture was substantially less than that removed in an average crop. Beef production would have provided some economic benefit to offset the foregone cropping opportunities.

Surface soil fertility has also declined under grazing over the same period but in a different pattern to that observed under cropping. Organic carbon showed clear fluctuation but it was not until the natural variation in soil fertility over time was separated from the anthropogenic effects of land use change that a significant decline was observed. Total nitrogen declined by 22% and in the absence of a legume in the pasture, no fertility restoration occurred. Total phosphorus declined by 14%, equating to only half of the decline under cropping. Bicarbonate-extractable phosphorus declined by 64% and acid-extractable phosphorus declined by 66%; both greater than the decline observed under cropping, possibly due to immobilisation as organic phosphorus. Total sulfur declined by 23%; less than half of the decline under cropping. A similar decline in total potassium was observed under both land uses with a 10% decline under grazing. Exchangeable potassium declined by 59%. As for cropping, this fertility decline has limited pasture production and hence beef production. Despite these production limitations, the grazing system is representative of much of the extensive grazing undertaken in northern Australia. The incorporation of legumes into grazing systems within the Brigalow Belt bioregion has been shown to increase both soil fertility and enterprise profitability; however, broad-scale adoption within the grazing industry is still evolving.

The primary mechanism of nutrient loss depended on the land use and nutrient in question but included removal in grain and beef; mineralisation and oxidation; redistribution and stratification within the soil profile and nutrient pools due to plant growth and litter recycling; uptake and storage in above ground biomass; and loss in runoff and leaching. The addition of legumes into both the cropping and grazing systems would assist in fertility restoration however, particularly in the case of

cropping, may not enable continued production without fertility decline. In contrast to the fertility decline of the agricultural land uses, surface soil fertility of the brigalow scrub remained in relative equilibrium.

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Chapter 5 – Heavy grazing of buffel grass pastures in the Brigalow Belt bioregion of Queensland, Australia, more than tripled runoff and suspended solid loss compared to that from conservative grazing

STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

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My contribution to the paper involved:

Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Writing, - Original Draft, Writing - Review & Editing.

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5.1 Abstract

Loss of sediment and particulate nutrients in runoff from the extensive grazing lands of the Fitzroy Basin, central Queensland, continue to contribute to the declining health of the Great Barrier Reef. This study measured differences in hydrology and water quality from conservative and heavy grazing pressures on rundown improved grass pastures in the Fitzroy Basin. Conservative grazing pressure was defined as the safe long-term carrying capacity for rundown buffel grass pasture, whereas heavy grazing pressure was defined as the recommended stocking rate for newly established buffel grass pasture. Heavy grazing of rundown pasture resulted in 2.5 times more bare ground and only 8% of the pasture biomass compared to conservative grazing. Heavy grazing also resulted in 3.6 times more total runoff and 3.3 times the peak runoff rate compared to conservative grazing. Loads of total suspended solids, nitrogen and phosphorus in runoff were also greater from heavy than conservative grazing.

5.2 Introduction

The Fitzroy Basin is Queensland's largest coastal catchment and is almost entirely contained within the Brigalow Belt bioregion of Australia. Both the basin and the wider bioregion have experienced some of the highest rates of land clearing in the world, with up to 93% of vegetation communities dominated by brigalow (*Acacia harpophylla*) cleared for agriculture since European settlement (Butler and Fairfax 2003; Cogger *et al.* 2003; Tulloch *et al.* 2016). Grazing is the dominant land use in the Fitzroy Basin, with more than 2.6 million cattle over 11.1 Mha (Australian Bureau of Statistics 2009; Meat and Livestock Australia 2017a). This is the largest cattle herd in any natural resource management region in both Queensland and Australia, accounting for 25% of the state herd and 11% of the national herd (Meat and Livestock Australia 2017a).

The 2017 Scientific Consensus Statement for Great Barrier Reef water quality identified the Fitzroy Basin as a high priority area for reducing fine sediment and particulate nutrients. This is due to their ongoing contribution to marine water quality decline and resultant damage to seagrass and coral reefs (Waterhouse *et al.* 2017). Increased adoption of best management practices for agriculture was identified as a key strategy to reduce sediment and nutrient loads in runoff. Within the Grazing Water Quality Risk Framework for 2017 to 2022, the lowest risk to water quality from hillslope pasture management is achieved by practices such as forage budgeting to determine carrying capacity, ground cover monitoring and the adoption of wet season spelling (The State of Queensland 2020b). These practices are commonly recommended to maintain or improve ground cover (O'Reagain *et al.* 2011; Jones *et al.* 2016; Moravek *et al.* 2017), as high cover is known to reduce runoff, and hence also sediment and nutrients exported in runoff (Nelson *et al.* 1996; Murphy *et al.* 2008; Schwarte *et al.* 2011; Silburn *et al.* 2011). For example, light and heavy stocking rates were compared in the Burdekin Basin with 20 to 25% and 40 to 50% pasture utilisation, respectively (O'Reagain *et al.* 2008). A safe long-term carrying capacity is defined as the capacity of the pasture to sustainably carry livestock in the long-term whereas a safe pasture utilisation rate is defined as the proportion of annual forage growth that can be consumed by domestic livestock without adversely affecting land condition in the long-term (McKeon *et al.* 2009; Walsh and Cowley 2011).

In below average rainfall years, the heavy stocking rate had less ground cover, a greater frequency and intensity of runoff, and higher sediment concentrations in runoff. However, there was little difference between the two stocking rates in high rainfall years due to high ground cover (O'Reagain *et al.* 2008). This reflects international literature from at least the last 100 years that demonstrates heavy continuous grazing accelerates runoff and erosion (Hubbard *et al.* 2004). Multiple global meta-analyses have shown that grazing decreases ground cover and increases compaction, which consequently decreases protection from raindrop impact, aggregate stability and infiltration while

increasing runoff. These impacts were greater from heavy grazing than conservative or rotational grazing (Eldridge *et al.* 2016; Byrnes *et al.* 2018; Sirimarco *et al.* 2018; Xu *et al.* 2018; McDonald *et al.* 2019; Wang and Tang 2019; Lai and Kumar 2020). Thus, erosion and sediment transport are primarily associated with high-density stocking and/or poor forage stands on grazed landscapes (Hubbard *et al.* 2004). Globally, degradation by overgrazing is estimated to effect 20 to 35% of permanent pastures, which total about half of the earths terrestrial surface (Byrnes *et al.* 2018; Lai and Kumar 2020).

Although spelling pasture has been shown to increase biomass, seasonal conditions can actually have a stronger effect on ground cover and pasture biomass (Jones *et al.* 2016). This further highlights the importance of managing grazing pressure to maintain landscape resilience, particularly during periods of below average rainfall (Edwards 2018). Managing grazing pressure is typically undertaken by varying stocking rate, as it is the most powerful management tool available to the grazier (Lawrence and French 1992).

These interrelated land use and land management issues were a focus of the Reef 2050 Water Quality Improvement Plan (The State of Queensland 2018). This plan seeks to improve Great Barrier Reef health and resilience by facilitating increased adoption of lower risk land management practices to achieve specific water quality targets. Progress towards these targets is measured via the Paddock to Reef Integrated Monitoring, Modelling and Reporting program (Paddock to Reef program) (Waterhouse *et al.* 2018). The Paddock to Reef program is underpinned by a modelling framework that ranges in scale from individual paddocks though to entire basins with real-world validation provided by numerous studies (Waterhouse *et al.* 2018). The Brigalow Catchment Study is a paddock scale study that is used to validate the effects of hillslope grazing management on water quality from the Fitzroy Basin. This long-term study has a paired catchment design where catchments are

adjacent within a uniform landscape, whereas other paired catchment studies often have sites located further apart in the landscape which confounds interpretation due to inherent differences in soil, slope, vegetation and climatic sequences.

Despite the existence of about 200 paired catchment studies world-wide (Peel 2009), only 13 of them are based in Australia and only three of these have any form of pasture treatment (Best *et al.* 2003). Two of the three pasture studies were based in Mediterranean climates (cool wet winters and hot dry summers) and are now both inactive (Mein *et al.* 1988; Best *et al.* 2003), whereas the third at the Brigalow Catchment Study was based in a semi-arid, subtropical climate (warm wet summers and cool dry winters) and remains active. Bartley *et al*. (2012) noted that there is a limited amount of Australian runoff and water quality data that is urgently required for modelling activities, such as determining progress towards achieving the Reef 2050 Water Quality Improvement Plan targets. This study provides empirical data from the Fitzroy Basin to determine the effects of grazing management practices on paddock scale water quality. More specifically the study aims to:

1) Quantify the impact of conservative and heavy cattle grazing pressures on hydrology and both event mean concentrations (EMCs) and loads of total suspended solids, nitrogen and phosphorus in hillslope runoff over four hydrological years (2015 to 2018);
2) Determine the anthropogenic impact of cattle grazing by comparing hydrology and both EMCs and loads of total suspended solids, nitrogen and phosphorus in hillslope runoff from a conservatively grazed pasture and virgin brigalow woodland which is representative of the pre-European landscape; and
3) Quantify the impact of conservative and heavy cattle grazing pressures on pasture biomass and ground cover over four hydrological years (2015 to 2018).

5.3 Methods

5.3.1 Site description

This study was undertaken at the Brigalow Catchment Study which is representative of both the Fitzroy Basin and the Brigalow Belt bioregion (Cowie *et al.* 2007) (Figure). It is a paired, calibrated catchment study located near Theodore in central Queensland (24°48'S and 149°47'E), Australia, which was established in 1965 to quantify the impact of land development for agriculture on hydrology, productivity and resource condition (Cowie *et al.* 2007). The hydrological cycle of this study site is extensively documented (Thornton *et al.* 2007; Silburn *et al.* 2009; Thornton and Yu 2016), as are the impacts of land clearing and land use change on runoff water quality (Thornton and Elledge 2013; Thornton and Elledge 2016; Elledge and Thornton 2017). Data from this site is representative of hillslope runoff and erosion processes without any scalds, gullies, streams or streambanks.

In its native state, the study site was dominated by brigalow (*Acacia harpophylla*), either in a monoculture or in association with other species, such as belah (*Casuarina cristata*) and Dawson River blackbutt (*Eucalyptus cambageana*) (Johnson 2004). This vegetation association is colloquially known as brigalow scrub (Cowie *et al.* 2007). The extant uncleared vegetation of the Brigalow Catchment Study is classified as regional ecosystems 11.4.8, *Eucalyptus cambageana* woodland to open forest with *Acacia harpophylla* or *Acacia argyrodendron* on Cainozoic clay plains, and 11.4.9, *Acacia harpophylla* shrubby woodland with *Terminalia oblongata* on Cainozoic clay plains (The State of Queensland 2020d). Slope of the land averages 2.5% (range 1.8% to 3.5%) for Catchments 1 and 3 (Cowie *et al.* 2007), and based on an aerial LiDAR survey of the Brigalow Catchment Study in 2019, slope of Catchment 5 averages 5.7%. Soils are an association of Vertosols, Dermosols and Sodosols which are representative of 67% of the Fitzroy Basin under grazing; that is, 28% Vertosols, 28%

Sodosols and 11% Dermosols (Roots 2016). The region has a semi-arid, subtropical climate and mean annual hydrological year (October 1965 to September 2018) rainfall at the site was 648 mm.

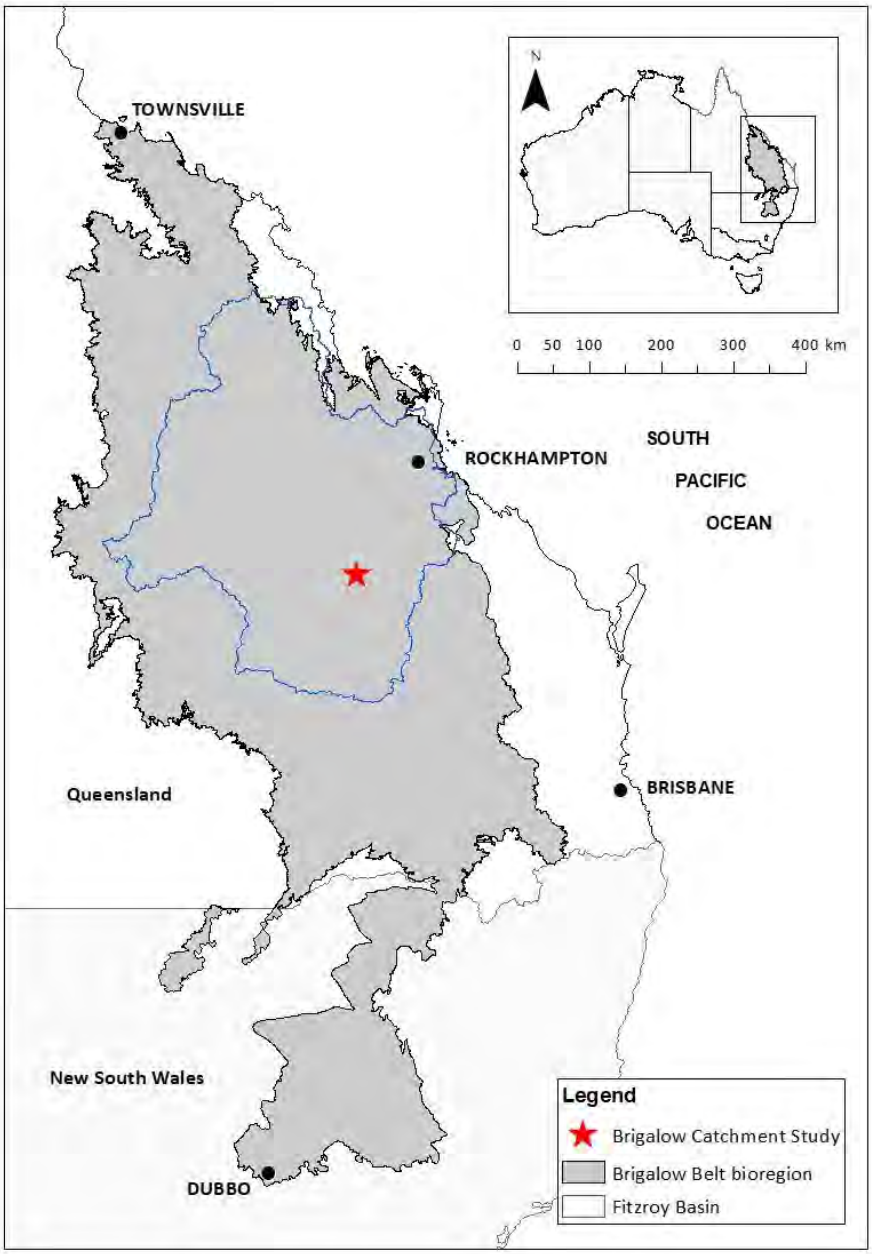

Figure 5.1. Location of the Brigalow Catchment Study within the Brigalow Belt bioregion of central Queensland, Australia.

5.3.2 Site history and monitoring period

The Brigalow Catchment Study can be separated into four experimental stages: Stage I, calibration of three catchments in an uncleared state from 1965 to 1982; Stage II, development of two catchments for agriculture from 1982 to 1983; Stage III, comparison of cropping and grazing land use to virgin brigalow scrub from 1984 to 2010; and Stage IV, a comparison of leguminous and non-leguminous pastures to virgin brigalow scrub during the adaptive land management phase from 2010 to 2018. Further details on these experimental phases are documented in other sources (Cowie *et al.* 2007; Radford *et al.* 2007; Thornton *et al.* 2007; Thornton and Elledge 2013). Data in this study is from Catchments 1, 3 and 5 during the adaptive land management phase for the 2015 to 2018 hydrological years (01 October 2014 to 30 September 2018). Catchments 1 and 3 were established during Stage I and Catchment 5 was incorporated into the long-term Brigalow Catchment Study during Stage IV. in 1965 but in a cleared state planted to pasture in 1969, 1977 and 1984 (The State of Queensland 1965; Commonwealth of Australia 1969; The State of Queensland 1977; The State of Queensland 1984). It was a common management practice to have a period of cropping following the initial development of improved pasture on brigalow lands to physically control regrowth of brigalow suckers (Johnson 1968; Johnson and Back 1974). Use of this strategy at the Brigalow Research Station was demonstrated by land use maps in annual reports and program reviews which classify Catchment 5 as cultivation in 1988 and 1989, in addition to written records for the planting of forage sorghum in 1989 and barley in both 1990 and 1991 (Queensland Department of Primary Industries 1988; Queensland Department of Primary Industries 1989; Queensland Department of Primary Industries 1990; Queensland Department of Primary Industries 1991). Aerial photography in 1991 shows the catchment in a tilled state which supports the written records (The State of Queensland 1991). Catchment 5 was then planted to buffel grass (*Cenchrus ciliaris*) and purple pigeon grass (*Setaria incrassata*) in January 1992 which remains today (Queensland Department of Primary Industries 1992).

Table 5.1 outlines the land use history of these catchments over the four experimental stages, Figure 5.2 shows the location of these three catchments within the landscape, and Table 5.2 characterises the catchments and the treatments applied over this four year study.

Since the commencement of the Brigalow Catchment Study in 1965, Catchment 1 has been retained in a virgin uncleared state to provide a control treatment representative of the Brigalow Belt bioregion in its pre-European condition. Catchment 3 remained uncleared during Stage I. During Stage II it was cleared by bulldozer and chain in March 1982, the fallen timber burnt in October 1982 and then the catchment planted to buffel grass (*Cenchrus ciliaris*) pasture in November 1982.

Although all catchments reported in this study were previously part of the former Queensland Department of Primary Industries' Brigalow Research Station, Catchment 5 has a longer history of agricultural land use as it was not incorporated into the Department of Resources' Brigalow Catchment Study until 2014. Aerial photography shows that Catchment 5 was virgin brigalow scrub in 1965 but in a cleared state planted to pasture in 1969, 1977 and 1984 (The State of Queensland 1965; Commonwealth of Australia 1969; The State of Queensland 1977; The State of Queensland 1984). It was a common management practice to have a period of cropping following the initial development of improved pasture on brigalow lands to physically control regrowth of brigalow suckers (Johnson 1968; Johnson and Back 1974). Use of this strategy at the Brigalow Research Station was demonstrated by land use maps in annual reports and program reviews which classify Catchment 5 as cultivation in 1988 and 1989, in addition to written records for the planting of forage sorghum in 1989 and barley in both 1990 and 1991 (Queensland Department of Primary Industries 1988; Queensland Department of Primary Industries 1989; Queensland Department of Primary Industries 1990; Queensland Department of Primary Industries 1991). Aerial photography in 1991 shows the catchment in a tilled state which supports the written records (The State of Queensland

1991). Catchment 5 was then planted to buffel grass (*Cenchrus ciliaris*) and purple pigeon grass (*Setaria incrassata*) in January 1992 which remains today (Queensland Department of Primary Industries 1992).

Table 5.1. Land use history of the three catchments monitored over the 2015 to 2018 hydrological years.

Catchment	**Land use by experimental stage**			
	Stage I **Jan 1965 to** **Mar 1982**	**Stage II** **Mar 1982 to** **Sep 1983**	**Stage III** **Sep 1984 to** **Jan 2010**	**Stage IV** **Jan 2010 to** **Oct 2018**
Catchment 1	Brigalow scrub	Brigalow scrub	Brigalow scrub	Brigalow scrub
Catchment 3	Brigalow scrub	Development	Grass pasture	Grass pasture
Catchment 5	Not monitored	Not monitored	Not monitored	Grass pasture

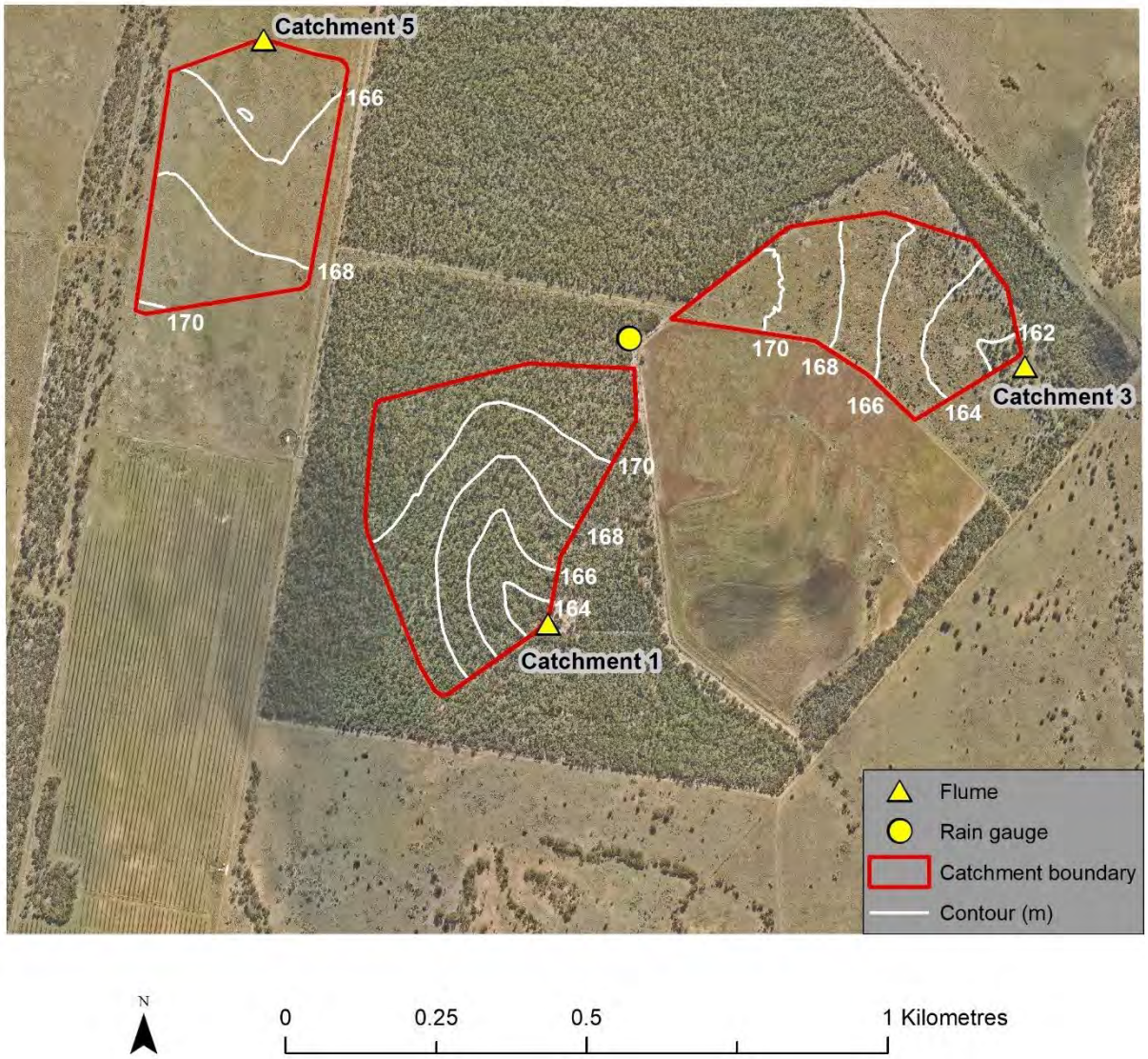

Figure 5.2. Aerial photograph of the Brigalow Catchment Study which shows catchment boundaries, topography and location of monitoring equipment.

Table 5.2. Description of the three catchments monitored over the 2015 to 2018 hydrological years.

Parameter	Brigalow scrub	Conservative grazing	Heavy grazing
Alternative catchment name	Catchment 1	Catchment 3	Catchment 5
Soil type (% of catchment)	Vertosols and Dermosols (70%), Sodosols (30%)	Vertosols and Dermosols (70%), Sodosols (30%)	Vertosols and Dermosols (93%), Sodosols (7%)
Slope	2.5%	2.5%	5.7%
Land use	Virgin brigalow scrub	Improved grass pasture	Improved grass pasture
Cattle stocking philosophy	Ungrazed control	Conservative stocking rate	Heavy stocking rate
Catchment area (ha)	16.8	12.7	12.0
Total grazed area (ha)	Not applicable	17.0	25.0
Pasture spelling philosophy	Ungrazed control	Wet season spell	Limited spelling
Pasture biomass philosophy	Not applicable	Minimum 1,000 kg/ha	No minimum limit
Photo			

Beef cattle commenced grazing Catchment 3 in December 1983 at a stocking rate of 0.45 adult equivalent (AE)/ha/yr which decreased to 0.26 AE/ha/yr over the next 21 years (Radford *et al.* 2007). An adult equivalent is considered to be a non-lactating animal of 450 kg live weight (McLean and Blakeley 2014). Stocking rates varied between 0.06 and 0.23 AE/ha/yr from February 2005 to September 2011, averaging 0.14 AE/ha/yr. The catchment was spelled from September 2011 to December 2013, and then grazed at 0.19 AE/ha/yr from December 2013 to February 2014.

While not incorporated into the Brigalow Catchment Study until 2014, management of Catchment 5 was taken over by the Department of Resources in 2008. Although exact stocking rates prior to this period were unknown, cattle stocking philosophies for the broader Brigalow Research Station can be used as a surrogate. In 1965 it was stated that the Brigalow Research Station could carry 800 head of cattle once cleared and developed (Queensland Department of Primary Industries 1965). This was later revised to an aspirational range from 800 to 1,000 head of grown cattle in 1976 (Stringer 1976) which remained until 1989 whilst land development was still in progress (Nasser 1986; Queensland Department of Primary Industries 1987; Queensland Department of Primary Industries 1988; Queensland Department of Primary Industries 1989). Carrying capacities were not published in annual reports from 1990 to 1995; however, from 1996 to the final technical report in 2004 it was stated that the station had a sustainable carrying capacity of 1,200 adult equivalents (Queensland Department of Primary Industries 1990; Queensland Department of Primary Industries 1991; Queensland Department of Primary Industries 1992; Loxton *et al.* 1994; Loxton and Boadle 1995; Loxton and Boadle 1996; Loxton and Boadle 1997; Jeffery and Loxton 1998; Jeffery and Loxton 1999; Loxton and Forster 2000; Sinclair and White 2004).

Early carrying capacities expressed as grown cattle can be converted to adult equivalents using carcase specifications for the brigalow lands of Queensland combined with dressing percentages.

Carcase weights averaged 269 kg (range 250 to 300 kg) (Strachan 1976) and an appropriate dressing percentage to convert live weight to carcase weight is 53% (Meat and Livestock Australia 2017b). The average dressing percentage of 53% for heavy steers with a fat score of three was selected, as Strachan (1976) states that steers with a low fat carcass were the most common animal produced for slaughter. For example, a carcase weight of 269 kg and a dressing percentage of 53% suggests that the live weight of a grown animal was about 508 kg, equal to 1.13 adult equivalents. Thus, the aspiration to carry 800 to 1,000 head of grown cattle equates to carrying capacities of 896 and 1,120 adult equivalents, respectively, which were both lower than the 1,200 adult equivalent carrying capacities reported from 1996 to 2004. These carrying capacities translate into surrogate stocking rates of 0.33 AE/ha/yr, 0.41 AE/ha/yr and 0.45 AE/ha/yr, respectively (Figure 5.3).

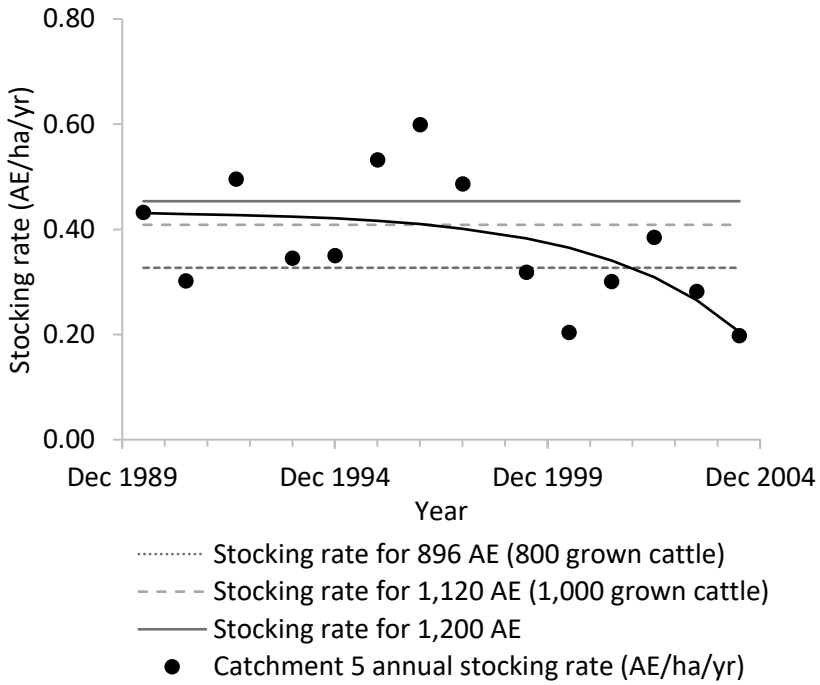

Figure 5.3. Aspirational and actual stocking rates for the Brigalow Research Station used to estimate stocking rates for Catchment 5 prior to the commencement of this study in 2014.

Although these calculated stocking rates can be used as a surrogate for Catchment 5 over one or more decades, they are less suited to estimate annual stocking rates. Brigalow Research Station documents from 1990 to 2004 noted an increase in both area of pasture and annual livestock returns over time (Queensland Department of Primary Industries 1990; Queensland Department of Primary Industries 1991; Queensland Department of Primary Industries 1992; Loxton *et al.* 1994; Loxton and Boadle 1995; Loxton and Boadle 1996; Loxton and Boadle 1997; Jeffery and Loxton 1998; Jeffery and Loxton 1999; Loxton and Forster 2000; Sinclair and White 2004). Thus, a surrogate annual stocking rate for Catchment 5 can be calculated as the number of cattle on the entire station during the year divided by the total area of available pasture to yield an AE/ha/yr (Figure 5.3). Annual livestock returns for the station reported both young cattle less than one adult equivalent and older cattle greater than one adult equivalent, so it is reasonable to assume that the total number of cattle reported could be expressed as adult equivalents. Annual calculations suggest that stocking rates for Catchment 5 decreased from 0.43 AE/ha/yr in 1990 to 0.20 AE/ha/yr in 2004 (Figure 5.3). Limited grazing occurred in Catchment 5 from 2004 until discussions to close the Brigalow Research Station in 2008. The catchment was spelled from June 2008 to July 2012 when it was grazed at 0.45 AE/ha/yr until September 2012, then grazed at 0.11 AE/ha/yr until December 2012.

5.3.3 Treatments

Over the four hydrological years of this study, Catchment 1 was retained in its virgin uncleared condition supporting brigalow scrub. Vertosols and Dermosols (clay soils) occupy approximately 70% of the catchment and Sodosols occupy the remaining 30% (Isbell 1996; Cowie *et al.* 2007). Catchment 3 continued as a conservatively grazed catchment with a buffel grass (*Cenchrus ciliaris* cv. Biloela) pasture. Vertosols and Dermosols (clay soils) occupy approximately 58% of the catchment and Sodosols occupy the remaining 42% (Isbell 1996; Cowie *et al.* 2007). Catchment 5 commenced

as a heavily grazed catchment with an existing buffel grass (*Chenchrus ciliaris*) and purple pigeon grass (*Setaria incrassata*) pasture. Vertosols occupy approximately 93% of the catchment and Sodosols occupy the remaining 7% (Isbell 1996). The Australian Soil Classification for Catchment 5 was determined by Land Resource Officers from the Department of Resources based on the soil survey of Webb (1971), the soil chemistry of Webb *et al.* (1977) and soil descriptions undertaken in 2018 which were extracted from the Soil And Land Information (SALI) system (Biggs *et al.* 2000).

The two pastures were spelled prior to the commencement of this study in October 2014. The conservatively grazed pasture was spelled from February 2014, while the heavily grazed pasture was spelled from December 2012. Conservative grazing pressure reflected the safe long-term carrying capacity for rundown buffel grass pasture, whereas heavy grazing pressure reflected stocking rates recommended for newly established buffel grass pasture. The Brigalow Catchment Study has been managed to maintain good (A) land condition and the estimated long-term carrying capacity was 0.22 AE/ha/yr (range 0.19 to 0.27 AE/ha/yr). This estimate was obtained from the Long Paddock FORAGE system which provides a property specific report based on climate data, satellite imagery and modelled pasture growth (The State of Queensland 2021a). Whereas published recommended stocking rates are about 0.50 AE/ha/yr for newly established buffel grass pasture and about 0.33 AE/ha/yr for rundown buffel grass pasture, which can occur in as little as five to ten years after establishment (Noble *et al.* 2000; Peck *et al.* 2011).

Stocking rates during this study were set based on measured pasture biomass, with pasture utilisation targets of less than 30% in the conservatively grazed pasture and greater than 50% in the heavily grazed pasture. Dietary intake was considered to be 2.2% of animal live weight (Minson and McDonald 1987). Actual stocking rates for this study have been presented as adult equivalents per hectare per year (AE/ha/yr) to account for differences in the size of cattle and the length of time the

pastures were grazed (Table 5.3). Spelling was defined as the number of days annually that pasture wasn't grazed (Table 5.4). Overall, the conservatively grazed pasture had lower stocking rates and greater periods of spelling.

Table 5.3. Annual stocking rates in adult equivalents (AE) per hectare per year for the two pasture treatments.

Year	Stocking rate (AE/ha/yr)	
	Conservative grazing	**Heavy grazing**
2013	Destocked	0.09
2014	0.19	Destocked
2015	0.20	0.83
2016	0.13	0.20
2017	0.19	0.26
2018	Destocked	0.86

Table 5.4. Annual number of non-grazed days (spelling) for the two pasture treatments.

Year	Pasture spelled (days/yr)	
	Conservative grazing	**Heavy grazing**
2013	365	303
2014	320	365
2015	80	33
2016	297	286
2017	76	180
2018	365	146

5.3.4 Hydrology

Rainfall and runoff were monitored over four hydrological years from October 2014 to September 2018. Rainfall was measured using a 0.5 mm tipping bucket rain gauge located at the head point of the three long-term catchments (Thornton *et al.* 2007). Each catchment was instrumented to measure runoff using a 1.2 m HL flume with a 3.9 x 6.1 m approach box (Brakenseik *et al.* 1979). Water heights through the flume were recorded using a pressure transducer with a mechanical float recorder backup. Stage heights were converted to discharge using a rating table (Brakenseik *et al.* 1979), while peak runoff rate was calculated on an event basis from instantaneous peak height. A runoff event commenced when stage height exceeded zero and finished when it returned to zero. Further details on calculating total runoff and peak runoff rates are documented in other sources (Thornton *et al.* 2007; Thornton and Yu 2016).

The 18 year calibration period for the three long-term catchments in Stage I meant that runoff from Catchment 3 can be estimated from measured runoff from Catchment 1 (Thornton *et al.* 2007). A calibration period for Catchment 5 was not possible as it had been developed for agriculture sometime between 1965 and 1969, which was at least 40 years prior to its inclusion in the study. Thus, although Catchment 5 has its own unique hydrological characteristics, its relationship to Catchments 1 and 3 in an uncleared state is unknown.

5.3.5 Water quality

Discrete water quality samples were obtained over four hydrological years (October 2014 to September 2018) using an auto-sampler located at the flume of each catchment. Auto-samplers were programmed to sample every 0.1 m change in stage height. Laboratory analyses of runoff samples were undertaken by Queensland Health Forensic and Scientific Services (Table 5.5), with some parameters calculated by difference (Table 5.6).

Event based water quality loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the resulting loads from all intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Total annual load was calculated by summing all the event-based water quality loads, and load in kg/ha was calculated by accounting for catchment area.

Table 5.5. Methods used by Queensland Health Forensic and Scientific Services for total suspended solids and nutrient analyses of runoff samples.

Parameter	Method
Total suspended solids	Method 18211 based on gravimetric quantification of solids in water
Total nitrogen and total dissolved nitrogen	Method 13802 by simultaneous persulfate digestion
Oxidised nitrogen	Method 13798 based on flow injection analysis of nitrogen as oxides
Ammonium-nitrogen	Method 13796 based on flow injection analysis of nitrogen as ammonia
Total phosphorus and total dissolved phosphorus	Method 13800 by simultaneous persulfate or Kjeldahl digestion
Dissolved inorganic phosphorus	Method 13799 by flow injection analysis

Table 5.6. Equations used to estimate nutrient parameters that were not directly measured.

Parameter	Equation
Particulate nitrogen	Total nitrogen minus total dissolved nitrogen
Dissolved inorganic nitrogen	Oxidised nitrogen plus ammonium-nitrogen
Dissolved organic nitrogen	Total dissolved nitrogen minus dissolved inorganic nitrogen
Particulate phosphorus	Total phosphorus minus total dissolved phosphorus
Dissolved organic phosphorus	Total dissolved phosphorus minus dissolved inorganic phosphorus

Event based EMCs were calculated by dividing total event load by total event flow, and mean annual EMCs were calculated by averaging the event-based EMCs within each year. Mean annual EMCs from 2000 to 2018 were used to calculate a long-term site EMC for each catchment using the method of Elledge and Thornton (2017). Where water quality data was not captured due to flows being too small to trigger auto-samplers, load estimations were obtained by multiplying the long-term EMC by observed flow. This method was applied to all events from brigalow scrub as flows were too small to trigger auto-samplers. Only observed (measured) event-based EMCs were included in the calculation of mean annual EMCs.

Dominant pathways of nitrogen and phosphorus loss in runoff were determined by the proportion of particulate and total dissolved fractions. That is, if total dissolved nitrogen was greater than 60% of total nitrogen it was considered to be transported primarily in a dissolved phase, and if less than 40% it was transported primarily in a particulate phase. If the value was between 40% and 60%, it was considered to have no dominant pathway of loss. The same method was applied to total phosphorus and total dissolved phosphorus.

5.3.6 Pasture biomass

The BOTANAL method of Tothill *et al.* (1978) was used to estimate pasture biomass one to two times per year over the total grazed area of the two pasture catchments, excluding the shade lines. Pasture assessments occurred in the late wet and/or the late dry season. The late wet season is typically the end of the pasture growing season, and the late dry season provides an indicator of the remaining pasture available for cattle grazing until suitable conditions for growth occur. Pasture biomass was visually estimated for up to 300 0.16 m^2 quadrats in each catchment at each sampling period. Visual estimates were calibrated against a set of 10 quadrats which were cut, dried and weighed.

5.3.7 Ground cover

Ground cover from the total grazed area of the two pasture catchments was compared from October 2012 to October 2018 using VegMachine® (Fitzroy Basin Association 2018). VegMachine is a simple tool for interrogating large raster time series ground cover datasets derived from Landsat satellite imagery (Terrestrial Ecosystem Research Network 2010; Beutel *et al.* 2019). The analysis of ground cover at or near ground level, which excludes taller cover such as tree and shrub canopies, required individual spatial polygons to define each catchment (Beutel *et al.* 2019). Polygons for the conservatively and heavily grazed catchments were defined as the fence line boundary for each paddock, which was identified via satellite imagery. Both catchment polygons were then manually imported into VegMachine and the "*Polygon Comparison"* tool used to perform a ground cover analysis of the conservatively and heavily grazed catchments. Seasonal deciles were also reported for total (green and non-green) cover, where total cover and bare ground equal 100%. These were calculated automatically within VegMachine using quarterly data from Autumn (March to May) 1988 to Summer (December to February) 2012/2013 as a baseline, with every season ranked (expressed as a decile) against all corresponding values for that season in the baseline period (Trevithick 2017).

For example, total cover from spring (September to November) 2015 was ranked against total cover from all the spring images from the baseline period.

5.3.8 Benchmarking ground cover to the Fitzroy Basin

VegMachine was also used to determine how representative ground cover from the Brigalow Catchment Study was to the wider Fitzroy Basin. This was achieved by comparing the conservatively and heavily grazed catchments to the six sub-basins of the Fitzroy Basin; that is, the Dawson, Comet, Nogoa, Isaac, Mackenzie and Fitzroy. Sub-basin comparisons were undertaken to better represent the range of covers within the Fitzroy Basin. Spatial layers for VegMachine analysis were prepared using a multi-step process in ArcGIS (Environmental Systems Research Institute 2020):

1) Boundaries for the six sub-basins were obtained from the "*Basin sub areas - Queensland*" spatial layer, accessed via the Queensland Spatial Catalogue (QSpatial) (The State of Queensland 2020c).
2) Landscapes that were comparable to the Brigalow Catchment Study were identified by interrogating the Regional Ecosystem Description Database to return Regional Ecosystems that contained the term "harpophylla" in the description (The State of Queensland 2019). These landscapes historically supported brigalow (*Acacia harpophylla*) vegetation communities on predominantly clay soils.
3) The "*Grazing land management land types V5"* spatial layer (accessed via QSpatial) was clipped to the six sub-basin boundaries defined in step one. This layer was used by VegMachine to determine the appropriate ground cover data for polygon comparisons.
4) The layer produced in step three was further clipped to the Regional Ecosystems identified in step two by using a definition query for "harpophylla" within the attribute table.
5) The "*Land use mapping – 1999 to 2017*" spatial layer (accessed via QSpatial) was clipped to landscapes with a secondary land use of "grazing" in the 2017 data to provide a relevant

comparison to the grazed pasture catchments in this study. This layer was further clipped to six sub-basin boundaries defined in step one.

6) The Regional Ecosystem layer created in step four was further clipped to the grazing layer produced in step five. The result was a spatial layer for each sub-basin that had multiple polygons displaying only grazing land supporting Regional Ecosystems containing *Acacia harpophylla.*
7) The layer produced in step 6 retained Regional Ecosystem classifications within the attribute table under the identifier "stratum". This stratum identifier is required by VegMachine to determine the appropriate ground cover data for polygon comparison and was listed as "FT05" or brigalow with melonholes for the Brigalow Catchment Study (Fitzroy Basin Association 2018; The State of Queensland 2021a). For each sub-basin, the stratum identifier FT05 was assigned to every polygon and then all polygons dissolved into a single polygon. The final result was a single polygon for each sub-basin displaying only grazing land supporting Regional Ecosystems containing *Acacia harpophylla* with the stratum identifier FT05.

Polygons for the conservatively and heavily grazed catchments in addition to polygons for all six sub-basins of the Fitzroy Basin were manually imported into VegMachine and the "*Polygon Comparison"* tool was used to perform ground cover analyses. Comparative ground cover analyses only considered time periods where ground cover observations, including deciles, occurred for all polygons.

5.4 Results

5.4.1 Hydrology

Total annual rainfall at the study site was below the long-term mean annual rainfall of 648 mm (October 1965 to September 2018) in all four hydrological years (Figure 5.4). Rainfall was in the 31st

percentile in 2015 (563 mm), the 29th percentile in 2016 (562 mm), the lowest on record in 2017 (272 mm) and in the 40th percentile in 2018 (584 mm).

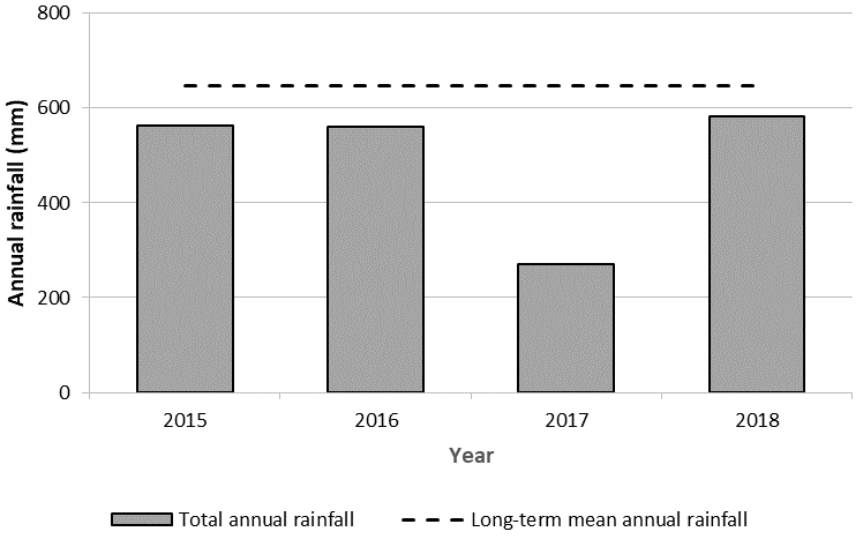

Figure 5.4. Total annual hydrological year rainfall for 2015 to 2018 relative to the long-term mean annual rainfall for the Brigalow Catchment Study.

Similar to rainfall, runoff for the four hydrological years was below the long-term mean annual runoff (1985 to 2018) for the brigalow scrub and conservatively grazed catchment (Figure 5.5). The heavily grazed catchment was only instrumented in 2014, at the commencement of this study, and mean annual runoff was based on four years (2015 to 2018) data. Runoff from brigalow scrub was in the 32nd percentile in 2015, no runoff occurred in 2016 and 2017, and in 2018 was in the 29th percentile. Runoff from the conservatively grazed catchment was in the 35th percentile in 2015, the 30th percentile in 2016, no runoff occurred in 2017, and in 2018 was in the 15th percentile.

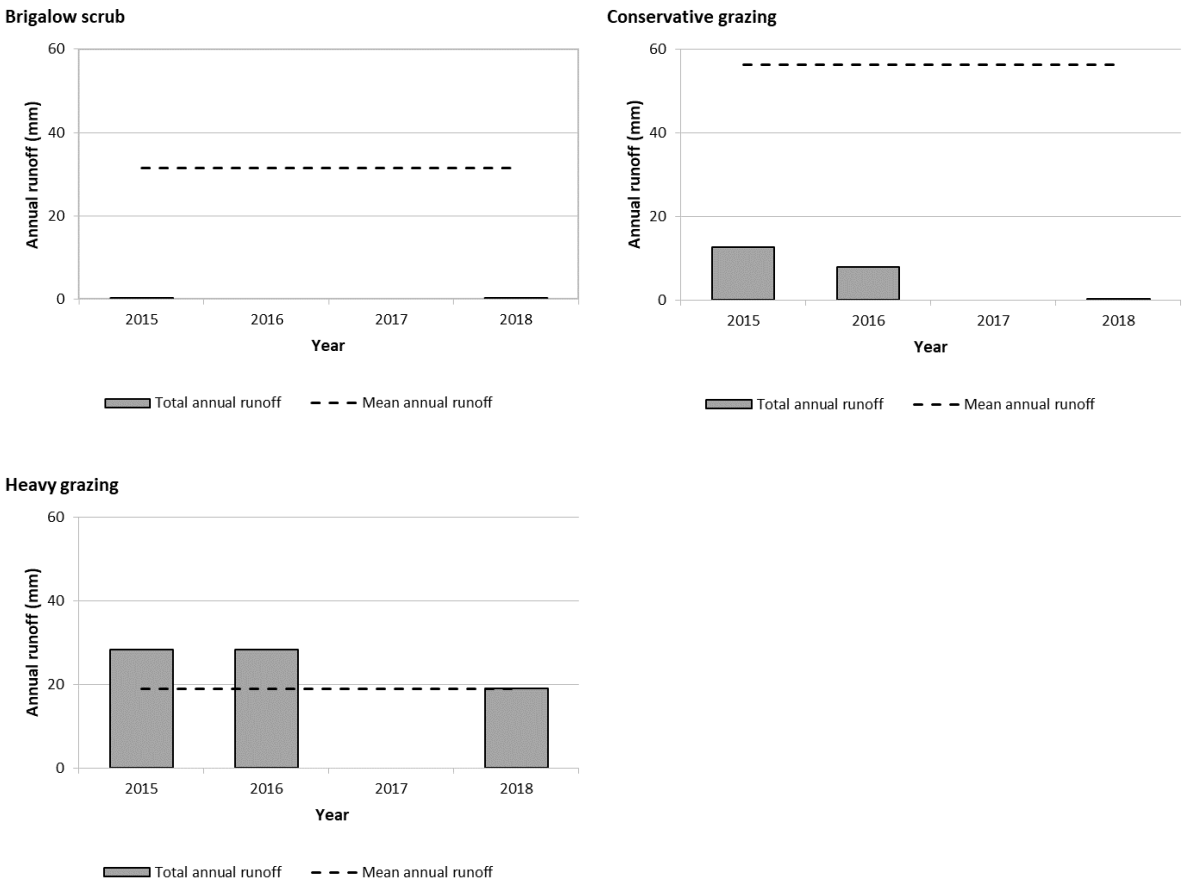

Figure 5.5. Total annual hydrological year runoff for 2015 to 2018 relative to mean annual runoff for the three catchments. Mean annual runoff for the brigalow scrub and conservatively grazed catchments were based on 34 years (1985 to 2018) data, but only four years data (2015 to 2018) for the heavily grazed catchment.

Hydrological data and water quality sampling effort for 2015 to 2018 are summarised in Table 5.7. Although the number of events and total runoff was low in these below average rainfall years, when runoff did occur, the heavily grazed catchment had at least double the runoff of the conservatively grazed catchment. A similar trend was also observed for peak runoff rates with both average and maximum values greatest from the heavily grazed pasture.

Table 5.7. Observed annual hydrological year summaries of runoff and sampling effort for three catchments.

Parameter	Year	Brigalow scrub	Conservative grazing	Heavy grazing
Number of events	2015	1	2	2
	2016	0	1	1
	2017	0	0	0
	2018	1	1	2
Number of samples	2015	0	3	21
	2016	0	2	6
	2017	0	0	0
	2018	0	0	4
Total runoff (mm)	2015	0.2	13	28
	2016	0	8	28
	2017	0	0	0
	2018	0.1	0.1	19
Average peak runoff rate (mm/hr)	2015	0.1	2.6	6.4
	2016	0	1.0	2.6
	2017	0	0	0
	2018	0.1	0.1	2.6
Maximum peak runoff rate (mm/hr)	2015	0.1	3.1	6.5
	2016	0	1.0	2.6
	2017	0	0	0
	2018	0.1	0.1	4.7

Using the hydrological calibration developed during Stage I (1965 to 1982), runoff characteristics for the conservatively grazed pasture (Catchment 3) can be estimated had it remained brigalow scrub (Table 5.8).

Table 5.8. Predicted annual hydrological year summaries of runoff from the conservatively grazed pasture catchment had it remained uncleared brigalow scrub.

Parameter	Year	Catchment 3
Estimated uncleared runoff (mm)	2015	0.2
	2016	0
	2017	0
	2018	0.1
Increase in runoff under pasture (mm)	2015	12
	2016	8
	2017	0
	2018	0
Estimated uncleared average peak runoff rate (mm/hr)	2015	0.2
	2016	0
	2017	0
	2018	0.4
Increase in average peak runoff rate under pasture (mm/hr)	2015	2.4
	2016	1.0
	2017	0
	2018	0

5.4.2 Water quality

5.4.2.1 Total suspended solids

Mean annual EMC for total suspended solids was greater from conservatively than heavily grazed pasture (Table 5.9). Mean annual load of total suspended solids from the heavily grazed pasture was 3.2 times greater than from the conservatively grazed pasture (Figure 5.6, Table 5.10). Brigalow scrub had no EMCs as flows were too small to collect runoff samples whereas loads were estimated by multiplying the long-term site EMC by observed flow.

Table 5.9. Event mean concentrations of total suspended solid, nitrogen and phosphorus parameters in runoff from 2015 to 2018.

Parameter	Event mean concentration (mg/L)		
	Brigalow scrub	**Conservative grazing**	**Heavy grazing**
Total suspended solids	No data	278	235
Total nitrogen	No data	6.49	2.39
Particulate nitrogen	No data	3.40	1.14
Total dissolved nitrogen	No data	3.08	1.25
Dissolved organic nitrogen	No data	1.28	0.66
Dissolved inorganic nitrogen	No data	1.81	0.59
Total phosphorus	No data	0.81	0.49
Particulate phosphorus	No data	0.50	0.22
Total dissolved phosphorus	No data	0.31	0.27
Dissolved organic phosphorus	No data	0.05	0.04
Dissolved inorganic phosphorus	No data	0.26	0.23

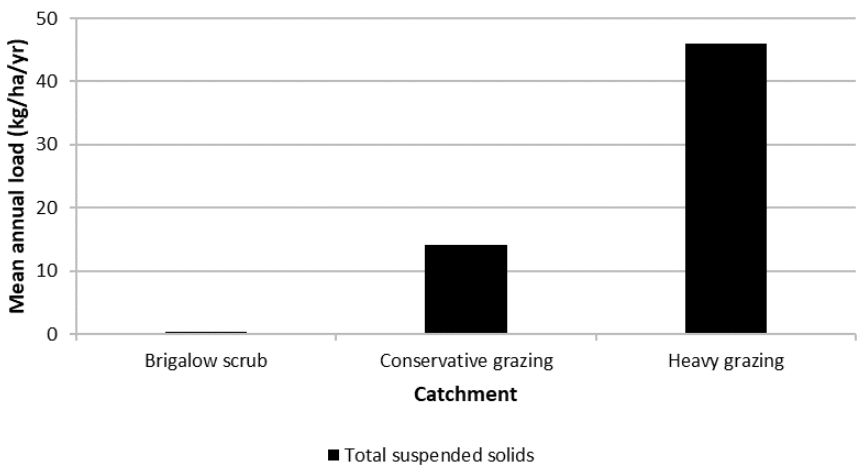

Figure 5.6. Mean annual load of total suspended solids in runoff from 2015 to 2018.

Table 5.10. Mean annual loads of total suspended solid, nitrogen and phosphorus parameters in runoff from 2015 to 2018.

Parameter	Mean annual load (kg/ha)		
	Brigalow scrub	**Conservative grazing**	**Heavy grazing**
Total suspended solids	0.4	14.2	46.0
Total nitrogen	0.01	0.29	0.46
Particulate nitrogen	<0.01	0.14	0.21
Total dissolved nitrogen	0.01	0.15	0.26
Dissolved organic nitrogen	<0.01	0.07	0.13
Dissolved inorganic nitrogen	<0.01	0.08	0.12
Total phosphorus	<0.01	0.04	0.10
Particulate phosphorus	<0.01	0.02	0.04
Total dissolved phosphorus	<0.01	0.02	0.06
Dissolved organic phosphorus	<0.01	0.00	0.01
Dissolved inorganic phosphorus	<0.01	0.01	0.05

5.4.2.2 Nitrogen

Mean annual EMC for total, particulate and total dissolved nitrogen were greater from conservatively than heavily grazed pasture (Table 5.9). Mean annual load of total nitrogen from the heavily grazed pasture was 1.6 times greater than from the conservatively grazed pasture (Figure 5.7, Table 5.10). Total nitrogen was composed of similar amounts of particulate and total dissolved nitrogen irrespective of grazing pressure; 49% and 51% for conservatively grazed pasture and 45% and 55% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of total dissolved nitrogen (64%) than particulate nitrogen (36%) towards total nitrogen. The dominant pathway of nitrogen loss was in a dissolved form from brigalow scrub but was unclear for the two pasture catchments (Table 5.11).

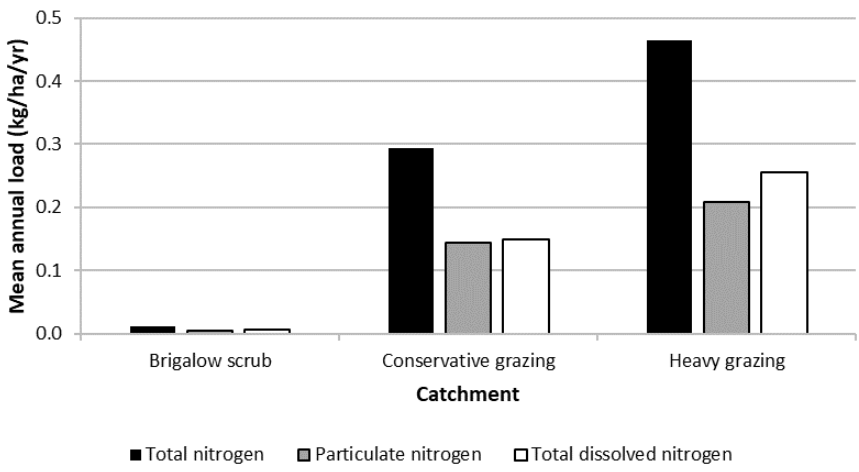

Figure 5.7. Mean annual load of total, particulate and dissolved nitrogen in runoff from 2015 to 2018.

Table 5.11. Dominant pathway of nitrogen loss in runoff from 2015 to 2018.

Year	Brigalow scrub	Conservative grazing	Heavy grazing
2015	Dissolved	No dominant	No dominant
2016	No runoff	No dominant	Dissolved
2017	No runoff	No runoff	No runoff
2018	Dissolved	Dissolved	Particulate

The mean annual EMC for dissolved organic and inorganic nitrogen were greater from conservatively grazed pasture than heavily grazed pasture (Table 5.9). Mean annual load of total dissolved nitrogen from the heavily grazed pasture was 1.7 times greater than from conservatively grazed pasture (Figure 5.8, Table 5.10). Dissolved organic and inorganic fractions contributed similar amounts towards total dissolved nitrogen from the two pasture catchments; 47% and 53% for conservatively grazed pasture and 53% and 47% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of dissolved inorganic nitrogen (66%) than dissolved organic nitrogen (34%) towards total dissolved nitrogen. Oxidised nitrogen was the greatest fraction of dissolved inorganic nitrogen from all catchments; 99% for brigalow scrub, 94% for conservatively grazed pasture and 88% for heavily grazed pasture.

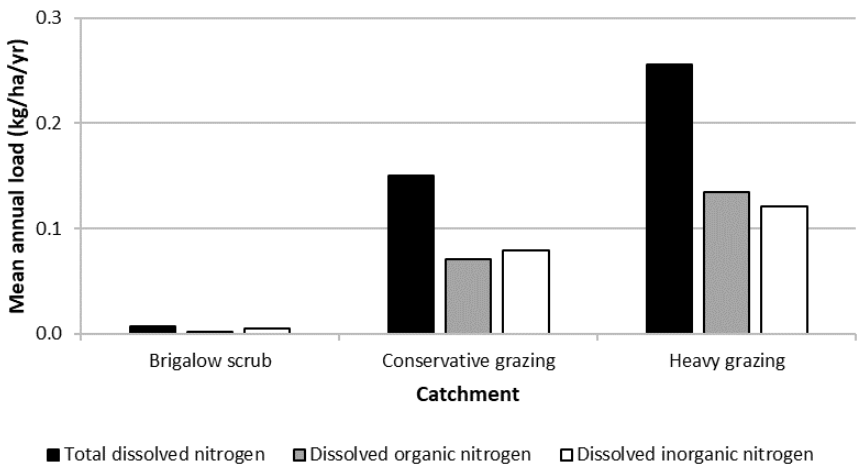

Figure 5.8. Mean annual load of dissolved nitrogen fractions in runoff from 2015 to 2018.

5.4.2.3 Phosphorus

The mean annual EMC for total, particulate and total dissolved phosphorus were greater from conservatively than heavily grazed pasture (Table 5.9). Mean annual load of total phosphorus from the heavily grazed pasture was 2.6 times greater than from conservatively grazed pasture (Figure 5.9, Table 5.10). Total phosphorus was composed of similar amounts of particulate and total dissolved phosphorus irrespective of grazing pressure; 59% and 41% for conservatively grazed pasture and 43% and 57% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of particulate phosphorus (72%) than total dissolved phosphorus (28%) towards total phosphorus. The dominant pathway of phosphorus loss was in a particulate form from brigalow scrub but was unclear for the two pastures (Table 5.12).

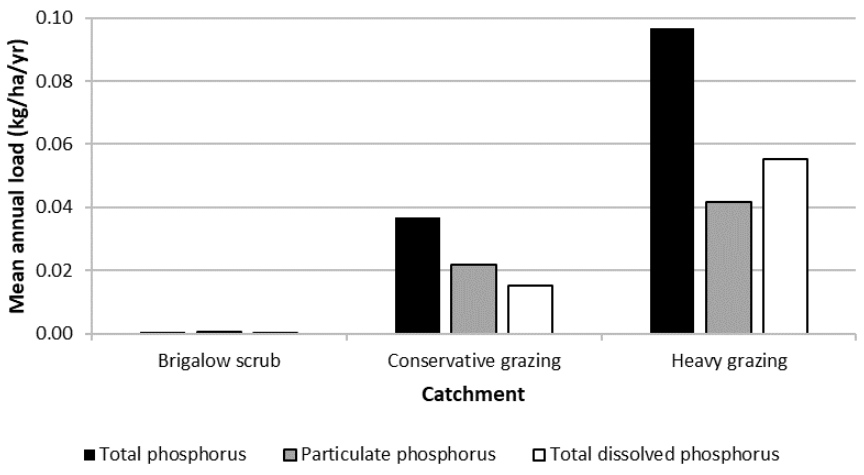

Figure 5.9. Mean annual load of total, particulate and dissolved phosphorus in runoff from 2015 to 2018.

Table 5.12. Dominant pathway of phosphorus loss in runoff from 2015 to 2018.

Year	Brigalow scrub	Conservative grazing	Heavy grazing
2015	Particulate	Particulate	No dominant
2016	No runoff	No dominant	Dissolved
2017	No runoff	No runoff	No runoff
2018	Particulate	No dominant	Particulate

The mean annual EMC for dissolved inorganic and organic phosphorus was greater from conservatively grazed pasture than heavily grazed pasture (Table 5.9). Mean annual load of total dissolved phosphorus from the heavily grazed pasture was 3.6 times greater than from conservatively grazed pasture (Figure 5.10, Table 5.10). Dissolved inorganic phosphorus was the greatest fraction of total dissolved phosphorus from all catchments; 78% from brigalow scrub, 84% from conservatively grazed pasture and 86% from heavily grazed pasture.

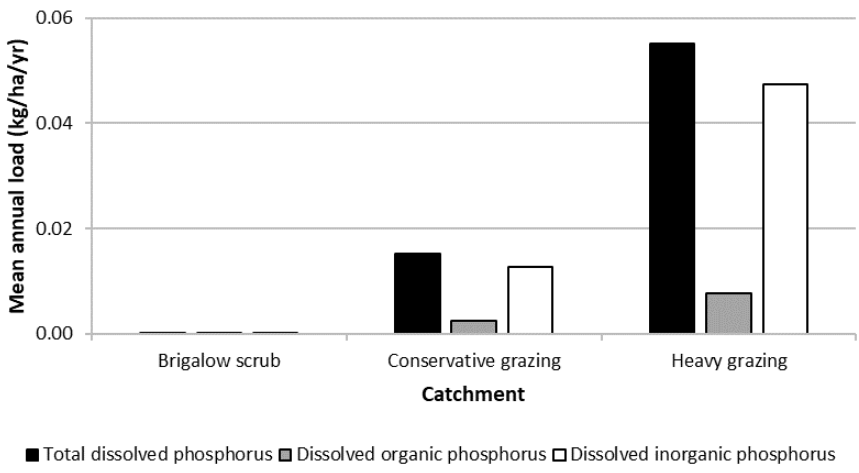

Figure 5.10. Mean annual load of dissolved phosphorus fractions in runoff from 2015 to 2018.

5.4.3 Pasture biomass

Overall, the heavily grazed catchment had lower pasture biomass than the conservatively grazed catchment (Figure 5.11). In the 2014 late wet season, prior to the commencement of the study, there was similar biomass in both the conservatively (6.9 t/ha) and heavily grazed pastures (6.2 t/ha). Biomass in the 2015 late wet season had increased 2.7 t/ha in the conservatively grazed pasture (9.6 t/ha) with little change in the heavily grazed pasture (6.5 t/ha). Biomass in the heavily grazed pasture went from 90% of the biomass in the conservatively grazed pasture in 2014 to 68% in 2015.

In the 2016 late wet season, biomass had reduced 53% under conservative grazing (4.5 t/ha) and 57% under heavy grazing (2.8 t/ha) compared to the previous year (Figure 5.11). The difference in biomass between the two pastures was 63%, similar to the previous year. Biomass continued to decline in both pastures over the next six months, with a 43% reduction in the conservatively grazed pasture to 2.5 t/ha and a much greater 83% reduction in the heavily grazed pasture to 0.5 t/ha. Biomass in the heavily grazed pasture during the 2016 late dry season was reduced to 19% of that from the conservatively grazed pasture.

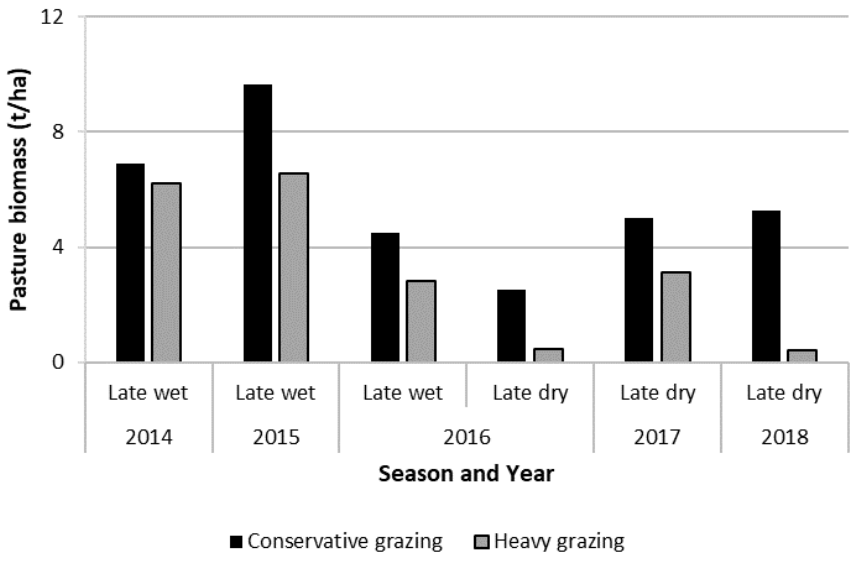

Figure 5.11. Pasture biomass in the two pastures from 2015 to 2018.

In the 2017 late dry season, biomass had increased to 5.0 t/ha under conservative grazing and 3.1 t/ha under heavy grazing (Figure 5.11). Pasture biomass in the heavily grazed catchment increased to 62% of that from the conservatively grazed catchment, similar to the 2015 and 2016 late wet seasons. In the 2018 late dry season, biomass had increased 5% under conservative grazing (5.3 t/ha) whereas biomass under heavy grazing (0.4 t/ha) had declined 86% compared to the previous year. Biomass in the heavily grazed pasture during the 2018 late dry season was reduced to 8% of that from the conservatively grazed pasture.

Table 5.13 provides a visual comparison of the conservatively and heavily grazed pastures during the late wet and late dry seasons over the 2015 to 2018 hydrological years. In each instance the photographs show that the heavily grazed pasture had less pasture biomass and ground cover than the conservatively grazed pasture.

Table 5.13. Photographic comparison of ground cover and pasture biomass from the two pastures in the late wet and late dry seasons from 2015 to 2018.

Year	Late wet season		Late dry season	
	Conservative grazing	**Heavy grazing**	**Conservative grazing**	**Heavy grazing**
2015				
2016				
2017				
2018				

5.4.4 Ground cover

In the two years prior to the commencement of this study, the two pastures were extensively spelled with less than nine weeks of grazing at conservative stocking rates. During this time, the effect of season on cover can be observed with both pastures having higher proportions of bare ground in the late dry season (Figure 5.12). At the commencement of this study in October 2014, the

proportion of bare ground was similar in the conservatively (12.3%) and heavily grazed pastures (13.4%). At this time, 95% of the conservatively grazed pasture had cover levels of 78% or higher and 95% of the heavily grazed pasture had similar cover levels of 73% or higher. In October 2018, the amount of bare ground in the heavily grazed pasture (23.5%) was 2.4 times greater than in the conservatively grazed pasture (9.9%). Ground cover in the conservatively grazed pasture remained relatively constant during the study with 95% of the pasture having cover levels of 80% or higher in October 2018. However, cover levels across 95% of the heavily grazed pasture decreased to 57% or higher by January 2018 before increasing to 69% or higher in October 2018, which was slightly lower than the distribution of cover at the commencement of the study. This analysis showed that the conservatively and heavily grazed pastures started in a similar condition, but an increase in bare ground and a corresponding decrease in ground cover were observed over time in the heavily grazed pasture.

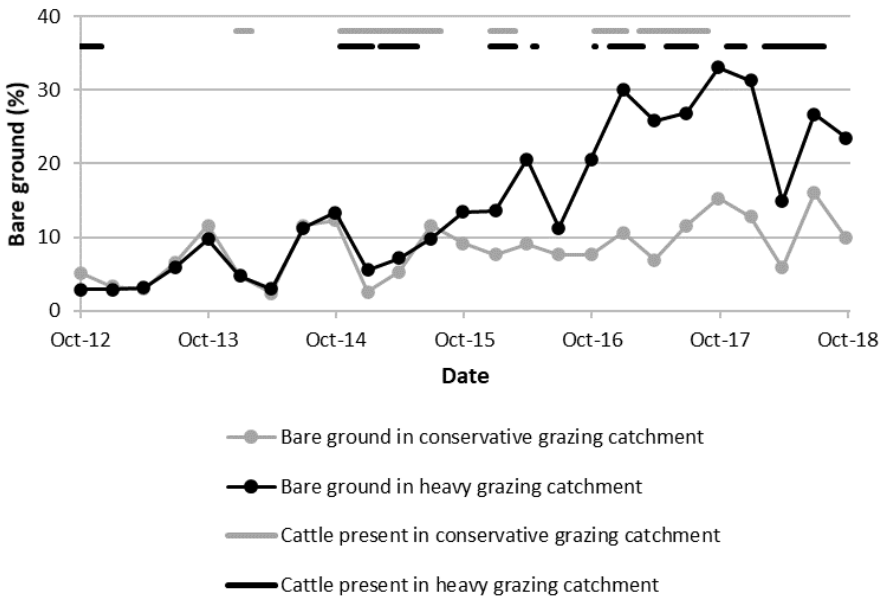

Figure 5.12. Measurements of bare ground in the two pastures related to periods of cattle stocking.

5.4.5 Benchmarking ground cover to the Fitzroy Basin

Regional Ecosystems that contain brigalow (*Acacia harpophylla*) account for 32% of the Fitzroy Basin. Grazing is the predominant land use in these Regional Ecosystems, as it occurs on 86% of land that historically supported *Acacia harpophylla* in the Fitzroy Basin (Figure 5.13).

VegMachine ground cover analysis provides outputs from May 1990. Since then, median VegMachine derived ground cover for the conservatively grazed catchment exceeded the lowest 80th percentile for the six Fitzroy sub-basins 95% of the time and exceeded the lowest 95th percentile 85% of the time (Figure 5.14). Since the heavy grazing treatment was planted to the current pasture in 1992 until commencement of this study in 2014, median ground cover in the catchment equalled or exceeded the conservatively grazed catchment 40% of the time. During this period, ground cover exceeded the lowest 80th percentile for the six Fitzroy sub-basins 89% of the time and exceeded the lowest 95th percentile 70% of the time. Within five years of heavy grazing commencing, ground cover in that catchment was within the 5th percentile range of covers for the six Fitzroy sub-basins 44% of the time (Figure 5.14).

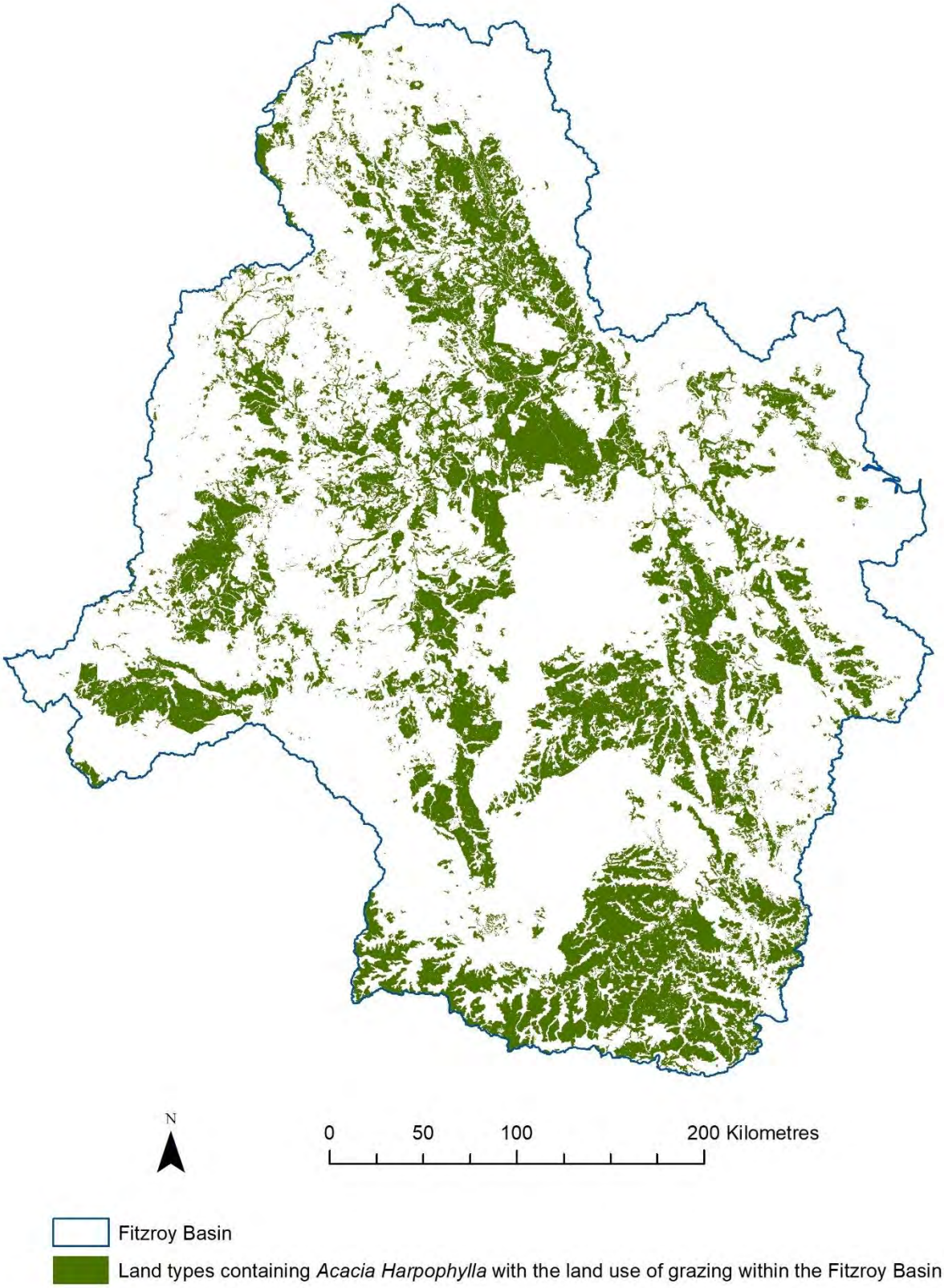

Figure 5.13. Land types containing brigalow (Acacia harpophylla) with the land use of grazing (green) within the Fitzroy Basin (blue outline).

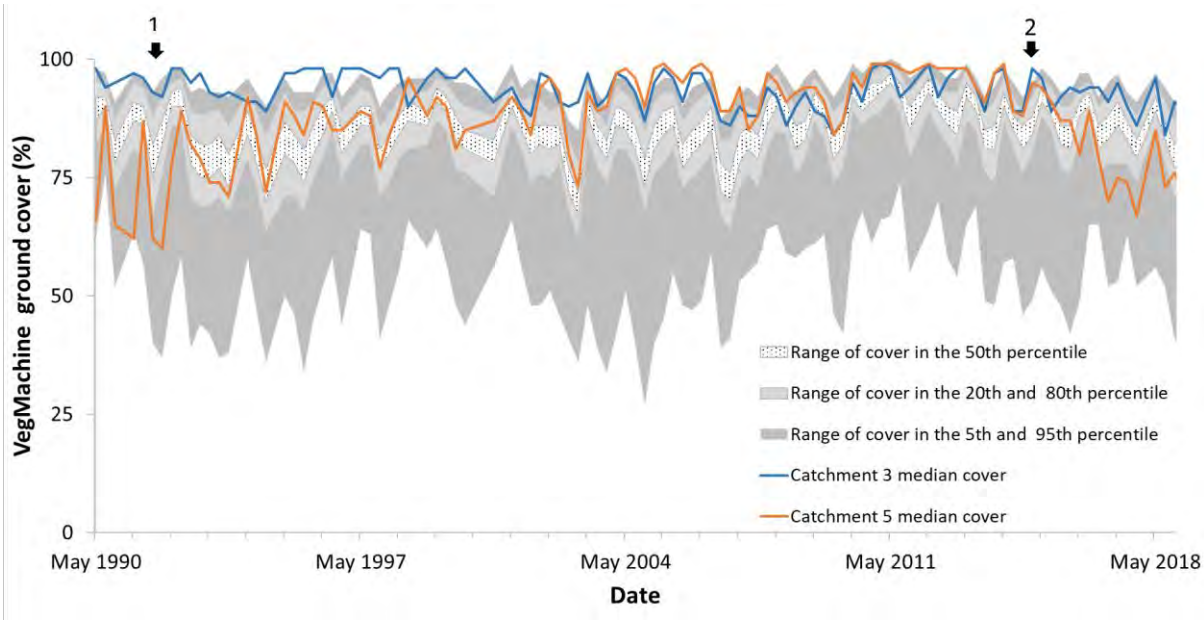

Figure 5.14. Median satellite derived ground cover for the conservatively (blue line) and heavily (orange line) grazed catchments of the Brigalow Catchment Study compared to the range of cover percentiles for the Fitzroy Basin. Arrow 1 indicates planting of pasture in Catchment 5 following three years of cropping and arrow 2 indicates the commencement of heavy grazing in Catchment 5.

5.5 Discussion

5.5.1 Stocking rates and safe long-term carrying capacity

Published recommended stocking rates for buffel grass pastures on brigalow lands vary from 0.1 AE/ha/yr to 0.5 AE/ha/yr (Lawrence and French 1992), with observed stocking rates reported to be in the same range (Graham *et al.* 1991; Lawrence and French 1992; Partridge *et al.* 1994; Noble *et al.* 2000; Paton *et al.* 2011; Peck *et al.* 2011). Some authors acknowledge that stocking rates should be adjusted for landscape and seasonal variability (Graham *et al.* 1991; Lawrence and French 1992; Paton *et al.* 2011), while others note that stocking rates should be reduced over time as pasture productivity declines (Partridge *et al.* 1994; Noble *et al.* 2000; Peck *et al.* 2011). For example, Noble *et al*. (2000) recommends 0.5 AE/ha/yr on newly established buffel grass pastures and 0.33 AE/ha/yr on rundown buffel grass pastures. Daily live weight gains of 0.5 kg/head are considered possible

from newly established pastures (Lawrence and French 1992; Radford *et al.* 2007); however, Partridge *et al.* (1994) states that stocking rates should be adjusted to achieve daily weight gains of 0.4 kg/head on rundown pastures as the plants are more likely to be damaged at higher stocking rates.

In line with these recommendations and to maintain industry relevance, the average stocking rate of the conservatively grazed pasture during this study was 0.17 AE/ha/yr. Historically, stocking rates for this pasture were 0.45 AE/ha/yr on newly established buffel grass pasture when the study commenced, which decreased to 0.26 AE/ha/yr over the next 21 years (Radford *et al.* 2007). The average long-term (1984 to 2017) stocking rate was 0.30 AE/ha/yr (unpublished data). Daily weight gains in the order of 0.5 kg/head were achieved initially and have been obtained periodically since (Radford *et al.* 2007; Thornton and Buck 2011). However, maintaining the 0.45 AE/ha/yr stocking rate during the first 11 years following pasture establishment saw daily weight gains decline to about 0.3 kg/head (Radford *et al.* 2007).

The average stocking rate in the heavily grazed pasture was 0.54 AE/ha/yr. Despite the age of the pasture (40 to 50 years old), this stocking rate was similar to recommended stocking rates for newly established buffel grass pastures. For three decades post-clearing but prior to the inclusion of Catchment 5 into the Brigalow Catchment Study, historical stocking rates were about 0.40 AE/ha/yr. These stocking rates decreased over the next decade to less than 0.25 AE/ha/yr, followed by extensive spelling over the next eight years. This management history is in line with published recommended and observed industry stocking rates for brigalow lands, which suggests that sustained heavy grazing prior to inclusion in this study was unlikely.

Given the difficulties encountered in changing the traditional paradigm of “more cattle means more money” towards lighter stocking rates, despite equal or greater economic return (Stockwell *et al.* 1991; O'Reagain *et al.* 2011; Moravek *et al.* 2017), it is likely that high stocking rates are still used within the industry. This is supported by the VegMachine ground cover analysis, which shows that while ground cover in the heavily grazed pasture of the Brigalow Catchment Study was often in the 5th percentile for grazed *Acacia harpophylla* landscapes in the Fitzroy Basin, ground cover was still higher than some properties within similar landscapes. Thus, the heavily grazed pasture in this study may overestimate pasture biomass and ground cover and underestimate hydrology and water quality compared to some properties.

The concept of a safe long-term carrying capacity for sustainable grazing management benefits productivity, land condition and runoff water quality by balancing pasture utilisation with pasture growth (O’Reagain *et al.* 2014). A pasture utilisation rate between 15 and 30% of pasture growth has been considered a safe long-term carrying capacity (O'Reagain *et al.* 2011; Peck *et al.* 2011). A safe long-term carrying capacity can be estimated using pasture biomass, dietary intake requirements of cattle and pasture utilisation rates. For the conservatively grazed pasture, a safe long-term carrying capacity was 0.29 AE/ha/yr based on a long-term pasture biomass of 3,500 kg/ha (Radford *et al.* 2007), an estimated dietary intake of 2.2% bodyweight per day (Minson and McDonald 1987) and a high but still economically viable utilisation rate of 30% (Bowen and Chudleigh 2017). This was similar to the lower estimate of long-term carrying capacity of 0.27 AE/ha/yr for the Brigalow Catchment Study determined by the FORAGE system (The State of Queensland 2021a). This was expected given the Aussie GRASS model (Carter *et al.* 2000) used in the FORAGE system is based on the GRASP pasture simulation model (Rickert *et al.* 2000), and both models have been informed by long-term BOTANAL pasture assessments, stocking rate and animal production data from the Brigalow Catchment Study (Dalal *et al.* 2021). GRASP pasture simulation modelling for Catchment 3

shows that in order to maintain a long-term pasture biomass of 3,500 kg/ha, an average of about 7,400 kg/ha of pasture biomass needs to be grown each year (Dalal *et al.* 2021). Although a safe long-term carrying capacity can be calculated, stocking rates should still be adjusted annually at the end of the summer growing period to account for pasture biomass. This reduces environmental damage, workload and management stress while benefiting long-term financial viability for the grazing enterprises (Lawrence and French 1992).

5.5.2 Effect of grazing pressure on hydrology

The climatic sequence experienced in this study should not be considered atypical. Long-term records for the Brigalow Catchment Study show four consecutive below average rainfall years have occurred previously from 2006 to 2009 (Thornton *et al.* 2007; Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). While the lowest total annual rainfall in the history of the Brigalow Catchment Study occurred in 2017, resulting in no runoff from any catchment, there have been four years between 1965 and 2014 when there was also no runoff from both Catchments 1 and 3 (Thornton *et al.* 2007; Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). This highlights the need for long-term studies in semi-arid landscapes to capture both seasonal and annual rainfall variability, which is the key driver of most landscape processes (Cowie *et al.* 2007).

From first principles, heavy grazing pressure should decrease ground cover compared to conservative grazing pressure in the same landscape due to increased pasture utilisation and cattle trampling. It was hypothesised that a decline in ground cover combined with the deleterious effects of grazing on soil physical characteristics, such as structure and infiltration rate, would lead to increased runoff. This trend was demonstrated by the findings of Silburn *et al.* (2011) and Silcock *et al.* (2005) in the Fitzroy Basin, Bartley *et al*. (2014) and McIvor *et al*. (1995) in the Burdekin Basin,

and internationally in reviews such as those of van Oudenhoven *et al.* (2015). Increased runoff is noted as a driver for both increased erosion and nutrient loads in runoff by both Australian studies (Thornton *et al.* 2017; Koci *et al.* 2020) and international long-term paired catchment studies, such as those of the Santa Rita Experimental Watershed (Polyakov *et al.* 2010). For example, the long-term Santa Rita study determined that runoff was the best predictor of sediment yield and explained up to 90% of its variability. As runoff is known to increase with a decline in ground cover and/or biomass (McIvor *et al.* 1995; Bartley *et al.* 2010; Silburn *et al.* 2011; Koci *et al.* 2020), an increase in runoff from the heavily grazed catchment was expected. This reflects numerous other studies that have reported greater runoff from grazed than ungrazed areas and/or pastures with higher stocking rates (Filet and Osten 1996; Mapfumo *et al.* 2002; Silcock *et al.* 2005; O'Reagain 2011; van Oudenhoven *et al.* 2015; Duniway *et al.* 2018). This body of evidence suggested that the heavy grazing pressure in this study would ultimately lead to increased loads of sediment and nutrients in hillslope runoff compared to conservative grazing. Hillslope erosion is of particular concern, as it accounts for 22% of sediment loss from Great Barrier Reef catchments (McCloskey *et al.* 2021).

Changing land use from virgin brigalow scrub to conservatively grazed pasture at the long-term Brigalow Catchment Study doubled total runoff (Thornton *et al.* 2007) and increased both average and maximum peak runoff rates by 1.5 times and 3.0 times, respectively, when runoff occurred from both catchments (Thornton and Yu 2016). Over the four below average rainfall years of this study, heavy grazing of rundown pasture at stocking rates recommended for newly established pasture resulted in 3.6 times more total runoff and 3.3 times greater average peak runoff rate than the conservatively grazed pasture. At the end of this four-year study, the heavily grazed pasture had 2.4 times more bare ground and only 8% of the pasture biomass compared to the conservatively grazed pasture. In years when no runoff occurred from brigalow scrub, total runoff from the conservatively grazed pasture represents an absolute anthropogenic increase attributable to land use change.

Although Catchment 5 had a prior history of grazing before its inclusion in the Brigalow Catchment Study, both pasture catchments were managed according to recommended stocking rates. Satellite derived ground cover from VegMachine reflects this cattle stocking philosophy with similar cover for both the conservatively and heavily grazed pastures following the establishment of the current pasture in Catchment 5. Both Catchments 3 and 5 were dominated by clay soils (Vertosols and Dermosols) with a low slope (<6%), so inherent geomorphological differences are unlikely to override the grazing treatment effects on runoff and water quality. Furthermore, evidence that the runoff response from Catchment 5 is a treatment effect was supported by runoff responses from other catchments of the Brigalow Catchment Study.

For example, Catchment 4 of the Brigalow Catchment Study (Thornton and Elledge 2013) had the same land use history as Catchment 5 until 1998 when it was planted to a leucaena and grass pasture. If the runoff response to the heavy grazing treatment in Catchment 5 during this study was a legacy response to historical land use, then a similar runoff response was expected from Catchment 4. That is, Catchment 4, a conservatively grazed leucaena and grass pasture, would have about triple the runoff of Catchment 3, the conservatively grazed grass pasture. However, Catchment 4 had only 94% of the total runoff from Catchment 3 from 2010 to 2013 (Thornton and Elledge 2013; Thornton and Elledge 2014); 464 mm and 496 mm, respectively. Similarly, the calibration of the long-term catchments in Stage I showed that the greatest difference in pre-clearing runoff was 28% (Thornton *et al.* 2007). This is an order of magnitude less than the difference in runoff between Catchments 3 and 5 during this study. Thus, the impacts of heavy grazing pressure on hydrology and water quality were considered to be related to the treatment imposed in Catchment 5 rather than a legacy response to historical sustained heavy grazing.

While increases in runoff are commonly attributed to or observed in partnership with declining ground cover, the landscape response is more complex. For example, Thornton *et al.* (2007) showed that changed water use patterns was the primary driver of increased runoff when native vegetation was replaced with improved grass pasture, and that increased compaction and reduced ground cover, soil structure and infiltration rate were secondary drivers. It is also known that the effects of cover on runoff and erosion are more complicated than a simple presence or absence relationship, with additional drivers including the type, distribution and mass of cover (Bartley *et al.* 2014; Koci *et al.* 2020). Increased runoff, and subsequently increased loads of nutrients in runoff, are effectively a reduction in plant available water capacity and soil fertility which leads to reduced pasture growth.

Persistent heavy grazing is also known to change the composition of pasture species over time, which leads to a decline in desirable (perennial, palatable and productive) species and an increase in less desirable (annual, unpalatable and less productive) species. For example, studies in the Burdekin Basin have attributed the transition of productive native grass species, such as black speargrass (*Heteropogon contortus*) and desert bluegrass (*Bothriochloa ewartiana*), to the less productive and less drought tolerant Indian couch (*Bothriochloa pertusa*) to a combination of drought and heavy grazing (Bartley *et al.* 2014; Spiegel 2016). Thus, runoff, plant available water capacity, soil fertility, pasture growth and changes in pasture species composition are all intrinsically linked by the management of grazing pressure.

Intervention to break the cycle of declining land condition can be achieved with the adoption of improved management practices; however, the time required to restore healthy eco-hydrological function may vary from years to decades (Roth 2004; Silcock *et al.* 2005; Hawdon *et al.* 2008; Bartley *et al.* 2014). For example, a landholder in the Burdekin Basin reported improved land condition with the adoption of a safe long-term carrying capacity and pasture spelling (Landsberg *et al.* 1998). The

property had reduced income during the three-year transition phase, but became profitable with less cattle once the perennial grasses recovered. Other research in the Burdekin Basin indicates that sustainable grazing management is profitable over extended time periods and varying climatic cycles (O'Reagain *et al.* 2011). Nonetheless, from both an environmental and economic perspective, it is better to improve grazing management before a dramatic decline in land condition occurs (Rolfe *et al.* 2020).

5.5.3 Effect of grazing pressure on water quality

Heavily grazed pasture had higher loads and lower EMCs for all water quality parameters compared to the conservatively grazed pasture. In years when no runoff occurred from brigalow scrub, total runoff and subsequent loads of total suspended solids and all nutrients from the conservatively grazed pasture represent an absolute anthropogenic increase attributable to land use change. Over four below average rainfall years, this study typically had lower loads and higher EMCs than previously reported for the conservatively grazed pasture during wetter periods and over longer timeframes (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). These trends indicate that increased hillslope runoff, whether from above average rainfall or a treatment (grazing pressure) effect, results in dilution of total suspended solids and nutrients leading to lower EMCs. However, the dilution effect was not strong enough to result in reduced loads. Dilution effects have been reported for sediment and nutrient concentrations within events (Schepers and Francis 1982), within seasons (Schepers *et al.* 1982; Hay *et al.* 2006), in the transition from dry to wet seasons (Vink *et al.* 2007), and also on an annual basis over multiple years (Bartley *et al.* 2014; Miller *et al.* 2017). This study reflects other publications that have reported increased loads with increased flow (Schepers *et al.* 1982; Hay *et al.* 2006). It also reflects previous observations that high EMCs at this site do not necessarily equate to high loads (Thornton and Elledge, 2013).

5.5.3.1 Total suspended solids

Runoff from heavily grazed pasture had 3.2 times greater loads of total suspended solids than the conservatively grazed pasture. An increase in suspended solids with a decrease in ground cover reflected the trend observed between runoff and cover in this study, which is a relationship often cited in the literature (McIvor *et al.* 1995; Bartley *et al.* 2010; Silburn *et al.* 2011). VegMachine® analysis in this study also showed that ground cover decreased with increased grazing pressure. Despite similar cover levels in the two pastures initially, there was 2.4 times more bare ground in the heavily grazed pasture (23.5%) after four years compared to the conservatively grazed pasture (9.9%). Mean annual loads for both the conservatively (14 kg/ha/yr) and heavily grazed pastures (46 kg/ha/yr) during the four below average rainfall years were considerably lower than observed from the conservatively grazed pasture during an extremely wet period from 2010 to 2013 (Thornton and Elledge 2013), a return to average conditions from 2013 to 2014 (Thornton and Elledge 2014), and also modelled loads for the period 1984 to 2010 (Elledge and Thornton 2017). Mean annual load from the three previously reported periods was 258 kg/ha/yr (range 20 to 468 kg/ha/yr). Loads from this study were also lower than more erosive landscapes on shallower soils elsewhere in the Fitzroy Basin (Silburn *et al.* 2011) and also in the nearby Burdekin Basin (Hawdon *et al.* 2008; Bartley *et al.* 2014).

Mean annual EMCs of total suspended solids from both the conservatively (278 mg/L) and heavily grazed pastures (235 mg/L) were similar to those previously reported for the conservatively grazed pasture during wetter periods and over longer timeframes (301 mg/L; range 95 to 916 mg/L) (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). These values also fit within the ranges reported for grazing on both improved and native pastures dominated (>90%) by a single land use (Bartley *et al.* 2012). Bartley *et al*. (2012) reviewed water quality data from across Australia and found that EMCs of total suspended solids were lower from forests than

improved pasture, and both these land uses were lower than from native pastures. In contrast, EMCs from brigalow scrub of the Brigalow Catchment Study were generally higher than from conservatively grazed pasture when runoff occurred from both catchments (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). This highlights the importance that hydrological characteristics, vegetation type and landscape condition (i.e., ground cover) have on the resulting total suspended solids concentrations and loads. Data from the Brigalow Catchment Study can fill the knowledge gap of water quality from brigalow lands in the Fitzroy Basin to further refine estimations of the impact of grazing land management on Great Barrier Reef water quality.

5.5.3.2 Nitrogen

Similar to total suspended solids, loads of all nitrogen parameters during the four below average rainfall years were greater from heavily than conservatively grazed pasture while EMCs were lower from the heavily grazed pasture. This reflects other studies that have reported greater loads of nitrogen from grazed than ungrazed areas and from heavier than lighter grazing pressures (Daniel *et al.* 2006; Park *et al.* 2017). Mean annual loads of total nitrogen (0.29 kg/ha/yr) and dissolved inorganic nitrogen (0.08 kg/ha/yr) from the conservatively grazed pasture in this study were lower than previously reported during wetter periods (Thornton and Elledge 2013; Thornton and Elledge 2014) and over longer timeframes (Elledge and Thornton 2017); 2.6 kg/ha/yr (range 0.6 to 5.1 kg/ha/yr) and 0.37 kg/ha/yr (range 0.06 to 0.81 kg/ha/yr), respectively.

In contrast, EMCs of total nitrogen (6.49 mg/L) and dissolved inorganic nitrogen (1.81 mg/L) from the conservatively grazed pasture in this study were higher than previously reported; 2.4 mg/L (range 2.0 to 3.2 mg/L) and 0.41 mg/L (range 0.11 to 0.80 mg/L), respectively (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). EMCs for these two nitrogen parameters were within the range for improved pastures in Australia, but exceeded the range for native pastures

when the majority of the upstream area was under a single land use (Bartley *et al.* 2012). However, under the more rigorous criteria of upstream area dominated (>90%) by a single land use, the total nitrogen EMC in this study exceeded the ranges for both improved and native pastures. Comparable data was not available for dissolved inorganic nitrogen.

These high EMCs are likely a reflection of the high soil fertility of brigalow lands compared to the rangeland, savannah and woodland landscapes from which comparable data was available. This is supported by long-term total nitrogen (14.4 mg/L; range 9.9 to 20.2 mg/L) and dissolved inorganic nitrogen (4.82 mg/L; range 1.94 to 7.01 mg/L) EMCs from brigalow scrub (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017) which greatly exceed the ranges given for forest in Bartley *et al.* (2012). Furthermore, modelling of long-term water quality indicates that brigalow scrub has higher loads and concentrations of nitrogen (total and dissolved) compared to conservatively grazed pasture (Elledge and Thornton 2017). This contrasts with a number of Australian and international studies that have noted higher loads of nitrogen from pasture than forest (Quinn and Stroud 2002; Vink *et al.* 2007; Udawatta *et al.* 2011). This highlights the uniqueness of brigalow lands where nitrogen fixation by brigalow (*Acacia harpophylla*) leads to high soil fertility, and hence higher losses of nitrogen in runoff, compared to other landscapes (Webb *et al.* 1982; Yule 1989; Thornton and Elledge 2018).

The limited data collected during this study showed that nitrogen lost in runoff from brigalow scrub was predominately in the dissolved phase. This phase was dominated by dissolved inorganic nitrogen which in turn was dominated by oxidised nitrogen. In contrast, nitrogen from the two pastures was lost in both particulate and dissolved phases. Both dissolved organic and inorganic nitrogen made substantial contributions to the dissolved phase. Oxidised nitrogen dominated the dissolved inorganic nitrogen fraction. This reflects numerous authors that have highlighted the

importance of dissolved organic nitrogen when considering nitrogen losses (Alfaro *et al.* 2008; Robertson and Nash 2008; Van Kessel *et al.* 2009). This is certainly the case for grazed landscapes, as dissolved organic nitrogen is known to increase with the application of cattle urine and dung (Wachendorf *et al.* 2005; Van Kessel *et al.* 2009), and concentrations have also been shown to increase with increased grazing pressure (Owens *et al.* 1989).

5.5.3.3 Phosphorus

Similar to total suspended solids and nitrogen, loads of all phosphorus parameters during the four below average rainfall years were greater from heavily than conservatively grazed pastures while EMCs were lower from the heavily grazed pasture. This reflects other studies that have reported greater loads of phosphorus from grazed than ungrazed areas and from heavier than lighter grazing pressures (Daniel *et al.* 2006; Vink *et al.* 2007; Butler *et al.* 2008; Park *et al.* 2017). Mean annual loads of total phosphorus (0.04 kg/ha/yr) and dissolved inorganic phosphorus (0.01 kg/ha/yr) from the conservatively grazed pasture in this study were lower than previously reported during wetter periods (Thornton and Elledge 2013; Thornton and Elledge 2014) and over longer timeframes (Elledge and Thornton 2017); 0.38 kg/ha/yr (range 0.07 to 0.76 kg/ha/yr) and 0.20 kg/ha/yr (range 0.04 to 0.42 kg/ha/yr), respectively.

In contrast, EMCs of total phosphorus (0.81 mg/L) and dissolved inorganic phosphorus (0.26 mg/L) from the conservatively grazed pasture were higher than previously reported; 0.32 mg/L (range 0.23 to 0.41 mg/L) and 0.17 mg/L (range 0.10 to 0.22 mg/L), respectively (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017). The total phosphorus EMC fits within the range for both improved and native pastures within Australia (Bartley *et al.* 2012). Although the EMC for dissolved inorganic phosphorus was just above the range for improved pastures, it greatly exceeded the range for native pastures (Bartley *et al.* 2012). Similarly, the EMC for dissolved organic

phosphorus in this study (0.05 mg/L) greatly exceeded both the improved and native pasture ranges of Bartley *et al*. (2012).

Similar to the response for nitrogen, these high EMCs are likely a reflection of the high soil fertility of brigalow lands. This is supported by long-term EMCs of total phosphorus (0.79 mg/L; range 0.32 to 2.19 mg/L) and dissolved inorganic phosphorus (0.16 mg/L; range 0.10 to 0.29 mg/L) from brigalow scrub (Thornton and Elledge 2013; Thornton and Elledge 2014; Elledge and Thornton 2017) which greatly exceed the ranges given for forest in Bartley *et al.* (2012). Furthermore, soil phosphorus levels prior to land development at the Brigalow Catchment Study were considered moderate (13.7 mg/kg; range 13.3 to 14.0 mg/kg) based on the classification of Ahern *et al*. (1994). Levels increased rapidly becoming high to very high (34.7 mg/kg; range 24 to 44 mg/kg) following clearing and burning due to the resulting ash bed. However, soil phosphorus levels under grazing then declined back to a moderate level (12.6 mg/kg; range 11.0 to 14.6 mg/kg) over the next 32 years (Thornton and Shrestha 2021). This is in stark contrast to the low, deficient (very low) and acute (extremely low) status of soil phosphorus given to 72% of the central and north-east Queensland grazing lands (Ahern *et al.* 1994) and the deficient and acute status given to 68% of northern Australian soils (McCosker and Winks 1994).

Phosphorus loss from uncultivated fields and grazed pasture is typically in the dissolved phase, which is dominated by dissolved inorganic phosphorus (Gillingham and Gray 2006; Potter *et al.* 2006; Alfaro *et al.* 2008; Robertson and Nash 2008). The limited data collected during this study showed that phosphorus loss from brigalow scrub may be dominated by particulate phosphorus while the grass pastures lost phosphorus in both particulate and dissolved phases. Higher EMCs of dissolved inorganic phosphorus from conservatively grazed pasture compared to brigalow scrub has previously

been attributed to the presence of grazing animals and their dung (Elledge and Thornton 2017), which is in agreement with the literature (Schepers *et al.* 1982; Vadas *et al.* 2011).

5.5.4 Implications for the grazing industry

This study shows that grazing land management based on a safe long-term carrying capacity has a lower risk to water quality than heavily grazed pastures. This is essential knowledge for the grazing industry given the recent introduction of minimum practice agricultural standards for beef cattle grazing under the Reef protection regulation (Office of the Great Barrier Reef 2020; The State of Queensland 2021b). As per the regulation, where land has ground cover less than 50% at September 30 each year, measures must be undertaken to move land towards good (A) or fair (B) condition; that is, ground cover greater than 50%. This became enforceable under the Environmental Protection Act 1994 (The State of Queensland 2020a) in December 2020 for the Burdekin region, and will commence in December 2021 for the Fitzroy region followed by the Wet Tropics, Mackay Whitsunday and Burnett Mary regions in December 2022. This is in addition to minimum standard record keeping requirements that commenced for most graziers in December 2019.

Adoption of a safe long-term carrying capacity can assist landholders to demonstrate compliance with this legislation. For example, the Grazing Water Quality Risk Framework shows that hillslope pasture management has seven performance indicators where each indicator is weighted based on its relative influence on water quality leaving farms (McCosker and Northey 2015; The State of Queensland 2020b). Hillslope management based on a safe long-term carrying capacity combined with seasonal forage budgeting to ensure pasture utilisation rates are not exceeded accounts for 45% of the relative influence. Ground cover monitoring and pasture management decisions to achieve ground cover thresholds account for a further 30% of the relative influence.

5.6 Conclusion

Long-term data from the Brigalow Catchment Study suggests that a stocking rate of 0.29 AE/ha/yr is a safe long-term carrying capacity for well-managed, rundown (30 to 40 years old) buffel grass pasture established on predominantly clay soils previously dominated by brigalow woodland. This recommendation is based on long-term pasture biomass and cattle live weight gains from the study site; however, stocking rates may need to be reduced at other locations unable to maintain similar amounts of pasture biomass under grazing (average 3,500 kg/ha). Failure to reduce stocking rates on rundown pastures to match safe long-term carrying capacity led to increased hillslope runoff, and subsequently increased loads of total suspended solids, nitrogen and phosphorus in runoff. While limited water quality data was collected during the four below average rainfall years of this study, loads of total nitrogen and phosphorus both had substantial contributions of particulate and dissolved fractions. Although heavily grazed pasture had the highest runoff and greatest loads of total suspended solids and all nutrient parameters, it had the lowest EMCs. Heavy grazing pressure reduced ground cover which demonstrates the value of this indicator for assessing land condition. Continued monitoring would increase confidence in these findings by capturing more average and above average rainfall years, as wet years may produce different catchment responses. Continued monitoring to increase the dataset would enable statistical analyses of cover, hydrology and water quality interactions.

This study compliments other studies that have reported improved land condition and reduced economic risk by transitioning from heavy to conservative grazing pressures. Studies such as these underpin broader economic analyses that demonstrate long-term financial benefits for graziers who adopt improved management practices. This body of evidence demonstrates that reducing grazing pressure is a realistic economic option for landholders that will also have benefits for runoff water quality.

5.7 References

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Chapter 6 – Tebuthiuron movement via leaching and runoff from grazed Vertisol and Alfisol soils in the Brigalow Belt bioregion of central Queensland, Australia

STATEMENT OF CONTRIBUTION TO CO-AUTHORED PUBLISHED PAPER

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My contribution to the paper involved:

Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Writing, - Original Draft, Writing - Review & Editing.

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6.1 Abstract

Tebuthiuron is one of five priority herbicides identified as a water pollutant entering the Great Barrier Reef. A review of tebuthiuron research in Australia found 13 papers; six of which focused on water quality at the basin scale (>10,000 km^2) with little focus on process understanding. This study examined the movement of tebuthiuron in soil and runoff at the plot (1.7 m^2) and small catchment (12.7 ha) scales. The greatest concentration and mass in soil occurred from 0 to 0.05 m depth 30 to 57 days after application. Concentrations at all depths tended to decrease after 55 to 104 days. Runoff at the small catchment scale contained high concentrations of tebuthiuron (average 103 µg/L) 100 days after application, being 0.05% of the amount applied. Tebuthiuron concentrations in runoff declined over time with the majority of the chemical in the dissolved phase.

6.2 Introduction

In 2009, the Australian and Queensland Governments enacted the Reef Water Quality Protection Plan to reduce the risk of declining water quality entering the Great Barrier Reef (GBR). Five photosystem II (PSII) herbicides are targeted in Reef Plan: ametryn, atrazine, diuron, hexazinone and tebuthiuron (Department of the Premier and Cabinet 2009). The first four are registered for use in sugarcane while tebuthiuron is registered for use in grazing (Lewis *et al.* 2007). Tebuthiuron is a substituted urea herbicide; chemical name N-[5-(1, 1-dimethylethyl)-1,3,4-thiadiazol-2yl]-N,N´ dimethylurea and chemical formula $C_9H_{16}N_4OS$ (United States Environmental Protection Agency 1994). Internationally, tebuthiuron is registered for use in grasslands and grazing systems in South Africa and the United States of America;(United States Environmental Protection Agency 1994; du Toit and Sekwadi 2012) and in sugarcane in Brazil (Cerdeira *et al.* 2007; International Union of Pure and Applied Chemistry 2015). It is not approved or known to be used in European countries (International Union of Pure and Applied Chemistry 2015; European Commission 2016). Granular tebuthiuron has been registered in Australia since the 1980s and is used to control regrowth of

brigalow (*Acacia harpophylla*), tea tree (*Melaleuca spp*.) and other problem woody weeds on grazing lands in Queensland (Dow AgroSciences 2013b; Dow AgroSciences 2013a; King *et al.* 2013).

Tebuthiuron has been detected in GBR flood plumes from the Wet Tropics, Burdekin, Mackay-Whitsunday and Fitzroy catchments. The greatest concentration of tebuthiuron found in flood plumes was 0.014 µg/L from the Fitzroy Basin and 0.006 µg/L from the Burdekin Basin (Kennedy *et al.* 2012b). Kennedy *et al* (2012a) reported tebuthiuron concentrations exceeding the ANZECC trigger value of 0.02 µg/L for 99% ecological protection at sites 3 to 11 km from the mouth of the Burdekin River and up to 240 km from the mouth of the Fitzroy River. Despite regular detections of tebuthiuron in the catchments of the GBR, there is a paucity of information on how this herbicide behaves in soil and water in the Australian environment. A literature review using 'tebuthiuron' and 'Australia' in 2015 found 13 journal papers. Six of these studies focused on freshwater and/or marine water quality at the reef catchment scale (Lewis *et al.* 2011; Kennedy *et al.* 2012a; Kennedy *et al.* 2012b; Kroon *et al.* 2012; Lewis *et al.* 2012; Smith *et al.* 2012); five studies determined the impacts and toxicity of herbicides to a range of organisms, including plants, fish, algal, coral and seagrass (Lane *et al.* 1997; Jones and Kerswell 2003; van Dam *et al.* 2004; Bengtson Nash *et al.* 2005; Magnusson *et al.* 2010); one study assessed the role of herbicides on sustainability and water quality of forest ecosystems (Neary and Michael 1996); and another study considered the use of chemically reactive barriers for the treatment of runoff and drainage containing herbicides (Craig *et al.* 2015). Some of these studies focus on PSII herbicides as a group rather than quantifying the concentration and effects of tebuthiuron as an individual herbicide. Most of the papers, particularly those relating to water quality, have monitored large areas containing multiple land uses with interpretation of tebuthiuron data from grazing inferred rather than measured directly. Furthermore, the literature review found no Australian data relevant to the movement of tebuthiuron in soil or in runoff from grazed pastures at the small catchment scale. Review of the international literature indicates that

rainfall, and soil organic matter and clay content are linked to tebuthiuron dynamics (Chang and Stritzke 1977; Bovey *et al.* 1978; Scifres 1980). The current lack of data relating to tebuthiuron movements in the Australian grazing landscape, including loss in runoff, is a knowledge gap.

The objective of this study was to better understand the persistence and movement of tebuthiuron in grazing systems in GBR catchments by investigating: (1) the persistence of tebuthiuron in Vertisol and Alfisol soils under natural rainfall conditions; (2) the movement of granular and dry flowable tebuthiuron in runoff both soil types at the plot scale (1.7 m^2) under simulated rainfall conditions; and (3) the movement of granular tebuthiuron in runoff at the small catchment scale (12.7 ha) under natural rainfall conditions.

6.3 Materials and methods

6.3.1 Site description

This research was conducted at the Brigalow Catchment Study (BCS) which is a long-term (50 years) paired calibrated catchment study located in the Dawson sub-catchment of the Fitzroy Basin, central Queensland, Australia (24°48'29"S, 149 ° 47'50"E using the Geodetic Datum Australia(Australian Government - Geoscience Australia 2006)). An overview of the BCS is presented in Cowie *et al.* (2007), rainfall and runoff results are presented in Thornton *et al.* (2007) and Thornton and Yu (2016), agronomic and soil fertility results are presented in Radford *et al.*,(2007) and the deep drainage component of the water balance is presented in Silburn *et al.* (2009) The region has a semi-arid, subtropical climate. Annual average rainfall (October to September) from 1965 to 2014 was 661 mm. Summers are wet with 70% of the annual rainfall falling between October and March, while winter rainfall is low (Thornton *et al.* 2010).

6.3.2 Soil descriptions

The soils of the BCS are predominantly Vertisols and Alfisols with an average slope of 2.5%. In its virgin state the site was vegetated with brigalow scrub vegetation communities (Thornton and Elledge 2013). Tebuthiuron persistence in soil and its movement under simulated rainfall was investigated on two soil types; a Sodic Calciusterts Vertisol (Vertisol) and a Typic Natrustalfs Alfisol (Alfisol). The small catchment area of the natural rainfall study was 58% Vertisols and 42% Alfisols. In their virgin state, the Vertisols had an acid reaction trend with clay content increasing from 36% in the surface soil to 54% at 1.8 m (Northcote 1979). In contrast, the Alfisols had an alkaline reaction trend with clay content of 18% in the surface soil, 31% at 0.2 to 0.3 m, then decreasing with depth (Northcote 1979). The physio-chemical characteristics of the Vertisols and Alfisols at this site are given in Table 6.1.

Table 6.1. Average physio-chemical values for a Vertisol and Alfisol in their virgin state (after Cowie *et al.* (2007)).

depth (m)	pH	EC[a] (dS/m)	Cl[b] (µg/g)	OC[c] (%)	P[d] ($NaHCO_3$) (µg/g)	NO_3-N[e] (KCL) (µg/g)	TKN[f] (%)	TP[g] (%)	TK[g] (%)	TS[g] (%)	CEC (cmol/kg)	exchangable Ca^{++}	Mg^{++}	Na^{+}	K^{+} (cmol/kg)	clay (%)
							Vertisol soil									
0.0-0.1	6.56	0.16	75	1.58	12	2.7	0.16	0.03	0.15	0.03	34	12	11.1	1.4	0.4	36
0.1-0.2	7.54	0.48	450	0.95	8	1.2	0.11	0.04	0.15	0.02	36	12	14.6	3.2	0.2	40
0.2-0.3	8.14	0.68	730	0.52	4	0.5	0.06	0.02	0.14	0.02	35	10.0	15.4	4.1	0.2	44
0.5-0.6	5.70	0.77	1040	-	3	0.2	-	0.01	0.14	0.01	32	5.9	14.6	4.6	0.2	45
0.8-0.9	4.76	0.83	1145	-	1	0.2	-	0.01	0.14	0.01	32	4.1	13.7	4.9	0.1	46
1.1-1.2	4.64	0.83	1170	-	1	0.2	-	0.01	0.14	0	34	3.4	13.4	5.4	0.1	46
1.4-1.5	4.52	0.92	1320	-	2	0.1	-	0.01	0.14	0	38	3.4	15.0	6.6	0.2	50
1.7-1.8	4.48	0.98	1385	-	2	0.1	-	0.01	0.15	0	39	3.3	15.7	6.9	0.3	54
							Alfisol soil									
0.0-0.1	6.80	0.10	20	2.09	8	4	0.18	0.03	1.05	0.02	21	9.5	4.1	0.3	0.5	18
0.1-0.2	7.16	0.17	130	0.73	4	1.1	0.08	0.02	0.84	0.01	25	6.4	9.2	2.3	0.2	31
0.2-0.3	7.52	0.22	220	0.58	3	0.5	0.06	0.01	0.88	0.01	23	5.6	9.3	2.9	0.1	28
0.5-0.6	8.83	0.40	400	-	-	0.2	-	-	-	-	24	6.3	9.9	4.7	0.2	-
0.8-0.9	9.20	0.47	470	-	-	0.2	-	-	-	-	16	2.8	6.8	4.1	0.1	-

[a]electrical conductivity, [b]chloride, [c]organic carbon (Walkley and Black), [d]bicarbonate-extractable phosphorus (Colwell), [e]potassium chloride-extractable nitrate-nitrogen, [f]total Kjeldahl nitrogen, [g]total by x-ray fluorescence

6.3.3 Movement in soil under natural rainfall

The vertical movement of tebuthiuron was monitored in a Vertisol and an Alfisol under natural rainfall. On each soil type a row of 1.0 x 1.7 m adjacent unbounded plots was established. Graslan™ (200 g active ingredient (a.i.)/kg) is a tebuthiuron product registered for commercial application in Australia (Dow AgroSciences 2013a); however, as soil concentrations of tebuthiuron decrease with distance from the site where granular pellets are placed, results can be biased by the choice of sampling locations within a plot (Parry and Batterham 1999). To account for this sampling challenge, Spike® 80DF (800 g a.i./kg),(Dow AgroSciences 2013c) a dry flowable formulation of tebuthiuron, was applied to the plots at a rate of 3000 g/ha of a.i. instead of the granular product. Spike® 80DF is not registered for commercial application in Australia; however was approved for experimental use under a small-scale trial permit. Each plot was used for only one sampling interval with no plot sampled twice. Six soil cores were taken randomly from each plot using a hydraulic coring rig. Each core was divided into depth increments of 0 to 0.025 m, 0.025 to 0.05 m, 0.05 to 0.1 m then 0.1 m increments until a maximum of 0.4 m before the cores were combined to make a composite sample for analysis. Tebuthiuron concentration was determined by liquid chromatography mass spectrometry method KEP14D (Queensland Government 2015). In this method, the soil was shaken with acetone using a tabletop shaker for approximately 12 hours. The herbicide was then extracted using a QuEChERS procedure. The final extract was analysed by LC-MS/MS. The limits of detection, quantification and reporting for this method are 0.2 µg/kg, 0.5 µg/kg and 1 µg/kg respectively. Concentration of tebuthiuron in soil was converted into mass per sampling depth using measured soil bulk density. Dissipation of tebuthiuron was represented using a first-order equation (Wauchope *et al.* 1992). Half-lives of tebuthiuron in soil to 0.4 m were calculated by taking the natural log of soil tebuthiuron concentration at each sampling time, fitting a linear regression to the data, and then estimating the half-life by dividing the natural log of 0.5 by the slope of the regression line.

Sampling commenced in October 2011 with soil samples taken at 57, 104, 197 and 314 days after tebuthiuron application. This sampling strategy was chosen based on half-lives of one to two years reported in the literature (Worthing and Walker 1983; Weed Science Society of America 1989; United States Environmental Protection Agency 1994). Sampling was repeated in October 2012 with soil samples taken at 1, 16, 30, 55, and 104 days after tebuthiuron application. More intensive sampling was conducted to obtain data at shorter time intervals, particularly within the first 50 days after tebuthiuron application, to more accurately reflect the half-lives observed in the first sampling.

6.3.4 Movement in runoff at the plot scale under simulated rainfall

Simulated rainfall was used to investigate tebuthiruon concentrations in runoff from a Vertisol and an Alfisol. In October 2011, six plots 1.0 x 1.7 m on each soil type were treated with 3000 g a.i./ha of tebuthiuron; three with granular tebuthiuron (Graslan™) (200 g a.i./kg) and three with dry flowable tebuthiuron (Spike® 80DF) (800 g a.i./kg). Tebuthiuron was applied to the plots immediately before simulated rainfall. Rainfall was then applied to each plot at a target intensity of 80 mm/hr. Once runoff commenced, rainfall continued on the plot for a further 30 minutes, during which timed one litre runoff samples were collected at five minute intervals (0, 5, 10, 15, 20, 25 and 30 min) for the determination of runoff rate. Within each five minute interval, runoff was sampled for a set time to generate one 0.75 L composite flow weighted average sample for the determination of tebuthiuron concentration. Samples of the water used to simulate rainfall were also analysed for tebuthiuron to allow the calculation of a corrected runoff result if necessary.

Details on the rainfall simulation setup are given in Thornton and Elledge (Thornton and Elledge 2013). Each plot was encapsulated by a three-sided sheet metal edge (0.15 m high) placed approximately 0.05 to 0.07 m into the ground to achieve a hydraulic barrier. The short, downslope side of the plot had a separate metal plot end with a trough and spout for collecting runoff; the plot

end was pushed into the ground until the top edge was level with the soil surface. The rainfall simulator used was in an A-frame configuration. Three downward facing oscillating nozzles delivered a flat spray pattern of water across the plot with a fan angle of 80 degrees. A metal shroud positioned below each nozzle limited the lateral and longitudinal spray delivery, and also collected excess water which was returned to the pump delivery unit for recycling. The assembly was adjusted at each plot for adequate magnitude of nozzle sweep and symmetry of sweep relative to the simulator frame. Total runoff was calculated by a linear interpolation of the runoff rate of the seven one litre samples integrated for the duration of the event using Water Quality Analyser v2.1.2.4 (eWater. 2012). Tebuthiuron concentration was determined by liquid chromatography mass spectrometry (LCMS) method QIS 29937 (Queensland Government 2015). In this method an aliquot of water sample is extracted on a solid phase extraction cartridge prior to determination of herbicides by LC-MS/MS. The limits of detection, quantification and reporting for this method are 0.003 µg/kg, 0.01 µg/kg and 0.01 µg/kg respectively. Tebuthiuron loads in runoff were then calculated as follows:

$$\text{Load (g a.i./ha)} = \left[\frac{[\text{Concentration in runoff}(\mu\text{g/L}) * \text{Runoff Volume (L)}] \,/\, 1{,}000}{\text{Plot Length (m)} * \text{Plot Width (m)}}\right] * \; 10{,}000 \,/\, 1{,}000$$

Comparison of tebuthiuron load losses for the two formulations was made for each soil type using analysis of variance in Genstat v14.1 (VSN International 2011). The replicate and residual variances for soil types were then compared, determining that it was appropriate to pool variances; thus, allowing soil types to be compared.

6.3.5 Movement in runoff at the small catchment scale under natural rainfall

Tebuthiuron movement in runoff was investigated at the small catchment scale (12.7 ha) in a buffel grass pasture (*Cenchrus ciliaris* cv. Biloela) under natural rainfall conditions. Pasture cover is

consistently greater than 80%. There had been no control of regrowth vegetation since clearing in 1982. Granular tebuthiuron (Graslan™ Aerial 200 g a.i./kg) was applied by plane on 15 November 2011 by Dow AgroSciences at a rate of 12.5 kg/ha (2.5 kg a.i./ha), reflecting commercial practice (Dow AgroSciences 2013a; Dow AgroSciences 2015). The catchment was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 x 6.1 m concrete approach box. Water height through the flume was recorded using a mechanical float recorder. Rainfall was recorded at the head of the catchment (Thornton *et al.* 2007). A runoff event was defined as the period when water was flowing through the flume. Event based water quality samples were collected by automated samplers between November 2011 and January 2015 with a maximum of 12 samples per an event. Samples were collected every 0.1 m change in absolute flow height. Tebuthiuron concentration was determined by LCMS method QIS 29937 (as for the plot scale analysis) while total suspended solids was determined by gravimetric quantification of solids in water method 18211 (Queensland Government 2015). In this method a well-mixed sample is filtered through a pre-dried and pre-weighed glass fibre filter. The residue on the filter is washed to remove soluble salts and then dried to a constant weight at 105±2°C. The increase in weight represents the total suspended solids. The limit of reporting for this method is 2 mg/L.

Event based tebuthiuron loads and Event Mean Concentration (EMC) for each event are presented. Event loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the loads over all the intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Event based EMC was calculated by dividing total event load by total event flow. Regressions were undertaken using Genstat v14.1 (VSN International 2011).

6.3.6 Comparing tebuthiuron movement from simulated and natural rain studies

In order to explore if the data collected using rainfall simulation is representative of tebuthiuron movement under natural rainfall, the small catchment scale data was combined with the plot scale rainfall simulation data for analysis. The EMC of each plot from the rainfall simulation trial was treated as a separate "event". Additionally, data from related plot scale rainfall simulation studies described by Cowie *et al*. (2013) in the Wet Tropics, Burdekin, Fitzroy and Burnett-Mary basins were included, with average tebuthiuron concentration in runoff calculated for each of the study sites, irrespective of tebuthiuron formulation or plot treatments. A time series of data from the various studies was combined to explore tebuthiuron movement in runoff relative to time after application.

6.4 Results

6.4.1 Movement in soil under natural rainfall

A total of 174 mm of rain fell during the 104 days of the short sampling interval study, with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 30 days after application for both soils (Figure 6.1). The greatest concentration from 0.05 m to 0.4 m was measured 104 days after application in the Vertisol and 55 days in the Alfisol (Figure 6.1). The greatest mass of tebuthiuron from 0 to 0.4 m in both soils was also measured on day 30 (Figure 6.2). After 30 days the mass of tebuthiuron from 0 to 0.4 m tended to decline over time in both soils (Figure 6.2).

A total of 710 mm of rain fell during the long sampling interval study, again with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 57 days after application for both soils. Tebuthiuron concentration tended to decline with time and depth in both soils (Figure 6.3). Tebuthiuron mass from 0 to 0.4 m declined over time in

both soils (Figure 6.4). The change in tebuthiuron mass to 0.4 m equated to a half-life of 71 days in the Vertisol and 129 days in the Alfisol.

6.4.2 Movement in runoff at the plot scale under simulated rainfall

While the target intensity of simulated rainfall was 80 mm/hr, actual intensities varied between 59 and 81 mm/hr. When simulated rainfall was applied immediately after tebuthiuron application to Vertisols, 748 g/ha of granular formulation was lost in runoff (25% of applied tebuthiuron); significantly more than the 352 g/ha of dry flowable formulation lost in runoff (12% of applied tebuthiuron) (P <0.05) (Figure 6.5). Average tebuthiuron loss in runoff from Alfisols was 373 g/ha (12.5% of applied tebuthiuron) with no significant difference in runoff loss due to formulation (Figure 6.5). Runoff from Vertisols averaged 123% of runoff from Alfisols while tebuthiuron concentration in runoff was 125%; hence a significant trend for greater tebuthiuron loss from Vertisols compared to Alfisols (P <0.10).

6.4.3 Movement in runoff at the small catchment scale under natural rainfall

Tebuthiuron samples were collected from ten runoff events ranging from 100 to 1170 days after application (Table 6.2). These events accounted for greater than 90% of the runoff events with >1 mm of runoff that occurred in this period with the sampling pattern reflecting the seasonality of rainfall and runoff in this climate. Tebuthiuron EMC declined exponentially with time (Equation 1, R^2 = 0.998, P = <0.001), rainfall (Equation 2, R^2 = 0.999, P = <0.001) and runoff (Equation 3, R^2 = 0.985, P = <0.001) since application.

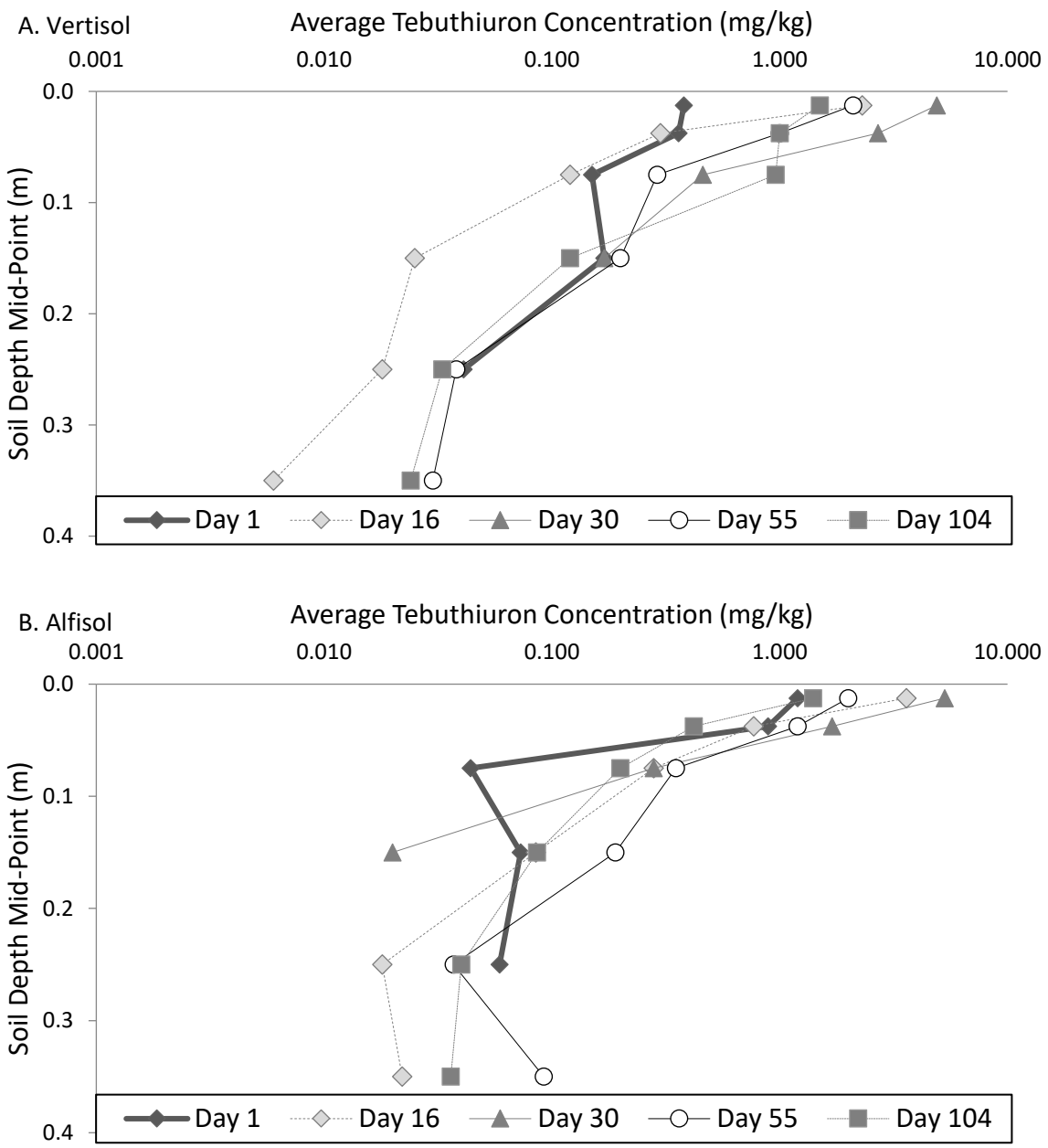

Figure 6.1. Tebuthiuron concentration (mg/kg) in the 0 to 0.4 m profile of Vertisol (A) and Alfisol (B) at 1, 16, 30, 55 and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

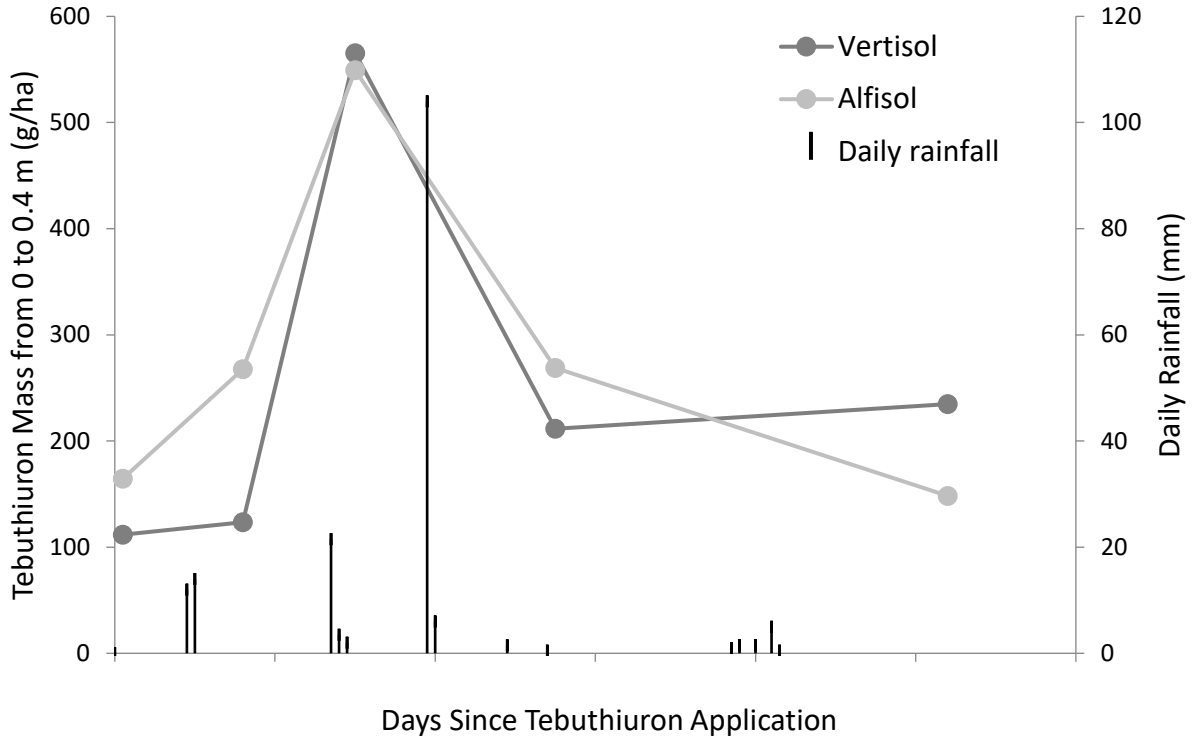

Figure 6.2. Tebuthiuron mass (g/ha) in the 0 to 0.4 m profile of the Vertisol and Alfisol at 1, 16, 30, 55 and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

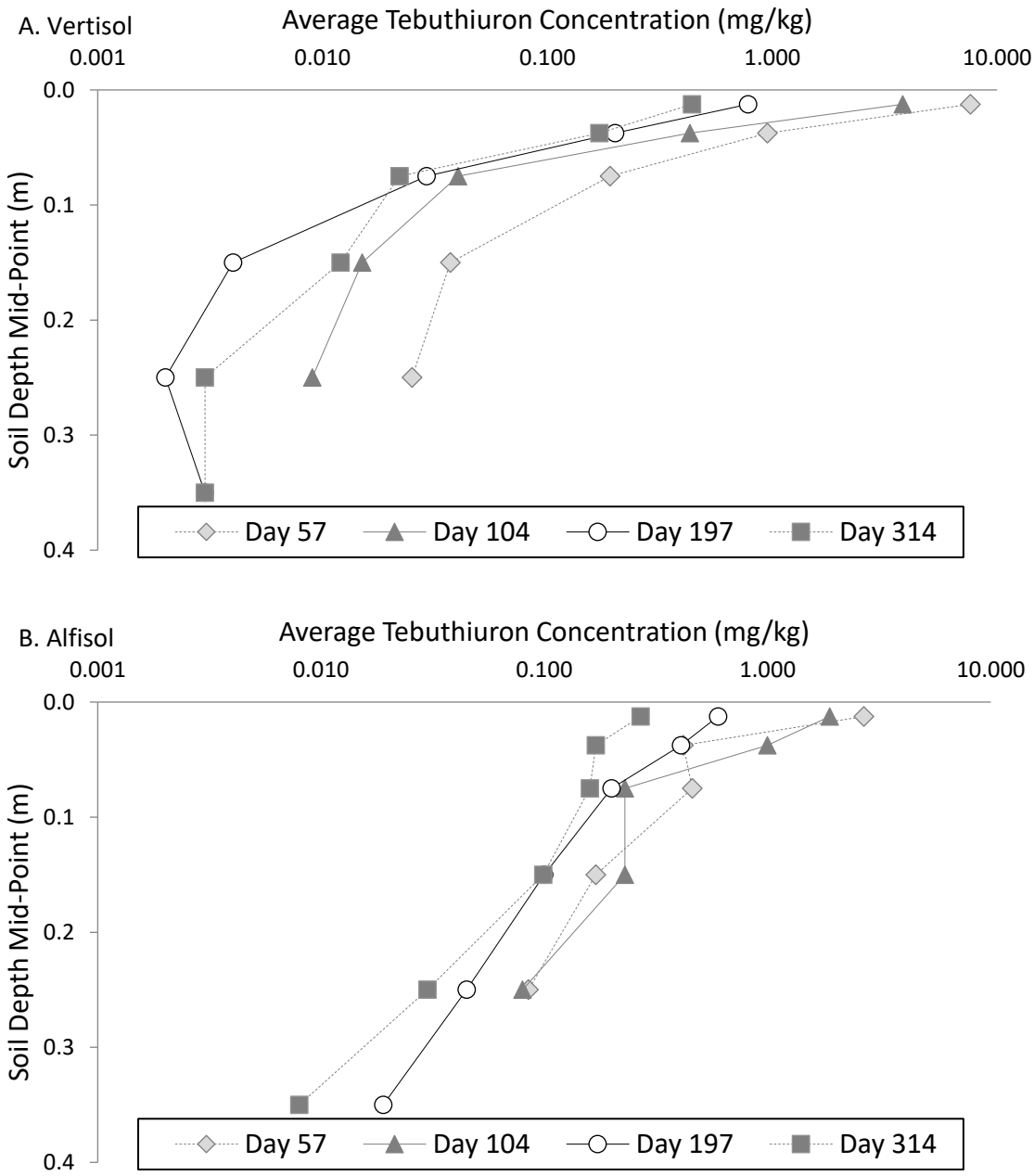

Figure 6.3. Tebuthiuron concentration (mg/kg) in the 0 to 0.4 m profile of Vertisol (A) and Alfisol (B) at 57, 104, 197 and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

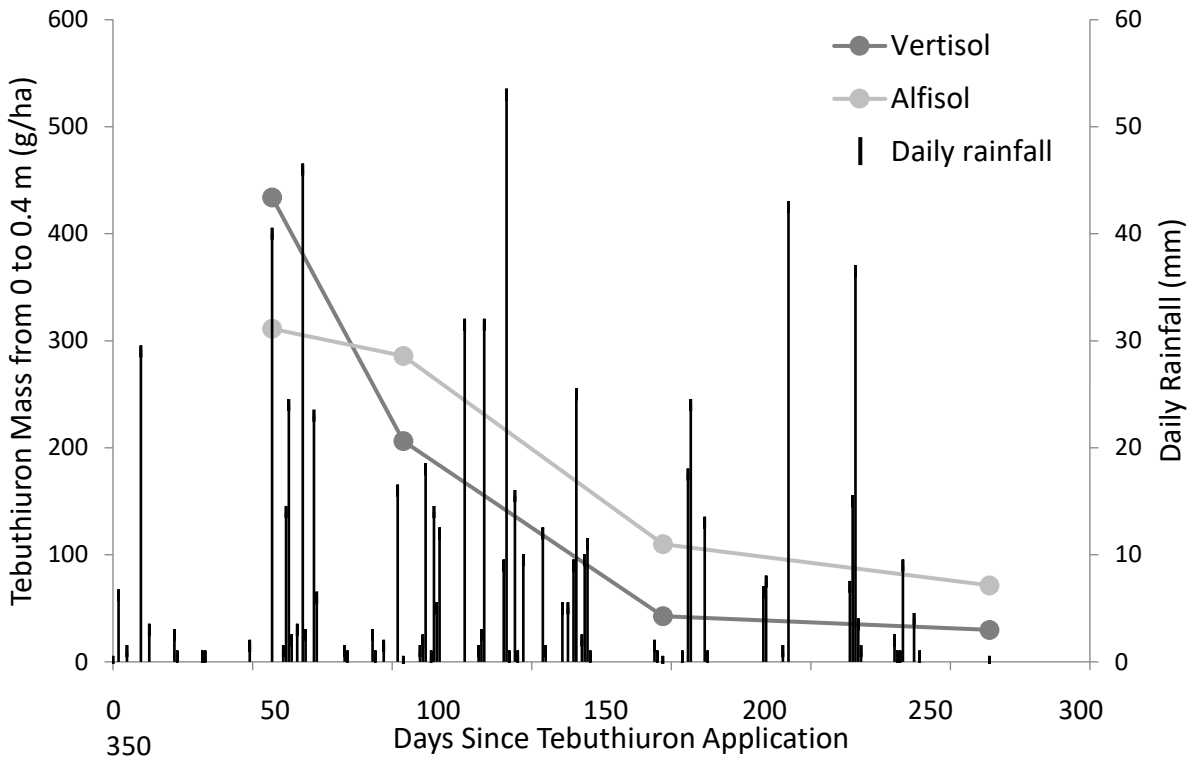

Figure 6.4. Tebuthiuron mass (g/ha) in the 0 to 0.4 m profile of the Vertisol and Alfisol at 57, 104, 197 and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

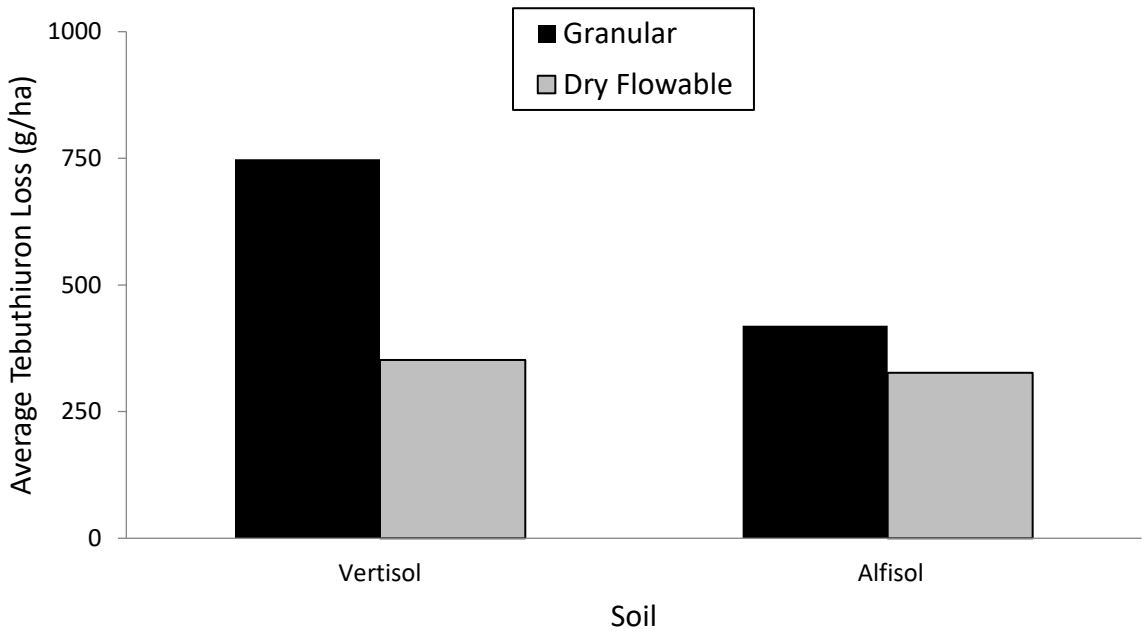

Figure 6.5. Average tebuthiuron loss (g/ha and percentage of tebuthiuron applied) in runoff from Vertisol and Alfisol soils under simulated rainfall conditions immediately after application. Tebuthiuron was applied at a rate of 3,000 g a.i./ha.

Table 6.2. Event based loads and concentrations of tebuthiuron and total suspended solids in runoff at the small catchment scale under natural rainfall conditions. Tebuthiuron was applied on 15 November 2011 at a rate of 12.5 kg/ha (200 g a.i./kg).

runoff event date	days since tebuthiuron application	cumulative rainfall since tebuthiuron application (mm)	total event discharge (mm)	number of samples	tebuthiuron				total suspended solids	
					event load (g/ha)	average sample concentration (µg/L)	event EMC (µg/L)	loss (% of applied)	event load (kg/ha)	event EMC (mg/L)
23/02/12	100	360	1.2	6	1.29	102.6	104.6	0.051	1.3	105.2
26/06/12	224	615	17.0	5	5.39	31.0	31.6	0.215	14.4	84.8
10/11/12	360	829	47.6	11	6.37	13.5	13.4	0.255	71.2	149.6
25/01/13	437	1006	138.1	2	11.30	8.0	8.2	0.450	-	-
01/03/13	472	1239	25.7	11	1.30	6.0	5.2	0.050	57.2	222.7
23/11/13	739	1581	21.1	12	0.67	3.0	3.2	0.027	40.5	191.8
12/12/13	758	1680	10.4	4	0.26	3.0	2.5	0.011	170.8	1640.3
31/03/14	867	1994	0.2	3	0.01	2.8	2.8	0.000	0.5	-
17/12/14	1128	2253	5.0	3	0.08	1.5	1.5	0.003	9.4	-
28/01/15	1170	2426	7.7	3	0.08	1.0	1.0	0.003	7.6	99.5
total	1170	2426	274.1		26.7			1.1	372.9	
average			27.4		2.7	17.3	17.4	0.1	41.4	356.3

$$EMC\ (mg/l) = 2.556 + 265.4 \times 0.99^{x\ (time\ in\ days)} \quad (1)$$

$$EMC\ (mg/l) = 2.482 + 573.3 \times 0.995^{x\ (rainfall\ in\ mm)} \quad (2)$$

$$EMC\ (mg/l) = 4.54 + 109.49 \times 0.289^{x\ (runoff\ in\ mm)} \quad (3)$$

The greatest decline occurred between the first two events; 100 and 224 days after application (Figure 6.6). The concentration of tebuthiuron in individual runoff samples within an event showed little variation thus event EMC was almost identical to the average of the individual sample concentrations. At 1170 days after application, a total of 2426 mm of rainfall and 274 mm of runoff had occurred and a total of 1.07% of the applied tebuthiuron had been exported in runoff (Table 6.2). Tebuthiuron loss during each event was less than 0.45% of the total applied to the catchment. No relationship was detected between tebuthiuron concentration and the total suspended solids concentration of individual runoff samples (P = 0.57) (Figure 6.7).

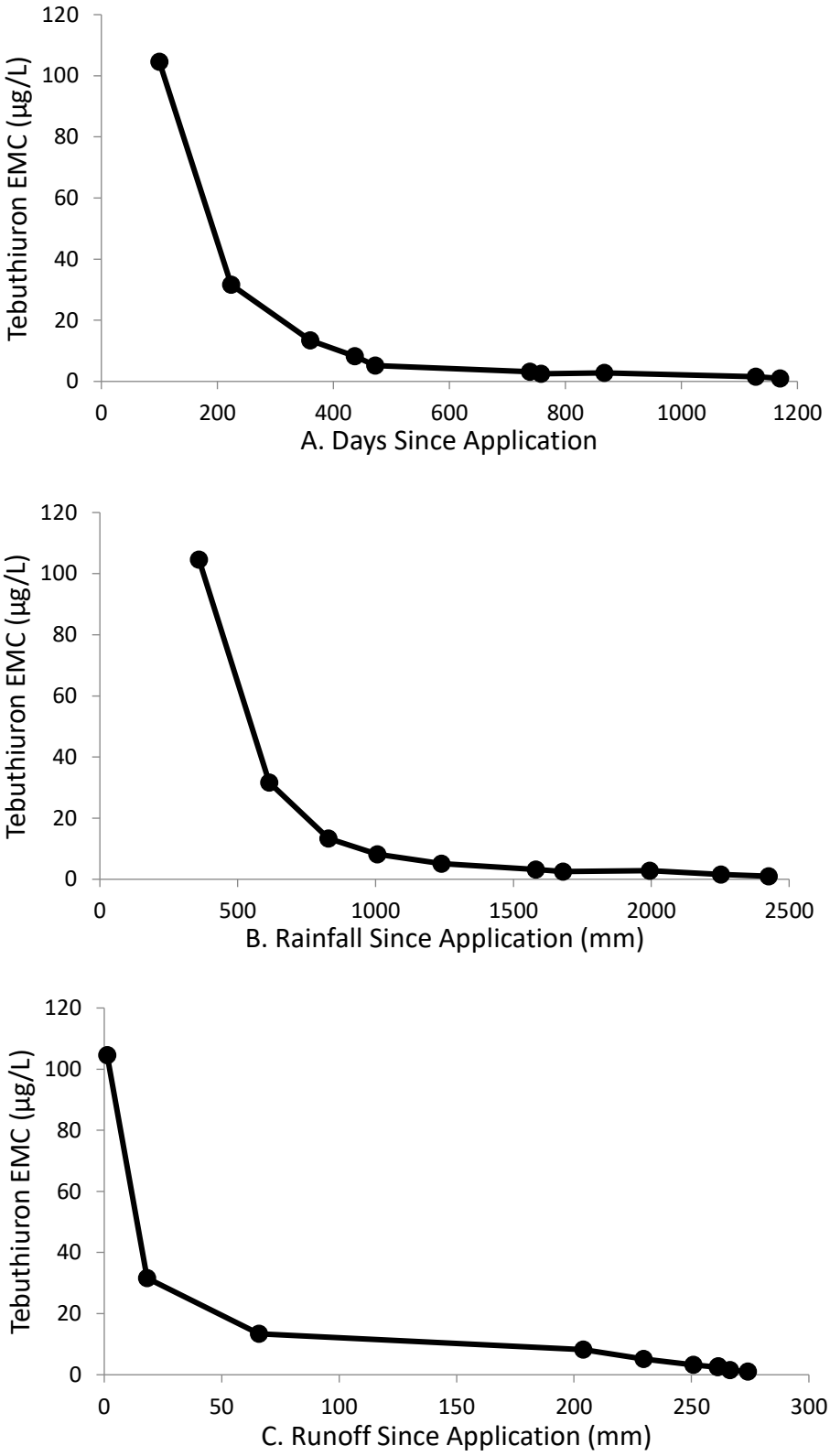

Figure 6.6. Event mean concentration (EMC) of tebuthiuron in runoff at the small catchment scale up to 1170 days (A), 2426 mm of rainfall (B) and 274 mm of runoff (C) following aerial application of 2500 g a.i./ha of tebuthiuron to the soil surface.

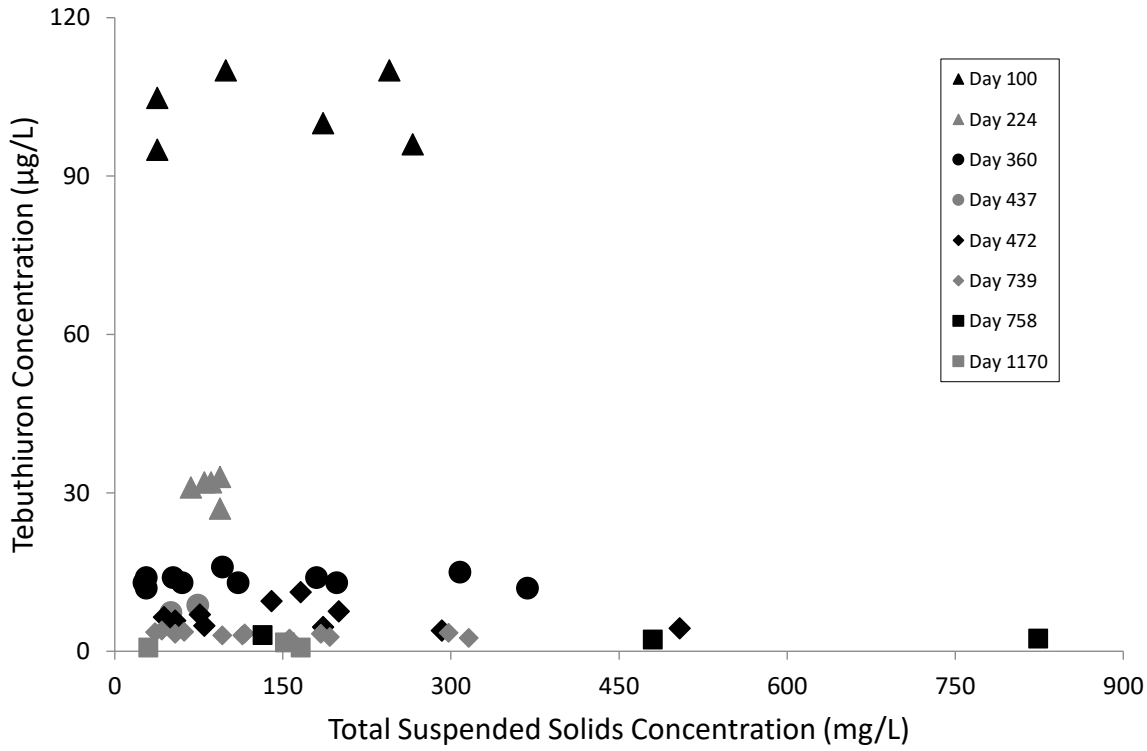

Figure 6.7. A comparison of total suspended sediment and tebuthiuron concentrations in individual runoff samples at the small catchment scale up to 1170 days after aerial application of tebuthiuron to the soil surface.

6.4.4 Comparing tebuthiuron movement from simulated and natural rain studies

The combined data set of tebuthiuron EMCs in runoff from the small catchment scale under natural rainfall (section above) and tebuthiuron EMCs in runoff from thirteen simulated rainfall studies at the plot scale (data presented in "Movement in Runoff at the Plot Scale Under Simulated Rainfall" combined with the data of Cowie *et al.* (2013)) showed an exponential decline over time since application (Equation 4, R^2 = 0.776, P = <0.001), (Figure 6.8). The shortest time between tebuthiuron application and runoff was 5 minutes (the rainfall simulation studies) whilst the longest was 1170 days (the small catchment scale study). However, the relationship developed at the small catchment scale substantially underestimated EMCs from the combined data set prior to 30 days after application. When the time series of data was limited to events occurring >30 days after tebuthiuron

application a significant exponential decline over time was found (Equation 5, R^2 = 0.916, P = <0.001).

$$EMC\ (mg/l) = 3.08 + 2349 \times 0.9432^{x\ (time\ in\ days)} \quad (4)$$

$$EMC\ (mg/l) = 4.32 + 314.94 \times 0.9849^{x\ (time\ in\ days)} \quad (5)$$

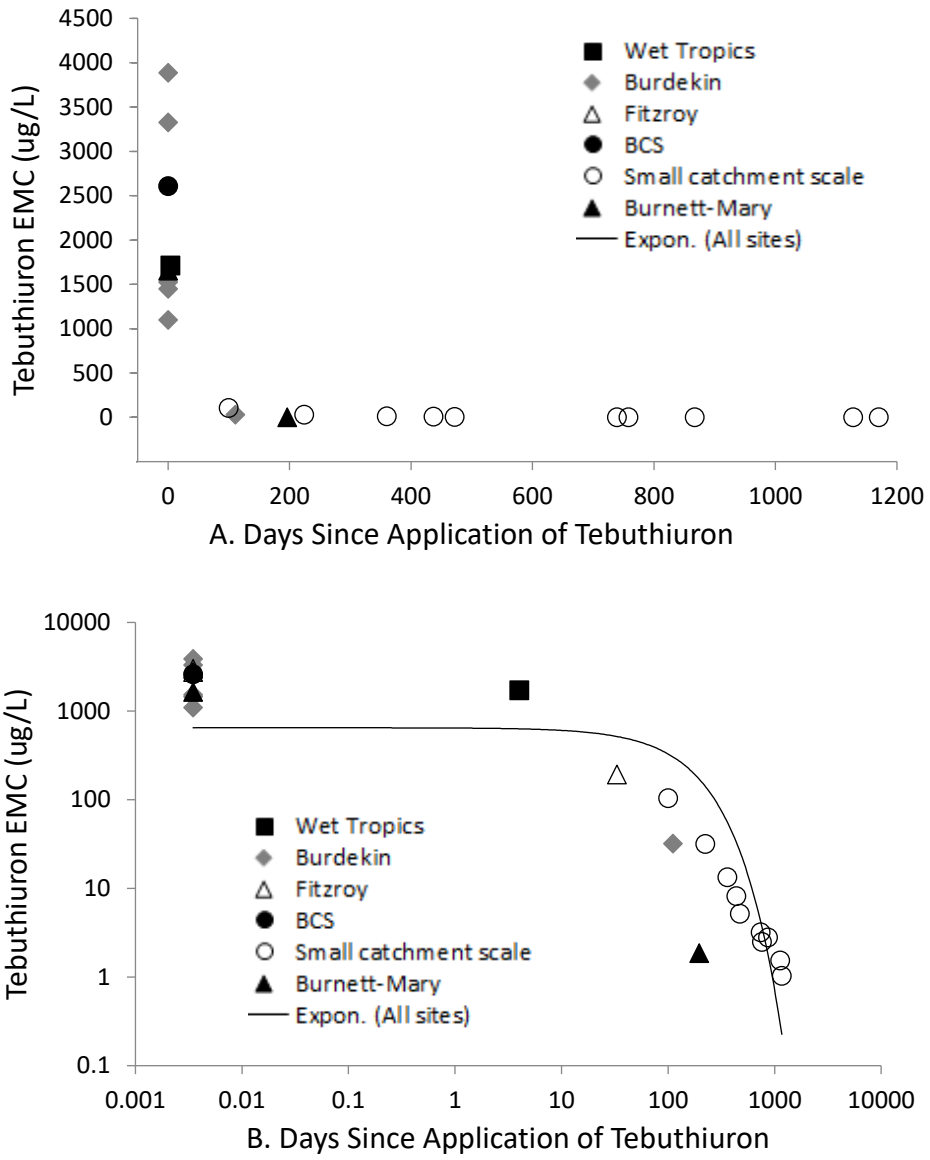

Figure 6.8. Linear (A) and logarithmic (B) plots of tebuthiuron event mean concentration in runoff from the small catchment scale and in runoff from thirteen simulated rainfall studies across five catchments. Note the fitted line is an exponential.

6.5 Discussion

Tebuthiuron was found to be mobile to depths of 0.4 m in both Vertisols and Alfisols. The greatest concentrations and greatest mass of tebuthiuron in both soils was measured 30 to 57 days after application to the soil surface. Movement down the soil profile is consistent with international literature which has reported tebuthiuron at depths of 0.15 to 0.6 m (Bovey *et al.* 1978; United States Environmental Protection Agency 1994; Desouza *et al.* 2001; Cerdeira *et al.* 2007). Movement of tebuthiuron to 1.8 m has been found in soil composed of 92% sand (United States Environmental Protection Agency 1994). Emmerich *et al* (1984) reported that tebuthiuron adsorbed to clay and organic matter in soil and that movement decreased as clay and organic matter content increased. This may explain the movement of tebuthiuron to 1.8 m in soil with an extremely high sand content. In contrast, Matallo *et al.* (2005) noted that tebuthiuron was poorly sorbed to soil; however, similar to the results of Emmerich *et al.* (1984), found less leaching from clayey soil than sandy soil. Given that tebuthiuron is highly soluble in water, its movement to depth in soil is likely a function of soil water holding capacity and hydraulic conductivity; both of which are heavily influenced by clay and organic matter content (United States Environmental Protection Agency 1994; Parry and Batterham 1999; Paterlini and Nogueira 2005). This is supported by the redistribution of tebuthiuron in the soil profile after rainfall which was observed in this study and earlier noted by Parry and Batterham (1999); and by the observation that the pattern of tebuthiuron redistribution differed between the two soils, which have differing clay and organic matter content.

Redistribution of tebuthiuron by rainfall is also likely responsible for two of the tebuthiuron dynamics observed in soil. Firstly, the maximum concentration of tebuthiuron in the soil at 0 to 0.05 m occurring at day 30 rather than at day 1 in the short sampling interval study and secondly for the fluctuating concentrations of tebuthiuron at depth in both studies. These dynamics are attributed to the interception of dry flowable tebuthiuron by plant residues during application and its subsequent

wash-off and hence delayed transport into the soil profile. Herbicide interception by trash and subsequent wash-off into soil is a well-documented process with significant amounts of herbicide able to be intercepted (Selim *et al.* 2003; Aslam *et al.* 2015). It is likely that this behaviour was absent from the long sampling interval study as the wash-off process had already occurred with the 85 mm of rainfall prior to the first sampling. This is supported by the apparent completion of the wash-off process in the short sampling interval study with the 53 mm of rainfall that occurred prior to the maximum soil concentration at 0 to 0.05 m.

Tebuthiuron half-lives in soil from this study were 71 and 129 days. This is considerably shorter than the one-to-two-year half-lives reported in the United States of America, but not as short as the 16 to 20 days found in Brazil (Worthing and Walker 1983; Weed Science Society of America 1989; United States Environmental Protection Agency 1994; Cerdeira *et al.* 2007). The half-lives from this study account for mass change of tebuthiuron in the soil profile irrespective of the change being attributed to breakdown, movement or uptake by vegetation.

Simulated rainfall at the plot scale showed a greater loss of tebuthiuron in runoff from Vertisols compared with Alfisols. This is consistent with the theory that tebuthiuron movement is a function of soil water holding capacity and hydraulic conductivity. Infiltration on Vertisols is expected to be lower than that of Alfisols due to higher clay content, which results in a shorter time to runoff and an increase in runoff volume (Thornton *et al.* 2007; Thornton 2012). A greater proportion of rainfall onto Vertisols interacts with highly soluble tebuthiuron that has not leached deeper into the soil prior to runoff, resulting in greater losses than from Alfisols.

The literature shows that pesticide decay after application generally exhibits a first order decay pattern; however, no reference to the pattern of tebuthiuron decay in runoff over time could be

found in the literature under natural rainfall conditions at the small catchment scale (Cook *et al.* 2013). This study appears to be the first to demonstrate this pattern. A common trend of an exponential decline in tebuthiuron EMC over time when undertaking combined analysis of small catchment scale and simulated rainfall data from this study gives confidence that the data that is obtained using simulated rainfall is reflecting that collected under natural conditions. Silburn and Kennedy(2007) presented the same conclusion when considering the suitability of simulated rainfall for pesticide research. Analysis of other simulated rainfall data from the Wet Tropics, Burdekin, Fitzroy and Burnett-Mary basins with results obtained in this study also gives confidence that the exponential trend of declining tebuthiuron EMC over time is not just site specific, but rather that it is indicative of the behaviour of tebuthiuron in the broader landscape.

It is clear that tebuthiuron concentrations in both soil and runoff are a function of time and rainfall since application; however, as this study did not consider the decay of tebuthiuron in the absence of rainfall it is difficult to separate the effect of each driver. Despite this limitation, the drivers can be inferred from the behaviour of tebuthiuron in soil at the plot scale and in runoff at both the plot and small catchment scale. It is likely that time since application is the greater driver of the exponential decay of tebuthiuron EMC in runoff given that cumulative rainfall tends to be linear. This is supported by the combined analysis of this study with the simulated rainfall studies of Cowie *et al*. (2013), which showed good correlation of EMC with time when runoff occurred greater than 30 days after tebuthiuron application. The first 30 days after application, when EMC in runoff was not well correlated with time since application, corresponds to the timing of peak soil tebuthiuron concentration in the surface layer and the greatest total mass in the profile for both soil sampling regimes. If time since application was the key driver in the first 30 days since application, it would be expected that the mass of tebuthiuron in soil at day 55 would have been similar for both samplings. This was not the case, with greater mass at day 55 in the long sampling interval study for both soils.

Rainfall to day 55 during the long sampling interval study was 85 mm, only 51% of the 165 mm of rainfall to day 55 in the short sampling interval study. This suggests that rainfall rather than time is the main driver of tebuthiuron mass in soil for at least the first eight weeks after application. From day 55 to day 104, rainfall in the long sampling interval study was 143 mm, while rainfall in the short sampling interval study was 9 mm. Despite the marked difference in rainfall totals during this 50-day period, a clearly proportional response in tebuthiuron mass was not found for either sampling. This suggests that rainfall is no longer the key driver of tebuthiuron mass in soil after about 55 days.

There are conflicting opinions on whether tebuthiuron is transported in dissolved phase in water or adsorbed to soil particles which are then lost from the catchment via erosion processes (Parry and Batterham 1999; Brodie *et al.* 2012). The lack of relationship observed between tebuthiuron and total suspended solids in this study indicates that the movement of tebuthiuron in runoff at the small catchment scale is occurring in a dissolved phase. This is consistent with the United States Environmental Protection Agency who state that the principle route of dissipation is mobilisation in water, which includes loss by solubilisation in runoff (United States Environmental Protection Agency 1994). The lack of variability in tebuthiuron concentrations in runoff samples within an event suggests that high frequency sampling may not be necessary to gain an accurate measure of tebuthiuron concentration in runoff.

It has been suggested that 0.5% of water soluble, soil applied herbicides will be lost in runoff (Wauchope 1978). The maximum tebuthiuron loss for an event at the small catchment scale in this study is similar to this figure, being 0.45% and averaging 0.1% of the amount applied. Despite the relatively small losses compared to application amounts, high solubility and low adsorption to soil can result in detectable levels of tebuthiuron downstream (Wauchope 1978). Strategies to minimise the risk of tebuthiuron loss in runoff are already in place under Queensland legislation, which

currently does not permit broad-scale applications between November 1 and March 31 to minimise losses in runoff during the high rainfall months.

Recommendations for tebuthiuron management in grazing lands to minimize water quality impacts should be based on the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ) water quality guidelines (Australian and New Zealand Environmental and Conservation Council and Agriculture and Resource Management Council of Australia 2000). The ANZECC and ARMCANZ freshwater guideline value for tebuthiuron concentrations at which 99% of species are protected is 0.02 µg/L. This value has also been adopted in the Great Barrier Reef Marine Park Authority Water Quality Guidelines for protection of the Great Barrier Reef (Australian and New Zealand Environmental and Conservation Council and Agriculture and Resource Management Council of Australia 2000; Great Barrier Reef Marine Park Authority 2010). However, the trigger value for tebuthiuron is considered to have low reliability. Lewis *at al.* (2012) state that if using the 0.02 µg/L guideline, tebuthiuron use in the Fitzroy Basin would require immediate management action. In contrast, photosystem inhibition data indicate that tebuthiuron is of much lower concern than other PSII herbicides used in the GBR, suggesting that additional toxicity data is required to provide further direction on the management of this herbicide (Lewis *et al.* 2012). This study supports the need for further ecotoxicology data given that tebuthiuron EMC in runoff at the small catchment scale was 5.2 µg/L 472 days after application. This exceeds the current freshwater guideline of 0.02 µg/L by a factor of 260, indicating that 260 ML of receiving water would be required to dilute 1 ML of runoff containing 5.2 µg/L of tebuthiuron to a concentration of 0.02 µg/L (Australian and New Zealand Environmental and Conservation Council and Agriculture and Resource Management Council of Australia 2000).

Recent synthesis of pesticide research in Great Barrier Reef catchments has clearly shown that ecosystems are simultaneously exposed to multiple pesticides with toxicity effects that may be additive, synergistic or antagonistic (Devlin *et al.* 2015). Simultaneous exposure is less applicable in upland catchments where grazing is the predominant, if not the sole, land use and where tebuthiuron is the most commonly used PSII herbicide. However, the risk of simultaneous exposure increases in the downstream transition from upland single land use catchments to multiple land use catchments and the marine environment. The stability of tebuthiuron in saltwater results in long residence times which increases the risk of simultaneous exposure (Mercurio *et al.* 2015).

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Chapter 7 – Conclusion

7.1 Research highlights addressing the key aims of this thesis

Millions of hectares of the heavily cleared Brigalow Belt bioregion drain into the Great Barrier Reef lagoon. The aim of this thesis was to quantify pre-European runoff water quality in the Brigalow Belt bioregion and the changes in water quality when brigalow (*Acacia harpophylla*) scrub was cleared and land developed for cropping or grazing land uses. Specific knowledge gaps in the understanding of runoff water quality from agricultural systems were losses of total suspended solids from grazing systems; dissolved inorganic nitrogen losses from cropping systems; and PSII herbicide losses from both cropping and grazing systems (Waterhouse *et al.* 2012). The importance of this aim was highlighted by the 2017 Scientific Consensus Statement which stated that "key Great Barrier Reef ecosystems continue to be in poor condition. This is largely due to the collective impact of land run-off associated with past and ongoing catchment development, coastal development activities, extreme weather events and climate change impacts" (Waterhouse *et al.* 2017).

Water quality is intrinsically linked to water quantity (Arora *et al.* 2017; Lintern *et al.* 2018). Historically, clearing brigalow scrub for cropping or grazing has doubled runoff and increased runoff rates (Thornton *et al.* 2007; Thornton and Yu 2016). These trends have persisted through the three runoff and water quality studies reported in Chapters 3, 5 and 6. In addition to hydrological change, land clearing and development for cropping or grazing has impacted water quality. Clearing brigalow scrub for cropping or grazing increased loads of total suspended solids, total phosphorus and dissolved inorganic phosphorus in runoff, with the magnitude of increase being greater for cropping than for grazing. Total nitrogen loss in runoff increased under cropping but decreased under grazing. Dissolved inorganic nitrogen loss in runoff was lower from both cropping and grazing than leguminous, nitrogen-fixing brigalow scrub, with losses from grazing an order of magnitude less than that from cropping. These changes in water quality were determined using data collected no less

than 17 years after land clearing and land use change (Chapter 3). During this time, significant nutrient fluxes occurred within the surface 0.1 m of the soil profile associated with clearing, burning and subsequent agricultural production over the next 32 years as shown in Chapter 4. These fluxes, in particular the nine-fold increase in ammonium-nitrogen, the eight-fold increase in nitrate-nitrogen and the two to three-fold increase in bicarbonate- and acid-extractable phosphorus immediately after clearing likely resulted in extremes in water quality loads and pollutant concentrations, exceeding the ranges reported in Chapters 3, 5 and 6.

Land management was also a key driver of change in hydrology and water quality, with land management effects able to exceed land use effects. In addition to the increases in runoff and total suspended solids lost in runoff as a result of land use change from brigalow scrub to grazed pasture, heavy grazing of improved pasture more than tripled runoff and total suspended solids loss compared to conservatively grazed pasture over four years (Chapter 5). The effect of land management on water quality was most easily determined where the input to the system was entirely anthropogenic, such as broadacre applications of herbicide. Unlike nutrients, with no confounding natural input herbicide loss in runoff was entirely contingent on herbicide use. Commercial application rates of tebuthiuron resulted in an average soil half-life of 100 days. Losses in runoff were primarily in the dissolved phase with no correlation to total suspended solids (Chapter 6). As the application of herbicides is wholly anthropogenic, management actions to reduce losses in runoff are easier to derive than for nutrient loss. For example, the risk of tebuthiuron loss in runoff decreases as the time from application to runoff increases, and by decreasing total runoff, rather than by decreasing total suspended solids loss in runoff (Chapter 6).

7.2 Beyond new knowledge: application of this thesis in modelling for the Reef 2050 Water Quality Improvement Plan 2017-2022

While Chapters 3 to 6 present new knowledge of the effects of land clearing, land use change and land management on runoff water quality at the small catchment scale in the Brigalow Belt bioregion, the use of models and modelling frameworks allows this knowledge to be applied at alternative locations both spatially and temporally. This approach was a cornerstone of the Reef 2050 Water Quality Improvement Plan 2017-2022, the overarching source of the key knowledge gaps targeted by this thesis (The State of Queensland 2018). The Reef 2050 Water Quality Improvement Plan 2017-2022 was supported by a robust monitoring and evaluation program known as the Paddock to Reef Integrated Monitoring, Modelling and Reporting program (Paddock to Reef program) (Carroll *et al.* 2012). A key consideration for the Paddock to Reef program was the ability to reflect changes in water quality due to changes in land management practices at the end-of-catchment in the context of a variable climate, and to assess this against targets set over relatively short time frames (Waterhouse 2018). A model framework supported by monitored data that links management action in catchments to water quality and ecological responses to receiving waters was required to report progress in the timeframes of the Reef 2050 Water Quality Improvement Plan 2017-2022 targets. This was fundamental to the Paddock to Reef program (Waterhouse 2018). The model framework ranged in scale from individual paddocks though to entire basins with real-world validation provided by numerous studies (Waterhouse 2018). The Brigalow Catchment Study was one paddock scale study that was used to validate the effects of land management on water quality from the Fitzroy Basin using the new knowledge presented in Chapters 3 to 6.

The contribution of this thesis to the design, calibration and validation of the Paddock to Reef model framework highlights that the data and knowledge are both relevant and accessible. This is best demonstrated on an industry and model basis. Within the framework, runoff water quality from

grain cropping was modelled using HowLeaky (Ghahramani 2021) to estimate sediment, particulate phosphorus, dissolved phosphorus and herbicide losses (Waterhouse 2018). Particulate nitrogen was estimated as a function of hillslope erosion within the Great Barrier Reef Dynamic SedNet (Dynamic SedNet) catchment model built in the eWater Source modelling platform (McCloskey *et al.* 2021b). Dissolved inorganic nitrogen and dissolved organic nitrogen were estimated using nutrient event mean concentrations and hydrology estimates within the Dynamic SedNet catchment model (Waterhouse 2018; McCloskey *et al.* 2021b). Hillslope erosion from grazing was modelled using the Revised Universal Soil Loss Equation within the Dynamic SedNet catchment model. Particulate nitrogen and phosphorus were estimated as a function of hillslope erosion within the Dynamic SedNet catchment model. Dissolved inorganic nitrogen, dissolved organic nitrogen and dissolved phosphorus were estimated using nutrient event mean concentration values and hydrology estimates within the Dynamic SedNet catchment model (Waterhouse 2018; McCloskey *et al.* 2021b; McCloskey *et al.* 2021a).

The Brigalow Catchment Study had a long association with the design, calibration, and validation of the HowLeaky model well before the commencement of this thesis. The HowLeaky model was based on the PERFECT water balance model (Littleboy *et al.* 1989), which was extensively validated at the study site (Lawrence 1990; Lawrence *et al.* 1991; Littleboy *et al.* 1992; Lawrence *et al.* 1993). Study data were also used to calibrate and validate the HowLeaky water balance sub-model and to design, calibrate and validate the phosphorus and pesticide sub-models (Thornton *et al.* 2007; Robinson *et al.* 2011; Shaw *et al.* 2011). Within the Paddock to Reef program, new knowledge presented in Chapter 3 was used to model runoff, erosion, dissolved inorganic nitrogen and atrazine loss from cropping (Ghahramani *et al.* 2020). It has been acknowledged that data from sites such as the Brigalow Catchment Study, and hence the new knowledge presented in Chapters 3 to 6, are critical

to ensure accuracy and credibility not only of HowLeaky, but of all paddock models within the Paddock to Reef program modelling framework (Jakeman *et al.* 2019).

The Brigalow Catchment Study was also used for the calibration and validation of the Dynamic SedNet catchment model both to estimate erosion from grazed hillslopes and to validate remotely sensed ground cover inputs to the model (Dougall and McCloskey 2017). New knowledge presented in Chapters 3 and 5 has been used to calibrate and validate Dynamic SedNet estimates of both erosion and nutrient loss estimations (McCloskey *et al.* 2021b; McCloskey *et al.* 2021a). New knowledge on the behaviour of tebuthiuron presented in Chapter 6 increased understanding of pesticide behaviour in the dry tropical regions of the Great Barrier Reef catchment (Lewis *et al.* 2016). Review of the Australian literature shows that this is still the only study of tebuthiuron loss from the immediate area of application at the catchment scale. Data from Chapters 3, 5 and 6, currently used to validate Dynamic SedNet outputs, facilitate the next iteration of model improvement for the Paddock to Reef program, similar to previous iterative model improvement reported by McCloskey *et al.* (2017b; 2017a). This is in addition to annual validation of modelling outputs against monitoring data, which also utilises the new knowledge presented in Chapters 3 to 6 (Australian and Queensland governments 2020). This continuous improvement approach acknowledges the feedback loop between identified gaps in knowledge required for modelling, and targeted research activities of paddock monitoring studies such as those reported in this thesis (McCloskey *et al.* 2021b; McCloskey *et al.* 2021a). The incorporation of research findings into model improvement highlights the value of the new knowledge presented in Chapters 3 to 6 for reducing model uncertainty, with flow on benefits when the models are used for decision making by government and other catchment managers.

7.3 Beyond new knowledge: application of this thesis in government policy for the Reef 2050 Water Quality Improvement Plan 2017-2022

The accumulation of scientific evidence alone will not ensure the survival of the Great Barrier Reef, or resolve any contemporary environmental issue, unless scientific knowledge is applied in policy and practice (Evans and Cvitanovic 2018). This was recognised by the Reef 2050 Water Quality Improvement Plan 2017-2022, which aimed to apply the best available science and knowledge to support policy, programs and practical on-ground management to improve water quality outcomes (The State of Queensland 2018). The new knowledge presented in Chapters 3, 5 and 6 has contributed to the development of Reef protection regulations, which are government policy designed to address land-based sources of water pollution flowing to the Great Barrier Reef (The State of Queensland 2021a).

Under the Environmental Protection Act 1994, cropping and grazing in specific reef regions are considered environmentally relevant activities (The State of Queensland 2021a). As such, they are subject to regulatory requirements for record keeping and minimum practice agricultural standards, which are termed reef protection regulations. Prior to the consultation regulatory impact statements (Office of the Great Barrier Reef 2017; Office of the Great Barrier Reef 2019), which were released for public consultation in 2017, the new knowledge presented in Chapters 3 and 5 were used by the Queensland Government to assist in the development of the reef protection regulations. In the first instance, this knowledge contributed to the development of the agricultural definitions and the minimum practice agricultural standards for all industries covered under the regulations. The new knowledge presented in Chapters 3 and 5 was also used to develop the minimum practice agricultural standards within specific industries. For example, a written submission containing knowledge from Chapters 3 and 5 was used to guide the regulatory requirements for record keeping and the minimum practice agricultural standards for beef cattle grazing (The State of Queensland

2021c). A written submission containing knowledge from Chapters 3 and 4 was also used to inform the environmentally relevant activity standard, commercial cropping and horticulture in the Great Barrier Reef Catchment (ERA13A) – Version 1, and the draft minimum practice agricultural standards for grains and horticulture (Queensland Government 2021; The State of Queensland 2021b).

The effectiveness of these policy instruments was scrutinised during the 2020 Senate Inquiry into the identification of leading practices in ensuring evidence-based regulation of farm practices that impact water quality outcomes in the Great Barrier Reef (Commonwealth of Australia 2020a). The new knowledge presented in Chapters 3 to 6 that assisted in the development of the reef protection regulations was presented to the Senate Inquiry in both written submissions (Independent Science Panel 2019; Morris 2019) and verbally by witnesses during public hearings (2020b). The tabling of knowledge generated during the completion of this thesis as evidence to a senate inquiry clearly demonstrates that the research has provided a substantial and original contribution to knowledge.

7.4 Recommendations for further research

The limitations of the research presented in this thesis are common to paired catchment studies. This type of study was traditionally limited by the period of record and the climatic sequence experienced during that period, the continuity of monitoring equipment and analytical techniques, and the lack of replication inherent in the experimental design.

The period of record for both the hydrology and water quality data presented in Chapter 3 greatly exceeds that obtained during a typical three-to-five-year project cycle. Both periods contained years with both above and below average rainfall, and as such, the data collected in these periods is considered representative of the study catchments at that time. However, as noted in Chapter 4, the monitoring period for water quality commenced nearly two decades after land clearing and land use

change. As soil nutrient fluxes associated with these perturbations had stabilised prior to the commencement of water quality monitoring, it is likely that measured sediment and nutrient loads in runoff would have been exceeded by losses that occurred soon after land clearing. Extending the analysis presented in Chapter 3 to include unpublished historical water quality data captured closer to the time of land clearing and land use change will assist in validating the assumption of greater sediment and nutrient loads in runoff compared to the monitoring period reported. Limitations to achieving this include the need to determine if the monitoring and analytical techniques used at the time are comparable to the contemporary techniques used in this thesis.

In contrast, the monitoring period for the hydrology and water quality data presented in Chapter 5 covers only four hydrological years, all of which experienced below average annual rainfall, including the lowest annual rainfall since the commencement of the Brigalow Catchment Study in 1965. It may be possible to extrapolate water quality results collected during extended periods of below average rainfall using known hydrological responses of the study site, which show that increased runoff associated with land development can still be detected in flood events (Thornton and Elledge 2012). However, with no data to test the assumption that water quality responses to high flows are similar to hydrological responses, this approach would be purely speculative. Monitoring during average and above average rainfall years is essential to determine if water quality responses to grazing management in wet years follows the trends reported in Chapter 5.

The tebuthiuron dynamics reported in Chapter 6 were investigated during a similarly short monitoring period of four years. However, as tebuthiuron was found to move predominantly in the dissolved phase in response to rainfall and runoff, the typically above average annual rainfall of the monitoring period allowed the collection of meaningful data. As a true replicated experimental design is not possible at the catchment scale, repeating the experiment, including potentially

conducting it in an alternative catchment, would be necessary to improve confidence in the findings or to capture responses to a different application rate, formulation or climatic sequence.

Even with decades of monitoring utilising standardised sampling methods and analytical techniques in a statistically valid experimental design, the understanding of soil fertility change presented in Chapter 4 poses new research questions. For example, the partial nutrient budgets used to determine the primary loss pathways of nutrients would be improved by consideration of fertility change throughout the soil profile rather than just the surface soil. This would yield a more holistic understanding of soil fertility and allow for more accurate parametrisation of both agronomic and water quality models. Revisiting and extending historical long-term data sets, such as those presented in Chapter 4, are likely to provide a more rapid and cost-effective way to generate new knowledge compared to undertaking new studies. Such approaches are already being undertaken to deliver new soil knowledge from existing long-term data sets to improve paddock scale water quality modelling within the Paddock to Reef program (Chamberlain *et al.* 2021).

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Appendix 1

Elledge A, Thornton C (2017) Effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland to a crop or pasture system on sediment, nitrogen and phosphorus in runoff over 25 years in subtropical Australia. *Agriculture, Ecosystems & Environment* **239**, 119-131.

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Effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland to a crop or pasture system on sediment, nitrogen and phosphorus in runoff over 25 years in subtropical Australia

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ABSTRACT

Native vegetation has been extensively cleared for agricultural systems worldwide, resulting in increased pollutant loads that often have adverse impacts downstream. This study uses 25 years of flow data and 10 years of sediment, nitrogen and phosphorus (total and dissolved) event mean concentrations from paired catchments to quantify the effect of changing land use from virgin brigalow (*Acacia harpophylla*) woodland in a semi-arid subtropical region of Australia into an unfertilised crop or conservatively grazed pasture system. Both the cropped and grazed catchments exported higher loads of sediment and phosphorus than the virgin brigalow catchment; however, the grazed catchment exported less total, oxidised and dissolved nitrogen than the virgin brigalow catchment. The cropped catchment exported higher loads of all water quality parameters compared to the grazed catchment. The simple hydrology and water quality model presented was effective for measuring the effect of land use change on runoff water quality. Variations in water quality between the three catchments are likely due to the presence of native legumes, ground cover, tillage practices and pasture rundown.

1. Introduction

Worldwide, the total area of forests in 2010 was estimated to be four billion hectares, or 31% of the total land area (Food and Agriculture Organization of the United Nations, 2010). Deforestation is typically associated with natural causes, such as fire and drought, and change of land use to agriculture. However, rates of net gain and loss vary between country and agro-ecological zones (Food and Agriculture Organization of the United Nations, 2010). For example, in Australia the Fitzroy Basin Land Development Scheme commenced in 1963 resulting in 4.5 Mha of virgin brigalow woodland being cleared for agriculture. This scheme continued through to the 1990s (Department of Lands, 1968; Partridge et al., 1994), with broad-scale clearing in Queensland only ceasing in 2006 (Thornton et al., 2012). In 2009, 74.8% (11.7 Mha) of the Fitzroy Basin was being used for agricultural purposes, with 71.5% grazed and 3.2% cropped (Australian Bureau of Statistics, 2009).

Pollutant loads exported in runoff have increased from natural rates as a consequence of broad-scale clearing of native vegetation and subsequent change of land use to agriculture. For example, Kroon et al. (2012) estimated that since European settlement mean annual loads exported from six catchments along the coast of Queensland, Australia, into the Great Barrier Reef have increased 5.5 times for total suspended sediment (17,000 kt yr^{-1}), 5.7 times for total nitrogen (80,000 t yr^{-1}) and 8.9 times for total phosphorus (16,000 t yr^{-1}). Transport of sediment and nutrients from the landscape into the Great Barrier Reef causes increased eutrophication and turbidity (Brodie et al., 2011; Hansen et al., 2002), which can lead to crown-of-thorns starfish (*Acanthaster planci*) outbreaks and coral mortality (Brodie and Waterhouse, 2012; De'ath et al., 2012). The impact of different agricultural activities on downstream water quality is an issue in common with other parts of Australia and the world (Barlow et al., 2007; Bossa et al., 2012; Brion et al., 2011; Dilshad et al., 1996; Jarvie et al., 2010; Lal, 1996; Singh and Mishra, 2014; Vink et al., 2007).

It is well documented that runoff volume and/or sediment load increase when native forest is cleared for agriculture (Cowie et al., 2007; Hunter and Walton, 2008; Siriwardena et al., 2006; Thornton et al., 2007). Numerous studies have also demonstrated higher runoff volume and/or sediment loads from cropped than grazed areas (Freebairn et al., 2009; Murphy et al., 2013; Stevens et al.,

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2006; Wilson et al., 2014). However, studies that have reported nutrient loads from agricultural systems tend to focus on total loads rather than dissolved loads (O'Reagain et al., 2005; Povilaitis et al., 2014; Stevens et al., 2006; Wilson et al., 2014). Dissolved nutrients pose a great risk to aquatic systems, as they are less likely to settle than nutrients bound to sediment (Silburn et al., 2007). For example, Devlin and Brodie (2005) mapped flood plumes from rivers exporting into the Great Barrier Reef over nine years and found that most suspended solids and associated particulate nutrients were deposited within 10 km of the river mouth while dissolved nutrients were transported with the plume 50–200 km from the river mouth.

Studies that have reported both total and dissolved nutrients are typically at the catchment scale (Joo et al., 2012; Li et al., 2014; Packett et al., 2009), but catchments often have multiple land uses within the monitored area so it is difficult to separate the impacts of each land use on water quality (Bartley et al., 2012; Li et al., 2014; Povilaitis et al., 2014). Bartley et al. (2012) reviewed 755 sediment, nitrogen and phosphorus data points from studies across Australia for use in catchment scale water quality models. They found that a catchment with less than 90% of a specific land use could have its water quality signature influenced by the other land uses, whereas a catchment dominated by a single land use (>90%) was a more appropriate representation of that specific land use. However, using data from sites with more than 90% of the area dominated by a single land use dramatically reduced the number of data points and also biased data towards smaller plot sizes for intensive land uses, such as sugar cane, which rarely cover large areas of a catchment (Bartley et al., 2012). Thus, there is currently a paucity of total and dissolved water quality data from areas greater than plot scale that are dominated by a single land use.

This study investigates the impact of changing land use from a virgin brigalow woodland into a crop or pasture system on runoff water quality. It models data based on a 17 year calibration period of three catchments in their virgin condition before changing the land use of two catchments to agriculture, and subsequent monitoring of all three catchments to collect 25 years flow and 10 years water quality data. The model presented uses long-term event mean concentrations (EMCs) with a regression based flow model described by Thornton et al. (2007). This research is unique as it: 1) reports on total and dissolved nitrogen and phosphorus in addition to sediment; and 2) compares both cropped and grazed catchments with a virgin woodland control catchment. This study improves understanding on the impact of agriculture on runoff water quality relative to the pre-European landscape and provides a comparison of water quality from crop and pasture systems.

2. Methods

2.1. Site description

The Brigalow Catchment Study (24°48′S and 149°47′E) is a paired, calibrated catchment study located near Theodore in central Queensland, Australia (Fig. 1). It was established in 1965 to quantify the impact of land development for agriculture on hydrology, productivity and resource condition (Cowie et al., 2007). The study site was selected to represent the Brigalow Belt Bioregion which covers an area approximately 36.7 Mha from Townsville in north Queensland to Dubbo in central-western New South Wales (Thornton et al., 2007). The site in its native state was dominated by brigalow (*Acacia harpophylla*) trees, either in a monoculture or in association with other species, such as belah (*Casuarina cristata*) and Dawson River blackbutt (*Eucalyptus cambageana*) (Johnson, 2004). The extant uncleared vegetation at the Brigalow Catchment Study is classified as regional ecosystems 11.4.8, woodland to open forest dominated by *Eucalyptus cambageana* and *Acacia harpophylla*, and 11.4.9, open forest and occasionally woodland dominated by *Acacia harpophylla* (Queensland Government, 2014). Slope of the land averages 2.5% (range from 1.8 to 3.5%) and soils are an association of black and grey Vertosols, black and grey Dermosols, and black and brown Sodosols. Vertosols and Dermosols (clay soils) cover approximately 70% of Catchments 1 and 2, and 58% of Catchment 3; Sodosols cover the remaining area (Cowie et al., 2007). These soil types are representative of 67% of the Fitzroy Basin under grazing: 28% Vertosols, 28% Sodosols and 11.3% Dermosols (Roots, 2016). The region has a semi-arid, subtropical climate and mean annual hydrological year (October 1965 to September 2014) rainfall at the site was 661 mm.

2.2. Calibration and development of catchments

Three contiguous catchments were monitored for rainfall and runoff from 1965 to 1982 (17 years). Each catchment was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 × 6.1 m concrete approach box. Water heights through the flumes were recorded using mechanical float recorders and converted to discharge using a rating table. Rainfall was recorded adjacent to each flume and at the top of the catchments using a tipping bucket rain gauge (Thornton et al., 2007). A runoff event was defined as commencing when stage height exceeded zero and finished when it returned to zero. These data were used to derive mathematical relationships to predict runoff from Catchment 2 (C2) and Catchment 3 (C3) given known runoff from Catchment 1 (C1) (Thornton et al., 2007). During this period, it was found that C2 and C3 in their uncleared state had 95% and 72% of the runoff from C1, respectively. Each catchment had its own intrinsic hydrological signature; for example, C3 had more runoff events but less total runoff volume on an annual basis compared to C1 and C2. Nonetheless, approximately 5% of the mean annual rainfall become runoff in all three catchments (Thornton et al., 2007).

Land development occurred between 1982 and 1983; that is, C1 remained virgin brigalow woodland to provide an uncleared control treatment, while C2 and C3 were cleared using a chain dragged between two dozers and the fallen timber burnt in-situ (Cowie et al., 2007). C2 was then developed for cropping with the construction of contour banks and grassed waterways, while C3 was developed for grazing by the planting of improved buffel grass pasture (Fig. 2).

2.3. Land use comparisons

Rainfall and runoff were monitored from the virgin brigalow woodland (C1), cropped (C2) and grazed (C3) catchments from 1984 until 2010 (Thornton and Elledge, 2013). This equates to 25 full hydrological years (October to September) monitoring and two incomplete hydrological years; July 1984 to September 1984, and October 2009 to January 2010. Over the 25 years, C2 had one sorghum crop followed by nine monoculture wheat crops, and then was opportunity cropped with sorghum (*Sorghum bicolor*), wheat (*Triticum* spp.), barley (*Hordeum vulgare*) or chick peas (*Cicer arietinum*). Zero or reduced till fallows were introduced in 1990. There were no fertiliser inputs in the cropped catchment (Radford et al., 2007). C3 was grazed at industry recommended stocking rates with utilisation to result in no less than 1000 kg ha^{-1} of pasture available at any time. Conservative management of this catchment has resulted in groundcover averaging 91% since 2000 (earlier data not available), which is greater than paddocks of the same land type within a 50 km radius which averaged only 74% (Fitzroy Basin Association, 2016). The foliage projective cover of tree regrowth in C3 has remained below 15% (Department of Science, Information Technology and Innovation, 2016). There was

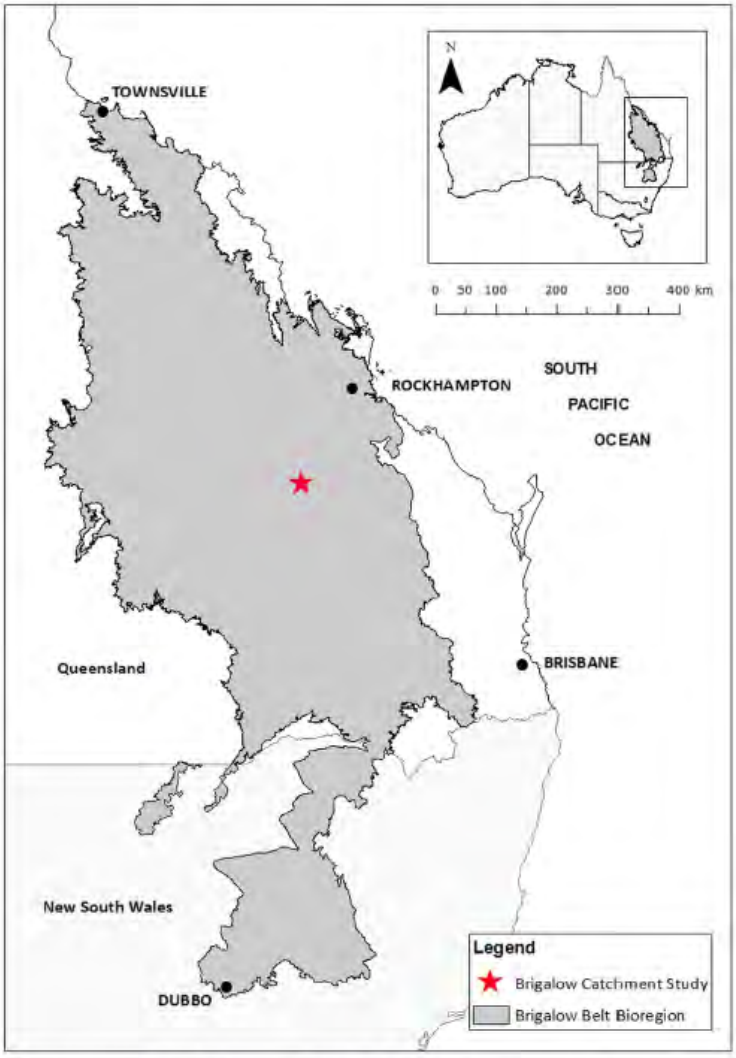

Fig. 1. Location of the Brigalow Catchment Study within the Brigalow Belt Bioregion of central Queensland, Australia.

no fertiliser inputs or supplement feeding in the pasture catchment (Radford et al., 2007).

Discrete water quality samples were obtained using auto-samplers from 2000 to 2010. Auto-samplers were programmed to sample every 0.1 m change in absolute stage height. Runoff samples were analysed for seven parameters by Queensland Health Forensic and Scientific Services (https://www.health.qld.gov.au/qhcss/qhss/) (Table 1).

Event based water quality loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the loads over all the intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Where samples were only collected on the rising limb of the hydrograph, the event peak was considered to be the end of the sampling interval for the last discrete sample, and the mean concentration of the discrete samples was applied to flow from the event peak to the event end. Event based EMCs were calculated by dividing total event load by total event flow.

Mean annual EMC was calculated by averaging the event based EMCs. These values were then averaged to determine the long-term EMC for each catchment. Where missing flow data occurred, estimations were obtained using the "HowLeaky?" modelling approach of Thornton et al. (2007). Where missing water quality data occurred, estimations were obtained by multiplying the long-

Fig. 2. Aerial photo of the three catchments monitored at the Brigalow Catchment Study following land use change of two catchments from virgin brigalow woodland to crop and pasture systems.

term EMC by the observed flow. Mean annual load was calculated by dividing the cumulative observed load for each catchment by the number of full hydrological years monitoring data (n = 25). The effect of changing land use from virgin brigalow woodland to crop or pasture systems on sediment, nitrogen and phosphorus loads (kg ha^{-1}) on an event basis were calculated by: (Table 2)

$$\left(\frac{(Q_{Obs} \times EMC_{Current}) - (Q_{Est} \times EMC_{Brigalow})}{1,000,000}\right) \div Area$$

Observed load was calculated by multiplying the observed event flow from 1984 to 2010 by the long-term EMC (2000 to 2010) for the respective catchment. Predicted load was calculated by multiplying the estimated flow of C2 and C3 had they remained virgin brigalow woodland (using the relationship of flow between the catchments during the calibration phase from 1965 to 1982; for example, C2 in an uncleared state had 95% of the runoff from C1) by the EMC for the virgin brigalow catchment. Mean annual land use change effect was calculated by dividing the cumulative difference in observed and predicted loads by the number of full hydrological years of monitoring data (n = 25). The assumptions of this approach are that water quality from the three catchments in their virgin state would have been similar, and that the long-term EMC values for C1 apply to all catchments had they remained virgin brigalow woodland.

3. Results

3.1. Hydrology

Total annual rainfall exceeded the long-term mean annual rainfall of 661 mm for the Brigalow Catchment Study in 10 out of the 25 full hydrological years monitored (Fig. 3). Observed mean annual runoff from the cropped and grazed catchments were 2.48 times (65.8 mm) and 1.97 times (52.2 mm) greater than observed runoff from the virgin brigalow woodland (26.5 mm), respectively. Similarly, observed runoff from the cropped catchment was 2.60 times greater than predicted runoff from this catchment had it remained uncleared (25.3 mm), and observed runoff from the

Table 1
Methods used by Queensland Health Forensic and Scientific Services for sediment, nitrogen and phosphorus analyses of water samples.

Parameter	Method
Total Suspended Solids	Method 18211 based on gravimetric quantification of solids in water.
Total Nitrogen	Method 13802 by simultaneous persulfate digestion. For the period 2000 to 2003, method 13804 based on simultaneous Kjeldahl digestion was reported and total nitrogen was manually calculated as total Kjeldahl nitrogen + oxidised nitrogen.
Oxidised Nitrogen	Method 13798 based on flow injection analysis of nitrogen as oxides.
Ammonium Nitrogen	Method 13796 based on flow injection analysis of nitrogen as ammonia.
Dissolved Inorganic Nitrogen	Manually calculated as oxidised nitrogen + ammonium nitrogen.
Total Phosphorus	Method 13800 by simultaneous persulfate or Kjeldahl digestion.
Dissolved Inorganic Phosphorus	Method 13799 by flow injection analysis; also known as orthophosphate.

Table 2
Model parameters were defined as follows.

Parameter		Description
Q_{Obs}	=	Observed discharge from the catchment under current land use (L event^{-1})
$EMC_{Current}$	=	Observed long-term event mean concentration from the catchment under current land use (mg L^{-1})
Q_{Est}	=	Estimated discharge from the catchment had it remained virgin brigalow woodland (L event^{-1}) (Thornton et al., 2007)
$EMC_{Brigalow}$	=	Observed long-term event mean concentration from the virgin brigalow catchment (mg L^{-1})
Area	=	Catchment area (ha)

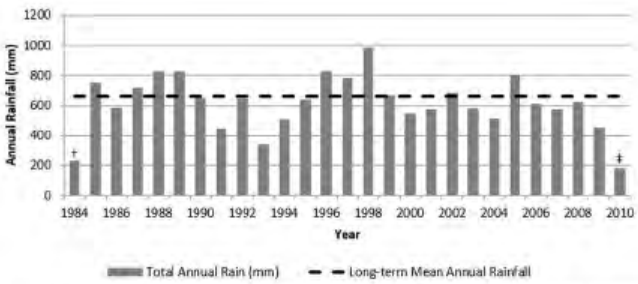

Fig. 3. Total annual hydrological year rainfall (mm) for 1984 to 2010 relative to the long-term mean annual rainfall for the Brigalow Catchment Study. † Total rainfall only from 25/07/1984, as this relates to the first runoff event recorded at the Brigalow Catchment Study following land development. ‡ Total rainfall only to 19/01/2015, as event data after this date was excluded from the presented model due to a change in management practices.

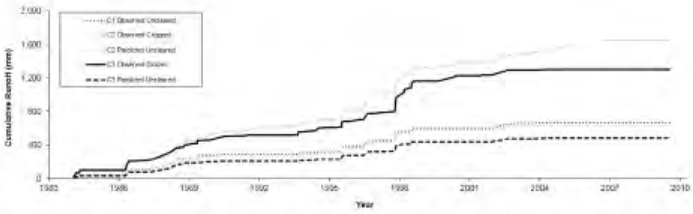

Fig. 4. Cumulative runoff (mm) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted runoff for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

grazed catchment was 2.74 times greater than predicted runoff from this catchment had it remained uncleared (19.0 mm). The rate of increase in cumulative runoff was greater in years with above average rainfall, particularly from 1987 to 1989 and 1996 to 1999 (Fig. 4). Over the 25 year period, the virgin brigalow catchment discharged a total of 663 mm runoff over 45 days, the cropped catchment discharged a total of 1647 mm runoff over 99 days, and the grazed catchment discharged a total of 1304 mm runoff over 80 days.

Table 3
Long-term event mean concentrations (mg L^{-1}) of sediment, nitrogen and phosphorus for the virgin brigalow woodland, cropped and grazed pasture catchments over 10 years (2000–2010).

Parameter	Event Mean Concentration (mg L^{-1})		
	Woodland (C1)	Crop (C2)	Pasture (C3)
Total Suspended Solids	307	798	229
Total Nitrogen	9.85	5.37	2.17
Oxidised Nitrogen	6.27	2.17	0.07
Ammonium Nitrogen	0.06	0.11	0.04
Dissolved Inorganic Nitrogen	6.32	2.27	0.11
Total Phosphorus	0.32	0.93	0.41
Dissolved Inorganic Phosphorus	0.12	0.35	0.22

3.2. Event mean concentrations

Long-term EMCs for the three monitored catchments from 2000 to 2010 are presented in Table 3. Concentrations of total, oxidised and dissolved inorganic nitrogen from virgin brigalow woodland were 1.83, 2.89 and 2.78 times greater than concentrations from the cropped catchment and 4.53, 95.10 and 59.89 times greater than concentrations from the grazed catchment, respectively. In contrast, concentrations of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen from the cropped catchment were 2.60, 2.90, 3.00 and 1.73 times greater than concentrations from the virgin brigalow catchment and 3.49, 2.26, 1.57 and 2.67 times greater than concentrations from the grazed catchment, respectively.

Overall, the proportion of dissolved inorganic phosphorus that comprised total phosphorus was 37% from the virgin brigalow catchment, 38% from the cropped catchment and 55% from the grazed catchment. The proportion of ammonium nitrogen that comprised dissolved inorganic nitrogen was 1% from the virgin brigalow catchment, 5% from the cropped catchment and 38% from the grazed catchment.

3.3. Sediment, nitrogen and phosphorus loads

Cumulative loads of sediment, nitrogen and phosphorus are presented in Figs. 5–11. Similar to runoff, the rate of increase in cumulative loads was greater in years with above average rainfall, particularly from 1987 to 1989 and 1996 to 1999.

The cropped catchment exported more sediment and nutrients (total and dissolved) than the grazed catchment over the 25 year period (Table 4). Changing land use from virgin brigalow woodland to either agricultural system increased loads of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen; the cropped catchment exported 6.45, 7.21, 7.45 and 4.29 times greater loads and the pasture catchment exported 1.46, 2.53, 3.75 and 1.27 times greater loads, respectively. In contrast, loads of oxidised and dissolved inorganic nitrogen were higher from virgin brigalow woodland than both agricultural systems; 1.16 and 1.12 times greater than loads from the cropped catchment and 48.34 and 30.44 times greater than loads from the grazed catchment, respectively. The virgin brigalow and cropped catchments exported 2.30 and 3.12 times greater total nitrogen than the pasture catchment, respectively.

Observed mean annual loads of total suspended solids, total phosphorus and dissolved inorganic phosphorus from the cropped catchment were 6.88, 7.70 and 7.95 times greater, respectively, than predictions from this catchment had it remained uncleared (Table 4). Total and ammonium nitrogen were also 1.42 and 4.57 times greater than uncleared predictions, whereas uncleared predictions of oxidised and dissolved inorganic nitrogen were conversely 1.09 and 1.05 times greater than the observed means from this catchment under cropping, respectively. Observed mean annual loads of total suspended solids, total and dissolved inorganic phosphorus, and ammonium nitrogen from the grazed catchment were 1.80, 3.11, 4.61 and 1.56 times greater, respectively, than predictions from this catchment had it remained uncleared (Table 4). In contrast, uncleared predictions of total, oxidised and dissolved inorganic nitrogen were 1.65, 39.36 and 24.79 times greater than the observed means from this catchment under grazing, respectively.

3.4. Effect of land use change on water quality

Over the 25 year period, the mean annual effect of changing land use from virgin brigalow woodland to crop or pasture resulted in 449 kg ha^{-1} yr^{-1} and 53 kg ha^{-1} yr^{-1} more total suspended solids in runoff, respectively (Table 5). Similarly, more total phosphorus, dissolved inorganic phosphorus and ammonium nitrogen were exported from crop and pasture systems than virgin brigalow woodland. Crops exported total nitrogen at an average rate of 1.04 kg ha^{-1} yr^{-1} more than if the catchment had remained uncleared, whereas pasture exported 0.74 kg ha^{-1} yr^{-1} less than if the catchment had remained uncleared. Although the cropped catchment exported more total nitrogen than its uncleared predictions, less oxidised and dissolved inorganic nitrogen were exported.

4. Discussion

4.1. Event mean concentrations

The simple hydrology and water quality model presented was effective at quantifying the effect of changing land use from virgin brigalow woodland to crop and pasture systems; however, it is likely that the results are an underestimate of the true change. Although 25 years (1984–2010) of flow data was available for these three catchments, comprehensive water quality data had only been collected for the last 10 years of this period (2000–2010). If sediment and nutrient EMCs from the agricultural catchments immediately after land use change were higher to that observed later in the study, the model would underestimate change. For example, wildfires in natural areas have been reported to increase sediment, nitrogen and phosphorus losses in runoff which typically remain high for about a year or until the soil stabilises and vegetation establishes (Ice et al., 2004; Smith et al., 2011; Stein et al., 2012). Historical cover data for the two agricultural catchments in this study indicate that plant cover was established by December 1983; C2 had 53% cover in June and 95% cover before the first crop was harvested in December, whereas C3 had 6.5% pasture cover in June and 96% cover by December. However, it is possible that the earlier runoff events may have had elevated sediment and nutrients in runoff as a residual impact of clearing and burning the catchments despite established cover.

Nonetheless, this study provides a rigorous estimate of sediment, nitrogen and phosphorus (total and dissolved) loads exported in runoff from these three catchments over 25 years. Bartley et al. (2012) reviewed sediment and nutrient concentration data from Australia suitable for catchment water quality models. Where upstream land use was dominated by more than 90% modified grazed pasture, they reported concentrations of 322 mg L^{-1} (10th and 90th percentiles 39 and 390 mg L^{-1}; n = 9 sites) for total suspended solids, 3.04 mg L^{-1} (10th and 90th 1.65 and 4.92 mg L^{-1}; n = 9 sites) for total nitrogen, and 0.73 mg L^{-1} (10th and 90th percentiles 0.17 and 2.17 mg L^{-1}; n = 17 sites) for total phosphorus. EMCs from the grazed catchment in this study for total suspended solids (229 mg L^{-1}), total nitrogen (2.17 mg L^{-1}) and total phosphorus (0.41 mg L^{-1}) are within the range of values reported by Bartley et al. (2012).

There were no dryland crop sites in the review by Bartley et al. (2012) that were dominated (> 90%) by a single upstream land use. However, plot and catchment scale data for sites with dryland crops as the main land use reported concentrations of 2501 mg L^{-1} (10th and 90th percentiles 162 and 5339 mg L^{-1}; n = 21 sites) for total suspended solids, 1.99 mg L^{-1} (10th and 90th 0.71 and 3.38 mg L^{-1}; n = 17 sites) for total nitrogen, and 0.85 mg L^{-1} (10th and 90th 0.096 and 1.65 mg L^{-1}; n = 17 sites) for total phosphorus (Bartley et al., 2012). As for the grazed catchment, EMCs from the cropped catchment in this study were within the range of values reported by Bartley et al. (2012) for total suspended solids (798 mg L^{-1}) and total phosphorus (0.93 mg L^{-1}), but total nitrogen (5.37 mg L^{-1}) values from the cropped catchment in this study were higher despite no fertiliser applications. The lower total nitrogen values reported by Bartley et al. (2012) may be partly explained by: (1) diversity of study locations, including variations in the physical and chemical structure of soil; (2) data collection from different spatial scales (plot versus small, medium and large catchments); and (3) less than 90% of the upstream catchment areas were dominated by dryland crops, which due to a potential matrix of soil type, land use and ground cover provide a less accurate comparison than if data was collected from a single land use.

Soil characteristics and land use history are of particular interest when comparing runoff water quality studies, as physically more sediment and particulate nutrients are expected from sodic soils which readily erode (Gray and Murphy, 2002) and chemically soil fertility declines over time. For example, total soil nitrogen (0–10 cm) has been shown to decline with an increase in cropping history ranging from 0 to 70 years (Dalal and Mayer, 1986a, 1986b). Following colonisation of Australia in 1788, clearing land for agriculture started in the southern states and slowly headed north to Queensland (Australian Government, 2015). For example, 85% (407,840 ha) of cropping in Australia was conducted in the southern states of Victoria, South Australia and New South Wales in 1860 with only 0.3% (1357 ha) occurring in Queensland

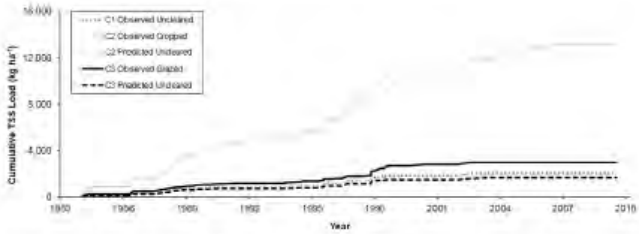

Fig. 5. Cumulative load (kg ha^{-1}) of total suspended sediments (TSS) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

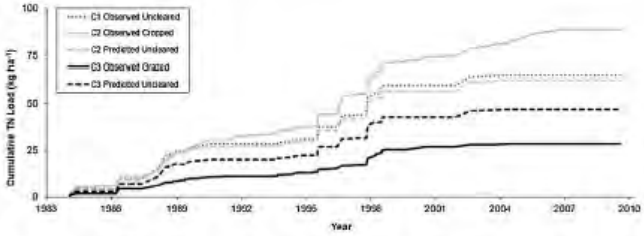

Fig. 6. Cumulative load (kg ha^{-1}) of total nitrogen (TN) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

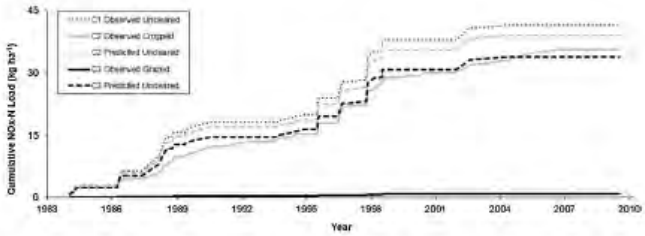

Fig. 7. Cumulative load (kg ha^{-1}) of oxidised nitrogen (NOx-N) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

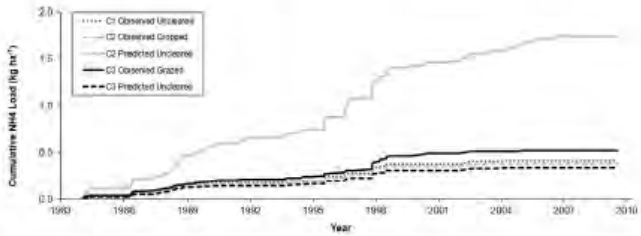

Fig. 8. Cumulative load (kg ha^{-1}) of ammonium nitrogen (NH_4-N) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

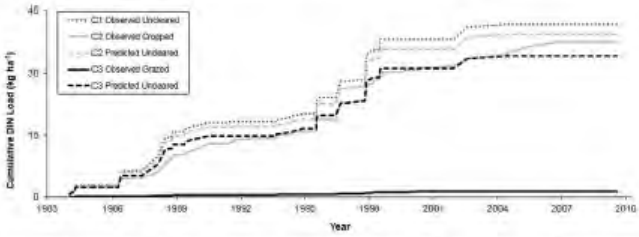

Fig. 9. Cumulative load (kg ha^{-1}) of dissolved inorganic nitrogen (DIN) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

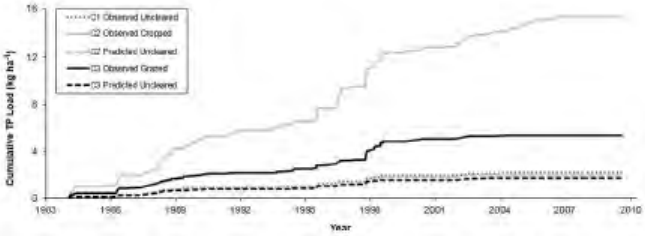

Fig. 10. Cumulative load (kg ha^{-1}) of total phosphorus (TP) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

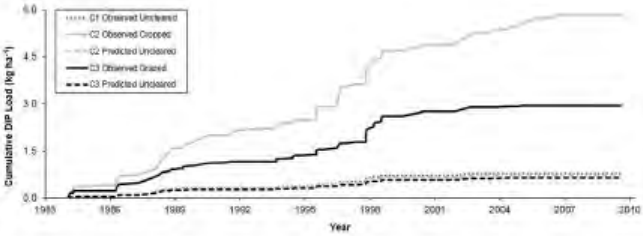

Fig. 11. Cumulative load (kg ha^{-1}) of dissolved inorganic phosphorus (DIP) from the virgin brigalow woodland (C1), crop (C2) and pasture (C3) catchments, and predicted loads for the cropped and grazed catchments had they remained virgin brigalow woodland. Data for the period July 1984 to January 2010; however, no events occurred between March 2007 and January 2010.

Table 4
Observed mean annual sediment, nitrogen and phosphorus loads (kg ha^{-1} yr^{-1}) from the virgin brigalow woodland, cropped and grazed pasture catchments over 25 years (1984–2010); and predicted mean annual loads from the cropped and grazed catchments had they remained virgin brigalow woodland.

Parameter	Load (kg ha^{-1} yr^{-1})				
	Woodland (C1)	Crop (C2)	Pasture (C3)	C2 Predicted Uncleared	C3 Predicted Uncleared
Total Suspended Solids	81	525	119	76	66
Total Nitrogen	2.61	3.53	1.13	2.49	1.87
Oxidised Nitrogen	1.66	1.43	0.03	1.56	1.35
Ammonium Nitrogen	0.02	0.07	0.02	0.02	0.01
Dissolved Inorganic Nitrogen	1.68	1.50	0.06	1.57	1.37
Total Phosphorus	0.08	0.61	0.21	0.08	0.07
Dissolved Inorganic Phosphorus	0.03	0.23	0.12	0.03	0.03

Table 5
Mean annual effect of changing land use from virgin brigalow woodland to crop and pasture systems on sediment, nitrogen and phosphorus loads (kg ha^{-1} yr^{-1}) over 25 hydrological years (1984–2010).

Parameter	Mean Annual Land Use Change Effect (kg ha^{-1} yr^{-1})	
	Crop (C2)	Pasture (C3)
Total Suspended Solids	449	53
Total Nitrogen	1.04	−0.74
Oxidised Nitrogen	−0.13	−1.32
Ammonium Nitrogen	0.05	0.01
Dissolved Inorganic Nitrogen	−0.07	−1.31
Total Phosphorus	0.53	0.15
Dissolved Inorganic Phosphorus	0.20	0.09

(Australian Bureau of Statistics, 2007). As a result, soils in the southern states where cropping has occurred for over 150 years are likely to be less fertile than in the Fitzroy Basin of Queensland where land development for cropping only commenced about 50 years ago. The shorter history of cropping at this study site in the Fitzroy Basin would also explain, at least in part, the higher total nitrogen in runoff compared to other areas of Australia which were included in the Bartley et al. (2012) review.

In contrast to total nutrients, there are limited data available on dissolved concentrations of nitrogen and phosphorus in runoff from cropped and/or grazed areas. Murphy et al. (2013) reported 5.9 mg L^{-1} oxidised nitrogen and 0.017 mg L^{-1} dissolved phosphorus from a cropped area over one wet season; whereas concentrations over 10 years used in this study were 2.17 mg L^{-1} and 0.14 mg L^{-1}, respectively. The paucity of studies that have reported on dissolved nutrients from comparative single land use systems over enough wet seasons to account for annual variability makes interpretation difficult at present. However, the EMCs used in the model presented in this study are within the range of sediment and total nitrogen and phosphorus values reported from other cropped and grazed sites. This suggests that the results are comparable to other areas dominated by similar agricultural systems.

4.2. Effect of land use change on water quality

Differences in runoff volume between the catchments can be attributed to variable water use patterns of the different vegetation types with ground cover, structural decline and surface roughness being secondary factors (Thornton et al., 2007). Clearing virgin brigalow woodland for agriculture is known to increase runoff volume (Siriwardena et al., 2006; Thornton et al., 2007), and it is well established that runoff volume and sediment loads are higher from cropped than grazed areas (Freebairn et al., 2009; Murphy et al., 2013; Sharpley and Smith, 1994; Silburn et al., 2007; Stevens et al., 2006). Both these trends were observed in this study. However, Australian literature currently provides an incomplete story on the impacts of changing land use for these two agricultural systems on nutrients in runoff. For example, Stevens et al. (2006) reported higher loads of total nitrogen and phosphorus from cropped than grazed areas but nothing on dissolved species, while Murphy et al. (2013) reported total and dissolved concentrations of nitrogen and phosphorus from cropped areas but nothing from grazed areas. This gap is also found in international studies; for example, in the southwestern United States of America, Sharpley and Smith (1994) reported higher loads of nitrogen and phosphorus (total and dissolved) following change of native grasslands to conventional tilled (fertilised) wheat but nothing from grazed areas. This highlights the uniqueness of this study's design which has collected long-term data on total and dissolved nutrients in runoff from both cropping and grazed areas concurrently with an uncleared control. In this study, more sediment and phosphorus (total and dissolved) were exported in runoff from both agricultural systems than virgin brigalow woodland. Changing land use to a pasture system also had less impact on runoff water quality than changing land use to a crop system for all sediment, nitrogen and phosphorus parameters reported.

The findings in this study also support other research which have reported a correlation between sediment and total phosphorus loss, and runoff and dissolved inorganic phosphorus loss (Gillingham and Thorrold, 2000; Hansen et al., 2002; Sharpley and Smith, 1990; Yuan et al., 2013). The considerably higher sediment loss from the cropped catchment is most likely the result of bare and/or low cover fallow management and tillage practices which are associated with erosion (Freebairn et al., 1993). Exports of sediment and total phosphorus increased at relatively proportional rates; however, the overall contribution of dissolved inorganic phosphorus to total phosphorus remained similar between the cropped catchment (38%) and its uncleared prediction (37%). This indicates that phosphorus from the cropped catchment was mainly exported in a particulate phase. Although this does not take into account the contribution of dissolved organic phosphorus which was not measured in this study, data from a nearby study has shown that dissolved organic phosphorus contributes only 3 to 5% of the total phosphorus load (Rogusz et al., 2013). This supports phosphorus from the cropped catchment being mainly exported in a particulate phase.

In contrast, the lower loss of sediment from the virgin brigalow and grazed catchments can be attributed to the higher proportion of litter and pasture cover, respectively, which protects the soil surface from raindrop impact. High ground cover also helps maintain high infiltration rates, which reduces runoff and subsequently erosion (Freebairn and Wockner, 1986; Silburn et al., 2011). Although conservative grazing of the unfertilised pasture resulted in only a 1.80 times increase in sediment compared to uncleared predictions for this catchment, total phosphorus increased 3.11 times and dissolved inorganic phosphorus 4.61 times. Furthermore, the overall contribution of dissolved inorganic phosphorus to total phosphorus increased from 37% for the uncleared prediction to 55% under grazing. The inclusion of dissolved organic phosphorus would increase the proportion of total phosphorus transported in the dissolved phase. The transport of phosphorus in mainly a dissolved phase is not surprising given the negative inverse relationship reported between dissolved phosphorus and sediment by Sharpley et al. (1981), and the management of this catchment to maintain high pasture cover and minimise erosion, which subsequently reduces particulate phosphorus loss (Sharpley et al., 1994).

The enrichment of dissolved phosphorus in runoff from the grazed catchment may also be explained by the presence of cattle, as grazing animals can return 60 to 99% of the nutrients they ingest back into the pasture system via dung and urine (Haynes and Williams, 1993). Dung is the main form that phosphorus is excreted from animals, and it often has a higher inorganic content than the pasture ingested (Haynes and Williams, 1993). For example, sheep dung has been shown to contain 80% inorganic phosphorus compared to only 64% from the pasture ingested

(Haynes and Williams, 1993). Australian data indicates that a 400 kg beef cattle steer maintaining body weight will excrete 2.8 kg of faecal dry matter per day (Department of Agriculture and Fisheries, 2011) which contains 2.1 g of phosphorus per kg of faecal dry matter (Jackson et al., 2012). Given the grazed catchment in this study is typically stocked at one 300 kg animal per 2.2 ha, approximately 0.71 kg ha^{-1} yr^{-1} of phosphorus is returned to the soil surface via dung.

Virgin brigalow woodland at this site is representative of the broader brigalow landscape in its pre-European condition, and the high nitrogen concentrations in runoff relative to the agricultural systems are likely due to the leguminous brigalow (*Acacia harpophylla*) tree which dominates the vegetation community. Although the concentration of total nitrogen in runoff from the virgin brigalow catchment was higher than the unfertilised cropped catchment, the mean annual load exported was less. This is a function of greater runoff volume and the number of days on which runoff occurred from the cropped catchment; that is, a total of 1647 mm was discharged over 99 days from the cropped catchment compared to only 663 mm discharged over 45 days from the virgin brigalow catchment over the 25 year period. This trend is similarly reported by Thornton et al. (2007) who found that in the same catchment 5.7% of rainfall become runoff in an uncleared state which increased to 11.0% under cropping.

In contrast to total nitrogen, oxidised and dissolved inorganic nitrogen both had higher concentrations and loads from virgin brigalow woodland compared to cropping. The contribution of particulate nitrogen to the total cumulative load of total nitrogen was 36% for virgin brigalow woodland and 58% for cropping; where particulate nitrogen was calculated as total nitrogen minus dissolved inorganic nitrogen. This indicates that total nitrogen load was dominated by a dissolved phase in the virgin brigalow woodland but a particulate phase in cropping. However, this does not take into account the contribution of dissolved organic nitrogen which was not measured in this study. The literature shows that dissolved organic nitrogen load in runoff can equal dissolved inorganic nitrogen loads (Heathwaite and Johnes, 1996; Martinelli et al., 2010; Rogusz et al., 2013), providing further evidence that the total nitrogen load from virgin brigalow woodland was dominated by a dissolved phase. It also suggests that total nitrogen load in cropping was likely to be equally comprised of both dissolved and particulate nitrogen if not dominated by a dissolved phase.

Although mean annual loads presented in this study are based on calculations using the 10 years of available EMC data, it is expected that total nitrogen concentrations in runoff would decline from the cropped catchment over the 25 years as nitrogen was removed from the system. Measurements of total soil nitrogen from 1981 to 2008 (the last sampling period before conversion of the cropped catchment into a ley pasture in 2010) shows that nutrient rundown occurred in the absence of fertiliser inputs and the export of nitrogen in grain and runoff. That is, concentrations of total soil nitrogen in the virgin brigalow catchment remained relatively stable (mean 0.176%) whereas concentrations in the cropped catchment declined from 0.197% in 1981 to 0.076% in 2008 (unpublished data). This result is expected given the previously reported declines in grain yield and grain nitrogen from the cropped catchment over 23 years (Radford et al., 2007).

Both agricultural systems had more ammonium nitrogen in runoff than the virgin brigalow woodland; 2% contribution to the total cumulative load of total nitrogen compared to less than 1%, respectively. However, the overall small contribution of ammonium to total nitrogen is most likely due to soil bacteria which rapidly convert ammonium into nitrate given ideal moisture and temperature conditions (Price, 2006). Cumulative losses of ammonium in runoff from this study were more similar to sediment, and hence phosphorus, than other nitrogen parameters. This trend has been reported in other studies and is attributed to the adsorption of ammonium onto sediment particles (Heathwaite and Johnes, 1996; Johnes and Burt, 1991). That is, ammonium (NH_4^+) is a positively charged cation which is attracted to the negatively charged surface of organic matter and clay particles, whereas nitrate (NO_3^-) is a negatively charged anion repelled by the soil and subsequently more readily lost via leaching and runoff.

The grazed catchment exported considerably less nitrogen than the virgin brigalow and cropped catchments. Loads of oxidised and dissolved inorganic nitrogen from pasture were almost negligible, and the higher total nitrogen loads can be attributed to particulate nitrogen. That is, dissolved inorganic nitrogen contributed only 5% to the total cumulative load of total nitrogen which indicates that particulate nitrogen strongly dominates transport from the grazed catchment. A dissolved organic nitrogen load equal to the dissolved inorganic nitrogen load would still result in particulate nitrogen strongly dominating transport from the grazed catchment. However, Radford et al. (2007) reported only 1.6 kg ha^{-1} yr^{-1} of nitrogen removal in cattle from the grazed catchment over 23 years compared to 36.1 kg ha^{-1} yr^{-1} nitrogen removal in grain from the cropped catchment. These observations imply that sown pasture in the grazed catchment is a sink for nitrogen. This is known as pasture rundown which occurs when mineral nitrogen becomes immobilised in soil organic matter and established grass plants, rather than a net loss from the system (Lawrence et al., 2014; Robertson et al., 1997). This is reflected in the soil mineral nitrogen data for the grazed catchment which remained relatively stable from 1983 to 2008 following an initial peak in 1982 due to clearing and burning of the catchment (unpublished data). Although rundown can lead to a decline in pasture productivity (Lawrence et al., 2014; Myers and Robbins, 1991), the grazed catchment in this study has always been conservatively managed to maintain high pasture cover.

Lower nitrogen from the grazed catchment compared to the cropped catchment can also be attributed to the higher percentage of nitrogen removed by pasture (3.5%) compared to cereal grains (1.8%) (The State of Victoria, 2015). As pasture tends to uptake more nitrate, a component of both oxidised and dissolved inorganic nitrogen, there is less available in the effective depth of interaction (0.1–4 cm) (Sharpley, 1985) to be dissolved and transported with water in runoff or as leachate. Loads of nitrogen in runoff have also been shown to be lower from pasture cut to 155 mm above the ground than 47 mm (Mundy et al., 2003). This supports the use of management practices that promote higher pasture biomass to reduce runoff volume and hence improve water quality, such as wet season spelling and conservative stocking rates based on feed availability.

4.3. Effect of management practices

Management practices, such as fertiliser application and tillage method, are two factors that affect the quality of surface runoff from crop systems. Sharpley and Smith (1994) found that fertiliser applications on conventionally tilled wheat resulted in a 17-fold nitrogen and 30-fold phosphorus increase in runoff. Physical and chemical degradation of soils from cropped land is a slow process (Silburn et al., 2007), and based on more than 25 years of fertility rundown at this site, soil fertility and consequently nutrient loads in runoff are expected to be lower than fertilised crops. For example, Murphy et al. (2013) reported 7–8 kg ha^{-1} oxidised nitrogen (approximately 20% of the total nitrogen applied at planting) in runoff from a fertilised crop, whereas this study in a similar area of central Queensland, Australia, reported 1.43 kg ha^{-1} oxidised nitrogen from an unfertilised crop.

Conventional tillage practices are reported to have higher runoff volume and/or erosion loss than no-till crop systems (Carroll et al., 1997; DeLaune and Sij, 2012; Ehigiator and Anyata, 2011). No-till practices have higher stubble cover which reduces overland flow velocity and the ability of water to detach and transport sediment (Rose and Freebairn, 1985). Cover levels above 30% have been suggested as critical for erosion control in crop systems (Carroll et al., 1997). Thus, management practices that retain cover and reduce runoff are also useful for reducing loads of sediment and some nutrients (Bartley et al., 2014a; Hansen et al., 2002; McIvor et al., 1995). For example, Sharpley and Smith (1994) found that changing a crop system from conventional to no-till reduced soil loss 18-fold, nitrogen loss four-fold and phosphorus loss three-fold, but an increase in bioavailable phosphorus was observed. Similarly, DeLaune and Sij (2012) reported a five-fold reduction in soil loss from no-till compared to conventional tilled systems. These authors also observed a trend of lower total phosphorus, dissolved phosphorus and ammonia nitrogen but higher nitrate nitrogen from no-till systems, although differences were not statistically different ($P < 0.05$) (DeLaune and Sij, 2012). Minimum tillage was introduced to the cropped catchment at the Brigalow Catchment Study in 1992 with intermittent use of conventional tillage practices in 1994, 1997 and 2007. Small increases in cumulative runoff and loads of sediment and nutrients can be seen around the periods when conventional tillage had been reintroduced; however, hydrology appears to be a stronger influence with the two main periods of an increased rate in cumulative loads (1991 to 1994 and 1996 to 1999) coinciding with periods of above average rainfall over multiple years. This supports the recommendation that management practices that reduce runoff also reduce sediment and nutrient loads.

Runoff water quality from pasture systems is similarly affected by cover. Silburn et al. (2011) suggested that more than 50% ground cover should be maintained in grazed areas to reduce excessive runoff and soil loss. This recommendation was based on a seven year study in a semi-arid area of Queensland which exported 30 to 50% of rainfall as runoff when cover was less than 20%, but averaged only 5.9% when cover was greater than 50%. The trend of reduced runoff, and hence reduced sediment and nutrients exported in runoff, from grazed land with higher ground cover is supported by numerous authors (Murphy et al., 2008; Nelson et al., 1996; Schwarte et al., 2011). Bare areas (scalds) have a low tolerance to soil erosion due to low total water-holding capacity which results in lower infiltration and hence increased runoff compared to areas with greater cover (Silburn et al., 2011). However, management practices such as reduced stocking rates and rotational wet season resting have been shown to increase ground cover (Bartley et al., 2010, 2014b). The pasture system at the Brigalow Catchment Study is conservatively grazed and aims to maintain at least 80% cover and less than 30% pasture utilisation, which is considered a well-managed system. Hence, the loads of sediment, nitrogen and phosphorus exported from this site may be lower than other areas which have higher stocking rates and greater pasture utilisation.

5. Conclusions

The simple hydrology and water quality model presented was based on a 17 year calibration period of the Brigalow Catchment Study in its native condition, and 25 years flow and 10 years water quality monitoring following land use change to agriculture. The model indicated that changing land use from virgin brigalow woodland to a well-managed (unfertilised) pasture system decreased nitrogen in runoff compared to runoff from virgin brigalow woodland which dominated the landscape during pre-European times; however, both crop and pasture systems increased loads of sediment and phosphorus. Overall, crops posed a greater risk to downstream water quality, and subsequently the end of catchment marine system, than pasture.

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Appendix 2

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The Brigalow Catchment Study: V*. Clearing and burning brigalow (*Acacia harpophylla*) in Queensland, Australia, temporarily increases surface soil fertility prior to nutrient decline under cropping or grazing

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Abstract. In the Brigalow Belt bioregion of Australia, clearing of brigalow (*Acacia harpophylla*) scrub vegetation for agriculture has altered nutrient cycling over millions of hectares. In order to quantify the effect of this vegetation clearing and land use change on soil fertility, the Brigalow Catchment Study commenced in 1965. Initial clearing and burning of brigalow scrub resulted in a temporary increase of mineral nitrogen, total and available phosphorus, total and exchangeable potassium and total sulfur in the surface soil (0–0.1 m) as a result of soil heating and the ash bed effect. Soil pH also increased, but did not peak immediately after burning. Soil fertility declined significantly over the subsequent 32 years. Under cropping, organic carbon declined by 46%, total nitrogen by 55%, total phosphorus by 29%, bicarbonate-extractable phosphorus by 54%, acid-extractable phosphorus by 59%, total sulfur by 49%, total potassium by 9% and exchangeable potassium by 63% from post-burn, pre-cropping concentrations. Fertility also declined under grazing but in a different pattern to that observed under cropping. Organic carbon showed clear fluctuation but it was not until the natural variation in soil fertility over time was separated from the anthropogenic effects of land use change that a significant decline was observed. Total nitrogen declined by 22%. Total phosphorus declined by 14%, equating to only half of the decline under cropping. Bicarbonate-extractable phosphorus declined by 64% and acid-extractable phosphorus by 66%; both greater than the decline observed under cropping. Total sulfur declined by 23%; less than half of the decline under cropping. A similar decline in total potassium was observed under both land uses, with a 10% decline under grazing. Exchangeable potassium declined by 59%. The primary mechanism of nutrient loss depended on the specific land use and nutrient in question.

Keywords: catchment management, cropping systems, dryland agriculture, tree clearing.

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Introduction

Soil fertility decline, soil structural decline and erosion are all considered to be consequences of changing land use from virgin forest to cropping and grazing. Traditionally, nutrient cycling in undisturbed virgin ecological systems was considered a steady-state closed system, where soil nutrients are consumed by the growing plants and then released back to the soil via leaf litter, wood debris and roots (Moody 1998). In contrast, cropping and grazing systems disturb this cycle by removing nutrients in harvested products and animals (Radford *et al.* 2007), via increased surface runoff (Thornton *et al.* 2007; Elledge and Thornton 2017), increased leaching (Silburn *et al.* 2009) and increased gaseous losses from soil and animals (Huth *et al.* 2010; Dalal *et al.* 2013). Disturbance of nutrient cycles and increased losses of soil nutrients affect the viability and sustainability of farming systems. Increased nutrient loads lost to the environment impacts ecosystem health, resulting in substantial investment in harm minimisation and remediation programs worldwide (Carroll *et al.* 2012). Contemporary nutrient cycling research suggests that disturbance and nutrient loss on a local scale have ramifications on a global scale. This is demonstrated by feedback mechanisms between increasing temperature, increasing atmospheric carbon dioxide and nitrogen concentrations, and fluxes of soil organic matter as a result of concomitant change in soil carbon and nitrogen concentrations (Crowther *et al.* 2016; Tipping *et al.* 2017; Schulte-Uebbing and de Vries 2018).

In the Brigalow Belt bioregion of Australia, clearing of brigalow (*Acacia harpophylla*) scrub and land use change has substantially altered nutrient cycling over a large area. The bioregion occupies 36.7 million hectares of Queensland and New South Wales, stretching from Dubbo in the south to Townsville in the north of Australia. Since European settlement, 58% of this bioregion has been cleared. The

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bioregion contains Queensland's largest catchment, the Fitzroy Basin, which drains directly into the Great Barrier Reef lagoon. In 1962, the Brigalow Land Development Fitzroy Basin Scheme commenced, resulting in the government-sponsored clearing of 4.5 million hectares for cropping and grazing. This clearing represents 21% of all clearing in the bioregion and 32% of the Fitzroy Basin area (Thornton *et al.* 2007). Broad-scale land clearing continued in the basin until 2006 (McGrath 2007). In the preceding decade, rates of land clearing in Queensland were among the highest in the world, with estimates of 425 000–446 000 ha cleared per year (Wilson *et al.* 2002; Lindenmayer and Burgman 2005; Reside *et al.* 2017). More than 60% of this clearing, or ~261 000 ha/year, was undertaken in the Brigalow Belt (Wilson *et al.* 2002; Cogger *et al.* 2003). It is estimated that up to 93% of brigalow scrub has been cleared since European settlement (Butler and Fairfax 2003; Cogger *et al.* 2003; Tulloch *et al.* 2016).

In order to quantify the effect of this scale of vegetation clearing and land use change on soil fertility, the Brigalow Catchment Study (BCS) commenced in 1965. The objective of this study was to evaluate whether clearing of brigalow scrub for cropping or grazing would alter the dynamics of soil organic carbon (OC), nitrogen, phosphorus, sulfur and potassium over time. It was hypothesised that land development for cropping would lead to a significant decline in soil fertility while less or no change was expected with land development for grazing. It was also expected that the trends noted by Radford *et al.* (2007), i.e. unchanged concentrations of soil OC and total nitrogen (TN) under brigalow scrub and grazing land uses but significant decline under cropping, would continue; however, the planting of legume ley pasture may enhance nutrient status in soil under the cropping land use.

As resourcing pressures limit the commencement and continuation of long-term studies there is an increasing trend towards modelling. This study facilitates modelling by numerically describing the starting condition of the landscape and mathematically defining fertility trends over time. Discussion on the mechanisms of change further informs process-based models, assisting in moving forward from traditional empirical black box models. The BCS continues today having adapted to answer new research questions, and having answered questions unanticipated at its inception more than five decades ago.

Materials and methods

The BCS is described in detail by Cowie *et al.* (2007); changes in runoff volume and peak runoff rate are given in Thornton *et al.* (2007) and Thornton and Yu (2016); agronomic and soil fertility results are given in Radford *et al.* (2007); the deep drainage component of the water balance is given in Silburn *et al.* (2009); and changes in water quality are given in Thornton and Elledge (2016) and Elledge and Thornton (2017).

Site location and climate

The study site is located at 24.81°S, 149.80°E at an altitude of 151 m above sea level, located within the Dawson subcatchment of the Fitzroy Basin, central Queensland, Australia. A locality map is presented in Cowie *et al.* (2007). The region has a semiarid, subtropical climate. Summers are wet, with 70% of the annual average (1964–2014) hydrological year (October–September) rainfall of 661 mm falling during October–March, and winter rainfall is low (Fig. 1). Average monthly temperature ranges from a minimum of 6.3°C in July to a maximum of 33.8°C in January (Fig. 1).

Experimental design

The BCS is a paired, calibrated catchment study consisting of three small catchments, C1, C2 and C3, ranging from 11.7 to 16.8 ha in size. Within each catchment, three permanent monitoring sites were established to monitor soil fertility. A map showing the location of the monitoring sites within the catchments is presented in Cowie *et al.* (2007). Establishment of the 20 m × 20 m sites was done using double stratification. Initial stratification was based on soil type and slope position with a monitoring site allocated to both an upper- and lower-slope position on Vertosols, and the third on a Sodosol irrespective of slope position. Secondary stratification was by way of 10 subunits, each 4 m × 10 m, within each monitoring site.

Soil types

Soil types were typically characterised by fine-textured dark cracking clays (Black and Grey Vertosols), noncracking clays (Black and Grey Dermosols) and thin layered dark and brown sodic soils (Black and Brown Sodosols) (Isbell 1996; Cowie *et al.* 2007). Approximately 70% of C1 and C2 and 58% of

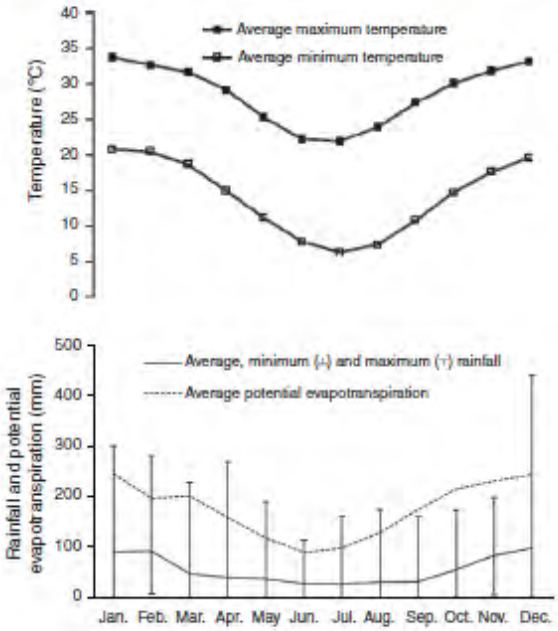

Fig. 1. Average monthly temperature, rainfall and potential evapotranspiration for the Brigalow Catchment Study site from 1964 to 2014.

C3 comprised Vertosols and Dermosols (clay soils); the remaining area in each catchment was occupied by Sodosols. The plant-available water holding capacity of these soils ranged from 130 to 200 mm in the surface 1.4 m of the soil profile (Cowie *et al.* 2007). Average slope of the catchments is 2.5%. The catchments consisted of good quality agricultural land, all equally suitable for cropping or grazing (Cowie *et al.* 2007). The physiochemical characteristics of an upper-slope Vertosol, and a Sodosol, both within C1, are given in Table 1 (adapted from Cowie *et al.* 2007). These sites were sampled in 1981 with sampling and sample handling procedures described in subsequent sections. Values for pH, electrical conductivity (EC) and Cl were determined using 1:5 suspensions in water (Hunter and Cowie 1989). Total carbon, TN and total OC were determined by Dumas high-temperature combustion as described in methods 6B2a, 7A5 and 6B5 respectively, in Rayment and Lyons (2011). Walkley and Black OC was determined according to method 6A1 in Rayment and Higginson (1992). Nitrate-nitrogen (NO_3-N) was determined by the potassium chloride extraction method described in method 7C2 in Rayment and Higginson (1992). Cation exchange capacity and exchangeable cations were determined by extraction with alcoholic one molar ammonium chloride at pH 8.5 as described in method 15C1 in Rayment and Higginson (1992). Clay content was determined by drink mixer physical dispersion (Bouyoucos 1951) followed by fine-fraction determination by hydrometer (Thorburn and Shaw 1987; Hunter and Cowie 1989).

Vegetation

Vegetation was typical of the Brigalow Belt bioregion, dominated by brigalow (*Acacia harpophylla*), as described in detail by Cowie *et al.* (2007). In their native 'brigalow' state, the catchments were composed of three major vegetation communities, identified by their most common canopy species: brigalow (*Acacia harpophylla*), brigalow–belah (*Casuarina cristata*) and brigalow–Dawson gum (*Eucalyptus cambageana*). Understoreys of all major communities were characterised by *Geijera* sp. either exclusively, or in association with *Eremophila* sp. or *Myoporum* sp.

Site history and management

The study has had four experimental stages (Table 2). Stage I, the calibration phase, monitored rainfall and runoff from the catchments, allowing an empirical hydrological calibration between catchments to be developed. The permanent monitoring sites were established in each catchment during this stage. Baseline measurements of soil fertility were taken in 1981 (Cowie *et al.* 2007; Radford *et al.* 2007).

Table 1. Average pre-clearing (1981) soil physiochemical characteristics for a Vertosol and a Sodosol within catchment 1 (adapted from Cowie *et al.* (2007))

EC, electrical conductivity; Cl, chlorine; TC, total carbon; TN, total nitrogen; NO_3-N, nitrate nitrogen; CEC, cation exchange capacity

Depth (m)	pH	EC (dS/m)	Cl (µg/g)	TC (%)	TN (%)	TOC[A] (%)	NO_3-N (KCl) (µg/g)	CEC	Exchangeable Ca^{2+}	Mg^{2+}	Na^+	K^+ (cmol/kg)	Clay (%)
							Vertosol						
0.0–0.1	6.56	0.16	75	2.01	0.16	1.58	2.7	34	11.8	11.1	1.4	0.41	36
0.1–0.2	7.54	0.48	450	1.37	0.11	1.34	1.2	36	11.5	14.6	3.2	0.23	40
0.2–0.3	8.14	0.68	730	0.69	0.06	0.66	0.5	35	10.0	15.4	4.1	0.16	44
0.5–0.6	5.70	0.77	1040				0.2	32	5.9	14.6	4.6	0.21	45
0.8–0.9	4.76	0.83	1145				0.2	32	4.1	13.7	4.9	0.12	46
1.1–1.2	4.64	0.83	1170				0.2	34	3.4	13.4	5.4	0.12	46
1.4–1.5	4.52	0.92	1320				0.1	38	3.4	15.0	6.6	0.16	50
1.7–1.8	4.48	0.98	1385				0.1	39	3.3	15.7	6.9	0.27	54
							Sodosol						
0.0–0.1	6.80	0.10	20	2.43	0.17	2.33	4	21	9.5	4.1	0.3	0.51	18
0.1–0.2	7.16	0.17	130	0.87	0.07	0.84	1.1	25	6.4	9.2	2.3	0.18	31
0.2–0.3	7.52	0.22	220	0.79	0.06	0.78	0.5	23	5.6	9.3	2.9	0.12	28
0.5–0.6	8.83	0.40	400				0.2	24	6.3	9.9	4.7	0.15	
0.8–0.9	9.20	0.47	470				0.2	16	2.8	6.8	4.1	0.13	

[A]Walkley and Black OC (0–0.1 m).

Table 2. The land use history of the three catchments of the Brigalow Catchment Study

Catchment	Area (ha)	Land use by experimental stage: Stage I (Jan. 1965 to Mar. 1982)	Stage II (Mar. 1982 to Sep. 1984)	Stage III (Sep. 1984 to Jan. 2010)	Stage IV (Jan. 2010 to June 2014)
C1	16.8	Brigalow scrub	Brigalow scrub	Brigalow scrub	Brigalow scrub
C2	11.7	Brigalow scrub	Development	Cropping	Ley pasture
C3	12.7	Brigalow scrub	Development	Grazing	Grazing

Stage II, the land development phase, commenced in March 1982 when vegetation in C2 and C3 was developed by clearing with traditional bulldozer and chain methods. Catchment 1 was retained as an uncleared, undisturbed control. In C2 and C3, the fallen timber was burnt *in situ* in October 1982. Following burning, residual unburnt timber in C2 was raked to the contour for secondary burning. Narrow-based contour banks were then constructed at 1.5 m vertical spacing. A grassed waterway was established to carry runoff water from the contour channels to the catchment outlet. In C3, residual unburnt timber was left in place, and in November 1982 the catchment was sown to buffel grass (*Cenchrus ciliaris* cv. Biloela). The second soil fertility assessment was undertaken in December 1982, soon after burning.

Stage III, the land use comparison phase, commenced in 1984. In C2, the first crop sown was sorghum (*Sorghum bicolor*) (September 1984), followed by annual wheat (*Triticum aestivum*) for nine years. Fallows were initially managed using mechanical tillage (disc and chisel ploughs), which resulted in significant soil disturbance and low soil cover. In 1992, a minimum tillage philosophy was introduced and in 1995 opportunity cropping commenced with summer (sorghum) or winter (wheat, barley (*Hordeum vulgare*) and chickpea (*Cicer arietinum*) crops sown when soil water content was adequate. No nutrient inputs were used. In C3, the buffel grass pasture established well with >5 plants/m^2 and 96% groundcover achieved before cattle grazing commenced in December 1983. Stocking rate was 0.3–0.7 head/ha (each stock typically 0.8 adult equivalent), adjusted to maintain pasture dry matter levels >1000 kg/ha without nutrient inputs, feed or nutrient supplementation. The catchment was continuously stocked until December 1996 at which point irregular pasture spelling commenced when pasture dry matter was likely to decline below 1000 kg/ha with further grazing.

Stage IV, the adaptive land management phase, commenced in 2010. To sustain productive agricultural systems representative of commercial enterprises in the Brigalow Belt bioregion, management strategies to maintain or enhance soil fertility were implemented. In C2, the legume butterfly pea (*Clitoria ternatea*) was planted as a ley pasture in January 2010. The butterfly pea was left ungrazed to establish and set seed until March 2011 when grazing commenced. In September 2011, cattle were removed from both C2 and C3 to allow spelling of the pastures over the 2011/12 and 2012/13 wet seasons. Grazing recommenced in December 2013 when the catchments were 'crash grazed' with high stocking rates of 0.5 adult equivalents/ha in C2 and 1.4 adult equivalents/ha in C3 for 45 days to reduce rank pasture growth. Subsequently, grazing continued at conservative stocking rates of ~0.3 adult equivalents/ha with regular periods of pasture spelling.

Soil sampling

Soil water in the surface 0.1 m of the soil profile was determined gravimetrically according to the methods of Cowie *et al.* (2007).

Soil samples for fertility analysis were collected from the surface 0.1 m of the soil profile at each monitoring site using manual coring tubes of 0.05 m diameter; samples were typically a composite of eight 0.05 m cores. The eight cores were comprised of two cores sampled adjacent to each of four fixed locations within each subunit. More intensive sampling was undertaken pre-clearing in 1981, and in 2008 and 2014. In these years, samples were a composite of 20 cores, with five cores sampled adjacent to each of the four fixed locations. Soil samples were collected annually from pre-clearing in 1981 to 1987 and then in 1990, 1994, 1997, 2000, 2003, 2008 and 2014, with samples retained after analysis in a long-term storage archive.

Measurements of agricultural productivity, nutrient removal and nutrient inputs

In the cropped catchment, grain yield and nitrogen and phosphorus contents were measured according to the methods of Radford *et al.* (2007). Grain sulfur content was estimated as grain nitrogen multiplied by 10% (Byers *et al.* 1987; Györi 2005). Grain potassium content was estimated as 0.46% of grain yield (Mengel and Kirby 1982).

In the grazed catchment, cattle liveweight gain was measured according to the method of Radford *et al.* (2007). Nutrient export in beef was estimated as liveweight gain multiplied by 2.4% for nitrogen (Radford *et al.* 2007), 0.71% for phosphorus (Gibson *et al.* 2002), 0.16% for sulfur (National Research Council 2003) and 0.2% for potassium (Whitehead 2000). Nitrogen volatilisation loss from cattle urine and faeces was estimated as nitrogen intake multiplied by 19.77% (Laubach *et al.* 2013). Nitrogen intake was estimated as dietary biomass intake multiplied by dietary nitrogen content. Daily dietary biomass intake was estimated as fasted animal liveweight at entry to the catchment multiplied by 2% per day of grazing (Minson and McDonald 1987). Dietary nitrogen content was determined using the FNIRS technique of Dixon and Coates (2010).

Estimates of nutrient input from rainfall were obtained using the data of Packett (2017) multiplied by the annual average rainfall of the BCS. An average of rainfall chemistry values for Rockhampton and Emerald (mean values) were used given both sites are a similar distance from the BCS.

Soil physical and chemical analyses

Soil bulk density was measured pre-clearing in 1981, then post-clearing in 1984, 1987, 1994, 1997, 2000 and 2014, using the soil samples collected for fertility analysis. The tip diameter of the coring tubes was measured in the field with the external wall of the tube marked at 0.1 m to indicate the depth of sampling. Intact soil cores not contaminated by rocks or organic matter >2 mm were dried at 40°C then weighed and subsampled, with the subsamples then dried at 105°C to a constant weight. Bulk density was calculated from the total sample mass corrected to the equivalent mass of 105°C oven-dry soil, per volume of core sampled.

Chemical analyses were performed by the Queensland Government soil laboratory network. Prior to analyses, soil samples were dried at 40°C and ground to pass through a 2 mm sieve. Samples were then analysed for soil pH, OC, TN, mineral nitrogen (ammonium-nitrogen (NH_4-N) and NO_3-N), total phosphorus (TP), available phosphorus (bicarbonate- and acid-extractable phosphorus; P(B) and P (A) respectively), total sulfur (TS), total potassium (TK)

and exchangeable potassium. Soil pH in a 1:5 soil/water suspension ($pH_{(w)}$) was determined according to the method of Tucker and Beatty (1974) from 1981 to 1983, in 1985 and from 1987 to 1997. In all other years, $pH_{(w)}$ was determined according to method 4A1 in Rayment and Higginson (1992). Soil pH in a 1:5 soil/calcium chloride suspension ($pH_{(Ca)}$) was determined according to the method of White (1969) from 1981 to 1983, in 1985 and in 1987. In all other years, $pH_{(Ca)}$ was determined according to method 4B1 in Rayment and Higginson (1992). For laboratory convenience, method 4B2 has been used interchangeably with 4A1, as there is no significant difference in the results obtained from either method (Rayment and Higginson 1992). Where pH values have been averaged, they are presented as a true average pH, not an arithmetic average (Rayment and Lyons 2011). Soil OC was determined by the dichromate oxidation method of Walkley and Black (1934), followed by titration. Post-1997, the titrimetric component of the procedure was replaced with a colourimetric procedure (Sims and Haby 1971) as described in method 6A1 in Rayment and Higginson (1992); these methods are well correlated (coefficient of determination (R^2) = 0.96) (Cowie *et al.* 2002). Soil TN was determined by macro-Kjeldahl digestion (Bremner 1965). Mineral nitrogen was determined by the potassium chloride extraction method described in method 7C2 in Rayment and Higginson (1992). Results less than the practical quantitation level of 2 mg/kg were set to a value of 0.5 mg/kg. Soil TP was determined using the X-ray fluorescence (XRF) method described in method 9A1 in Rayment and Higginson (1992). Soil P(B) was determined using a modification of the Colwell (1963) method described in method 9B2 in Rayment and Higginson (1992), while P(A) was determined using a modification of the Kerr and von Stieglitz (1938) method described in method 9G2 in Rayment and Higginson (1992). Soil TS and TK were determined using the XRF method described in methods 10 A1 and 17A1 respectively in Rayment and Higginson (1992). Exchangeable potassium (Exch. K) was determined by extraction with alcoholic one molar ammonium chloride at pH 8.5 as described in method 15C1 in Rayment and Higginson (1992).

The full suite of chemical analyses was typically performed soon after soil sampling. When this had not occurred, analyses were performed as required on the archived samples. Cowie *et al.* (2007) presented chemical data from C1 in 1981 for most of the analytes reported in this study. However, with the exception of mineral nitrogen and Exch. K, repeat analyses in this study did not reflect the previously reported values, which were typically lower despite having been conducted according to the same method and utilising best practice of the day. Where this occurred, the results of the repeat analysis have been accepted for use in this study.

The number of samples analysed varied between soil samplings (Table 3). At a minimum, a composite sample comprised of a subsample of each of the 10 subunits in a monitoring site was generated for analysis. This composite sample was representative of at least 80 soil cores from within a monitoring site. Alternatively, a sample from each of the subunits in a monitoring site was generated for analysis. This resulted in 10 samples, with each being representative of at least eight soil cores.

Approaches for assessing fertility decline

Comparison of observed soil fertility data

The observed soil fertility of a catchment was calculated as the average of the analytical results for all composite samples from the three monitoring sites within the catchment at the time of sampling. Changes in soil fertility over time since

Table 3. The number of soil samples analysed per parameter, per catchment, per sampling event

$pH_{(w)}$, soil pH in water suspension; $pH_{(Ca)}$, soil pH in calcium chloride suspension; OC, organic carbon; TN, total nitrogen; NH_4-N, ammonium nitrogen; NO_3-N, nitrate nitrogen; TP, total phosphorus; P(B), bicarbonate-extractable phosphorus; P(A), acid-extractable phosphorus; TS, total sulfur; TK, total potassium; Exch. K, exchangeable potassium

	Number of samples analysed per catchment											
Year	$pH_{(w)}$	$pH_{(Ca)}$	OC	TN	NH_4-N	NO_3-N	TP	P(B)	P(A)	TS	TK	Exch. K
1981	30	30	3	3	30	30	3	3	3	3	3	30
1982	30	30	3	3	30	30	3	3	3	3	3	30
1983	30	30	3	3	30	30	3	3	3	3	3	30
1984	3	3	30	30[A]	3	3	3	3	6	3	3	3
1985	30	30	3[B]	3	30	30	3	3	3	3	3	30
1986	3	3	30	3	3	3	3	3	6	3	3	3
1987	30	30	30	30	30[C]	30[C]	3	3	6	3	3	3
1990	3	3	30	3	30	30	3	3	6	3	3	3
1994	3	3	3	3	3	3	3	3	6	3	3	3
1997	30	3	30	3	30[D]	30[D]	3	3	6	3	3	3
2000	3	3	3	3	3	3	3	3	6	3	3	3
2003	3	3	3	3	3	3	3	3	6	3	3	3
2008	30	30	30	30	30	30	30	30	30	30	30	30
2014	30	30[E]	30	3	30	30	30	30	30	30	30	30

[A]C1 – 27
[B]C1 – 30
[C]C1 – 25, C3 – 17
[D]C2 – 29
[E]C1 – 29

burning were assessed using both linear, exponential, double exponential and quadratic regression analysis tools in the statistical software package GENSTAT (VSN International 2016).

Calibrating to account for natural fertility change

The paired catchment design of the experiment allowed for the natural variation in soil fertility over time to be separated from the anthropogenic effects of land use change. This was done by dividing the observed soil fertility of C2 and C3 by the observed soil fertility of the control catchment C1. Analysis of these ratios accounts for likely change in the soil fertility of C2 and C3 had they remained uncleared and provides a more accurate estimation of change rather than simply comparing the observed fertility over time to pre-clearing levels. As for the observed data, changes in soil fertility over time since burning were assessed using regression analysis.

Results

Grain and beef production and associated nutrient removal

Grain production in C2 yielded 49460 kg/ha of grain over 30 years (Fig. 2). This removed 958 kg/ha of nitrogen, 130 kg/ha of phosphorus, 96 kg/ha of sulfur and 228 kg/ha of potassium from the catchment. Removal of grain ($P<0.001$, $R^2=99\%$) (Eqn 1), nitrogen ($P<0.001$, $R^2=99\%$) (Eqn 2) and phosphorus ($P<0.001$, $R^2=99\%$) (Eqn 3) over time since the first crop was planted all showed exponential trends. Grazing of ley pasture in C2 at a stocking rate of 0.33 adult equivalent animals per hectare for 173 days produced 46 kg/ha of beef. This removed 1.1 kg/ha of nitrogen, 0.3 kg/ha of phosphorus, 0.07 kg/ha of sulfur and 0.1 kg/ha of potassium from the catchment. This grazing period was 47 days longer than the average crop length from planting to harvest; however, nitrogen, phosphorus, sulfur and potassium removal in beef was only 3%, 6.5%, 2% and 1% respectively of that removed in an average crop:

$$\text{C2 grain removal (kg/ha)} = 223373 - 220280 \times (0.999)^x \quad (1)$$

$$\text{C2 nitrogen removal (kg/ha)} = 1521 - 1460 \times (0.999^x) \quad (2)$$

$$\text{C2 nitrogen (kg/ha)} = 1044 - 1035 \times (0.999^x) \quad (3)$$

where x is years since the first crop was planted.

Beef production in C3 yielded 1910 kg/ha of beef over 31 years (Fig. 2). This removed 46 kg/ha of nitrogen, 14 kg/ha of phosphorus, 3 kg/ha of sulfur and 4 kg/ha of potassium from the catchment. A further 71 kg/ha of nitrogen was removed via volatilisation from urine and faeces. Removal of beef over time since grazing commenced showed an exponential trend ($P<0.001$, $R^2=99\%$) (Eqn 4) (Fig. 2). Because the nitrogen and phosphorus contents of beef were estimated based on a percentage of liveweight gain, the response curve for their removal from the catchment over time mirrored that of total beef removal:

$$\text{C3 beef removal (kg/ha)} = 2765 - 2786 \times (0.999^x) \quad (4)$$

where x is years since grazing commenced.

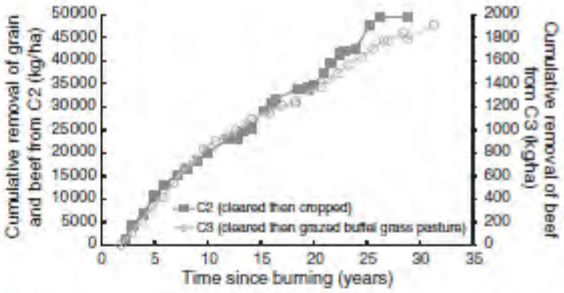

Fig. 2. Cumulative yield of agricultural commodities removed from C2 and C3 since land use change.

Trends in bulk density

Pre-clearing oven-dry bulk density for the three catchments in 1981 averaged 1.15 g/cm^3 (range 1.1–1.22 g/cm^3). Over the following 32 years there was no significant linear or exponential change in bulk density in C1 ($P = 0.498$ and $P = 0.773$ respectively). Clearing and burning followed by 30 years of cropping resulted in a significant linear increase in bulk density ($P = 0.062$, $R^2 = 44\%$). Fitting an exponential curve maintained the significance of the regression but improved R^2 ($P = 0.06$, $R^2 = 63\%$). Ratios of C2/C1 bulk density showed no significant linear or exponential change ($P = 0.136$ and $P = 0.292$ respectively). Clearing and burning followed by 31 years of grazing resulted in a linear increase in bulk density ($P = 0.097$, $R^2 = 35\%$); no significant exponential change was detected ($P = 0.14$). Ratios of C3/C1 bulk density mirrored both the linear and exponential results of the observed data ($P = 0.053$, $R^2 = 47\%$ and $P = 0.132$ respectively).

Observed bulk density in C2 and C3 post-clearing and burning was consistently higher than it was pre-clearing. Average bulk density post-clearing and burning was 116% of pre-clearing bulk density in C2 and 118% in C3. In the same period, bulk density in C1 declined to 98% of 1981 levels. Ratios of C2/C1 and C3/C1 bulk density were also higher post-clearing and burning, increasing to 119% and 120% of their respective pre-clearing ratios. As the average increase in bulk density in C2 and C3 equated to an additional 192 tonnes of soil in the surface 0.1 m of the soil profile, soil nutrient loss in kg/ha post-clearing and burning was calculated using the average bulk density of a catchment in that period, being 1.30 g/cm^3 in C2 and 1.34 g/cm^3 in C3.

In 1984 and 1987, soil water content was measured within two weeks of soil sampling occurring. In 1984, available soil water and bulk density at time of sampling was 5 mm and 1.18 g/cm^3 respectively in C1; 14 mm and 1.26 g/cm^3 in C2; and 17 mm and 1.30 g/cm^3 in C3. In 1987, available soil water and bulk density at time of sampling was 4 mm and 1.21 g/cm^3 respectively in C1; 23 mm and 1.21 g/cm^3 in C2; and 12 mm and 1.33 g/cm^3 in C3.

Trends in soil pH

Pre-clearing, $pH_{(w)}$ in the three catchments averaged 6.7 (range 6.6–6.9). From 1981 to 2014, $pH_{(w)}$ in C1 averaged 6.7 with no

significant linear or exponential trend ($P = 0.237$ and $P = 0.36$ respectively) (Fig. 3). Clearing and burning C2 and C3 in 1982 increased $pH_{(w)}$ in both catchments (Fig. 3). Visually, $pH_{(w)}$ continued to increase until 5 years post-burning in C2 and 11 years post-burning in C3. However, $pH_{(w)}$ had peaked within 2 years of burning, with no significant linear change in either catchment from 1.92 to 11.3 years post-burning ($P = 0.355$ and $P = 0.256$ respectively). The maximum

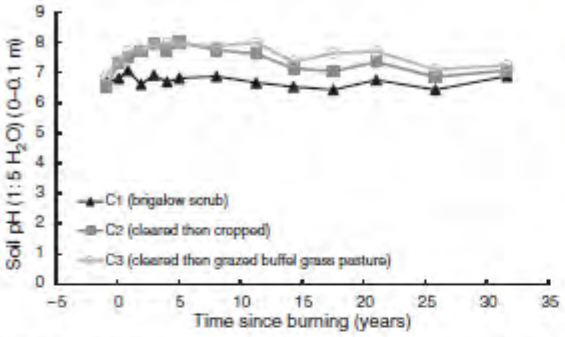

Fig. 3. Soil pH (1:5 soil/water) (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

$pH_{(w)}$ in both C2 and C3 was 8. Thirty-two years after burning, $pH_{(w)}$ in C2 was 7.1 and $pH_{(w)}$ in C3 was 7.3, both greater than their pre-clearing $pH_{(w)}$ of 6.6 and 6.9 respectively. The exponential rise in $pH_{(w)}$ post-burning, followed by a long-term linear decline was significant in both C2 ($P<0.001$, $R^2 = 79\%$) (Eqn 1 in Table 4) and C3 ($P<0.001$, $R^2 = 78\%$) when fitted with a double exponential curve (Eqn 2 in Table 4).

The behaviour of $pH_{(w)}$ in all catchments was mirrored by $pH_{(Ca)}$ (Fig. 4). From 1981 to 2014, $pH_{(Ca)}$ in C1 averaged 5.9 with no significant linear or exponential trend ($P = 0.357$ and $P = 0.069$ respectively). The exponential rise in $pH_{(Ca)}$ post-burning, followed by a long-term linear decline was significant in both C2 ($P<0.001$, $R^2 = 93\%$) (Eqn 3 in Table 4) and C3 ($P<0.001$, $R^2 = 72\%$) (Eqn 4 in Table 4). Values of $pH_{(Ca)}$ were 0.3–1.3 pH units less than $pH_{(w)}$.

Trends in observed soil fertility data

Organic carbon

Pre-clearing, OC concentrations in the three catchments averaged 2.08% (range 1.93–2.25%). From 1981 to 2014, OC in C1 averaged 2.15% with no significant linear or exponential trend ($P = 0.061$ and $P = 0.066$ respectively) (Fig. 5). Unlike C1, OC in C2 showed a significant exponential decline of 46%

Table 4. Equations describing trends in soil fertility over time, where x is years since burning
$pH_{(w)}$, soil pH in water suspension; $pH_{(Ca)}$, soil pH in calcium chloride suspension

Parameter	Catchment	Period	Trend equation	P	R^2	Equation number
$pH_{(w)}$	C1	1981–2014		NS		
	C2	1981–2014	C2 pH = 7.985 − 0.742 × (0.459^x) − 0.03708x	<0.001	0.79	1
	C3	1981–2014	C3 pH = 8.147 − 0.778 × (0.565^x) − 0.03144x	<0.001	0.78	2
$pH_{(Ca)}$	C1	1981–2014		NS		
	C2	1981–2014	C2 pH = 7.1952 − 0.706 × (0.3357^x) − 0.04163x	<0.001	0.93	3
	C3	1981–2014	C3 pH = 7.486 − 1.004 × (0.538^x) − 0.0369x	<0.001	0.72	4
Organic carbon	C1	1981–2014		NS		
	C2	1981–2014	C2 OC (%) = 1.203 + 0.842 × (0.823^x)	<0.001	0.88	5
	C3	1981–2000	C3 OC (%) = 1.53 + 0.207 × (0.49^x)	<0.001	0.79	6
Total nitrogen	C1	1981–2014		NS	0.39	
	C2	1981–2014	C2 TN (%) = 0.0866 + 0.104 × (0.84^x)	<0.001	0.91	7
	C3	1981–2014	C3 TN (%) = 0.12 + 0.028 × (0.611^x)	0.01	0.49	8
Total phosphorus	C1	1981–2014	C1 TP (%) = 0.0265 + 0.0023 × (1.035^x)	<0.001	0.77	9
	C2	1982–2014	C2 TP (%) = 0.0268 + 0.0097 × (0.875^x)	<0.001	0.91	10
	C3	1982–2014	C3 TP (%) = 0.027 + 0.0053 × (0.478^x)	0.009	0.53	11
Bicarbonate-extractable phosphorus	C1	1981–2014		NS		
	C2	1982–2014	C2 P(B) (mg/kg) = 18.14 + 15.7 × (0.852^x)	<0.001	0.88	12
	C3	1982–2014	C3 P(B) (mg/kg) = 12.62 + 22.86 × (0.744^x)	<0.001	0.92	13
Acid-extractable phosphorus	C1	1981–2014		NS		
	C2	1982–2014	C2 P(A) (mg/kg) = 31.02 + 29.75 × (0.849^x)	<0.001	0.91	14
	C3	1982–2014	C3 P(A) (mg/kg) = 21.3 + 39.42 × (0.818^x)	<0.001	0.97	15
Total sulfur	C1	1981–2014	C1 TS (%) = 0.0249 − 0.0043 × (0.984^x)	0.008	0.51	16
	C2	1982–2014	C2 TS (%) = 0.0135 + 0.0095 × (0.715^x)	<0.001	0.9	17
	C3	1982–2014		NA		
Total potassium	C1	1981–2014		NS		
	C2	1982–2014	C2 TK (%) = 0.457 + 0.039 × (0.893^x)	0.004	0.61	18
	C3	1982–2014	C3 TK (%) = 0.239 + 0.027 × (0.806^x)	<0.001	0.94	19
Exchangeable potassium	C1	1981–2014	C1 Exch. K ($cmol_c$/kg) = 0.4824 + (0.0367 + 0.00056x)/(1 − 0.07919x + 0.001865x^2)	<0.001	0.94	20
	C2	1982–2014	C2 Exch. K ($cmol_c$/kg) = 0.4081 + 0.3393 × (0.7678^x)	<0.001	0.8	21
	C3	1982–2014	C3 Exch. K ($cmol_c$/kg) = 0.3178 + 0.3454 × (0.8215^x)	<0.001	0.89	22

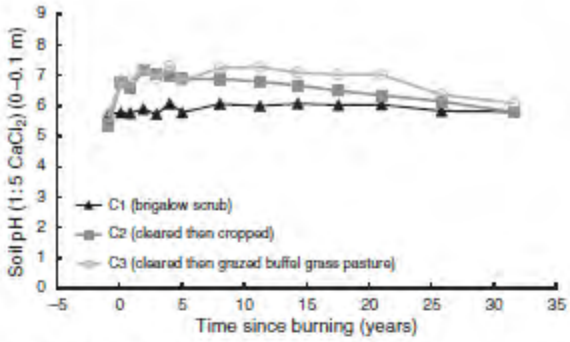

Fig. 4. Soil pH (1 : 5 soil/calcium chloride) (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

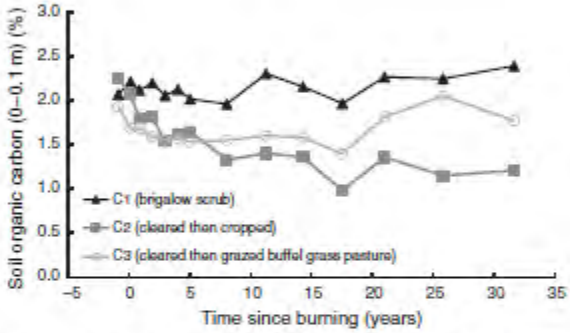

Fig. 5. Soil organic carbon (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

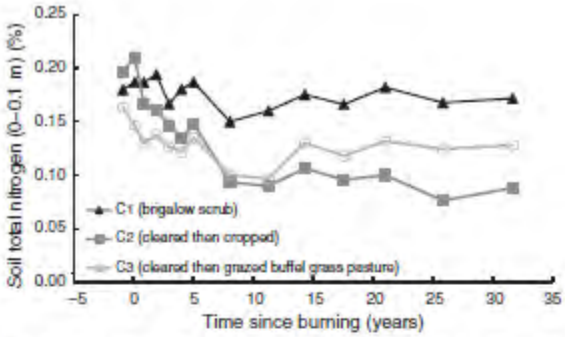

Fig. 6. Soil total nitrogen (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

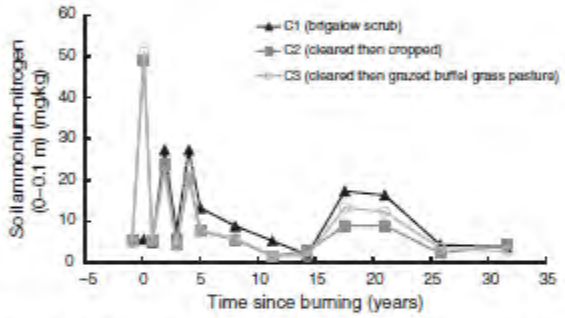

Fig. 7. Soil ammonium-nitrogen (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

from 2.25% in 1981 to 1.21% in 2014 ($P<0.001$, $R^2 = 88\%$) (Eqn 5 in Table 4) (Fig. 5). In C3, OC showed no significant linear or exponential trends from 1981 to 2014 ($P = 0.293$ and $P = 0.343$ respectively) (Fig. 5). However, this analysis masks a significant exponential decline of 28% from 1.93% in 1981 to 1.39% in 2000 ($P<0.001$, $R^2 = 79\%$) (Eqn 6 in Table 4) (Fig. 5) followed by an increase from 2000 to 2014.

Total nitrogen

Pre-clearing, TN concentrations in the three catchments averaged 0.18% (range 0.163–0.197%). From 1981 to 2014, TN in C1 averaged 1.75% with no significant linear or exponential trend ($P = 0.191$ and $P = 0.161$ respectively) (Fig. 6). Unlike C1, TN in C2 showed a significant exponential decline of 55%, or 1050 kg/ha, from 0.197% in 1981 to 0.088% in 2014 ($P<0.001$, $R^2 = 91\%$) (Eqn 7 in Table 4) (Fig. 6). Similar to C2, C3 showed a significant exponential decline of 22%, or 143 kg/ha, from 0.163% in 1981 to 0.128% in 2014 ($P = 0.01$, $R^2 = 49\%$) (Eqn 8 in Table 4) (Fig. 6).

These declines were exceeded when considering only the period 1981–2008, before the commencement of the adaptive land management phase to enhance soil fertility. In this period, TN in C2 showed a significant exponential decline of 61% or 1201 kg/ha, while TN in C3 showed a significant exponential decline of 24% or 192 kg/ha. From 2010 to 2014, the adaptive land management phase, TN in C1 and C3 had similar increases of 2.4% and 2.9% respectively; however, TN in C2 increased by 15.3% or 151 kg/ha.

Mineral nitrogen

Pre-clearing, NH_4-N concentrations in the three catchments averaged 5.19 mg/kg (range 4.87–5.5 mg/kg) and NO_3-N averaged 2.46 mg/kg (range 1.74–3.4 mg/kg). Average mineral nitrogen, being the sum of NH_4- and NO_3-N, was 7.65 mg/kg (range 6.61–8.58 mg/kg) (Figs 7–9). In the first sampling post-burning, NH_4-N in C2 and C3 spiked to an average of 8.9 times their pre-clearing concentrations when adjusted for the natural increase in NH_4-N observed in C1 (Fig. 7). This spike was short lived and by the following sampling, less than one year post-burning, NH_4-N concentrations in C2 and C3 declined back to that of C1. The NH_4-N concentrations fluctuated at all subsequent samplings, with C1 typically having highest concentrations and C2 and C3 having similar lower concentrations.

The NO_3-N in C2 and C3 had a similar spike post-clearing, increasing to an average of 7.5 times pre-clearing

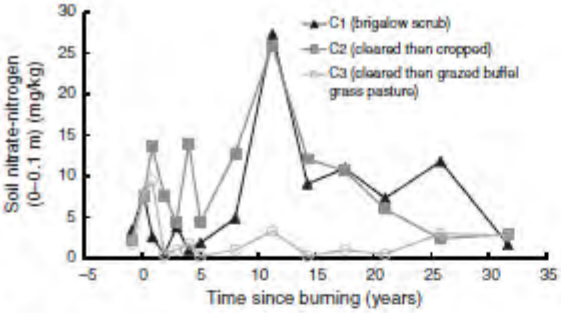

Fig. 8. Soil nitrate-nitrogen (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

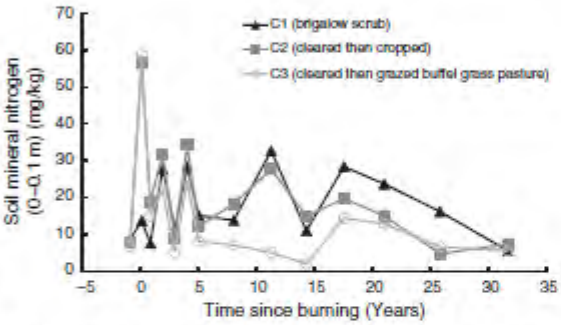

Fig. 9. Soil mineral nitrogen (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

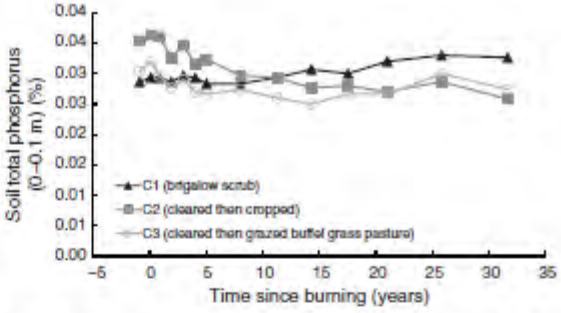

Fig. 10. Soil total phosphorus (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

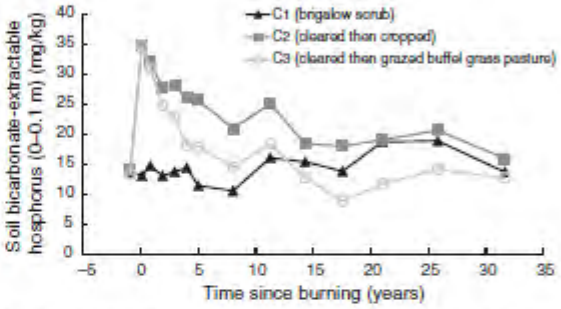

Fig. 11. Soil bicarbonate-extractable phosphorus (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

concentrations when adjusted for the natural decline in NO_3-N observed in C1 (Fig. 8). The spike was observed after the NH_4-N spike had declined back to pre-clearing concentrations. Elevated NO_3-N concentrations were observed in C2 for at least eight years post-burning, after which concentrations and fluctuations were similar to those observed in C1. Elevated NO_3-N concentrations in C3 declined within two years of burning and typically remained less than those observed in C1 with substantially less fluctuation.

Total mineral nitrogen showed a post-burning spike in C2 and C3 of 5.1 times their pre-clearing mineral nitrogen when adjusted for the natural increase in mineral nitrogen observed in C1 (Fig. 9). These increases declined substantially within one year post-burning and fluctuated similarly to mineral nitrogen concentrations in C1 up to five years post-burning. From this point mineral nitrogen in C1 and C2 had similar concentrations and fluctuations; however, concentrations in C3 were typically lower with less fluctuation.

Total phosphorus

Pre-clearing, TP concentrations in the three catchments averaged 0.031% (range 0.029–0.035%). In C1, TP showed a significant linear and exponential (Eqn 9 in Table 4) increase of 14% from 0.029% in 1981 to 0.033% in 2014 ($P < 0.001$, $R^2 = 76\%$ and $P < 0.001$, $R^2 = 77\%$ respectively) (Fig. 10). This increase was not constant over time, with no significant linear or exponential trend occurring before 2003 ($P = 0.082$ and $P = 0.15$ respectively).

Clearing and burning C2 and C3 increased TP by an average of 4%. Post-burning, TP in C2 showed a significant exponential decline of 29%, or 131 kg/ha, from 0.036% in 1982 to 0.027% in 2014 ($P < 0.001$, $R^2 = 91\%$) (Eqn 10 in Table 4) (Fig. 10). Similarly, TP in C3 showed a significant exponential decline of 14% or 59 kg/ha, from 0.032% in 1982 to 0.027% in 2014 ($P = 0.009$, $R^2 = 53\%$) (Eqn 11 in Table 4) (Fig. 10). Visually, the decline in C3 was most prevalent from 1982 to 1997 followed by an increase from 2000 to 2014. This is supported by linear regression showing increasing P-values and decreasing R^2 with each successive sampling from 1997 onwards. Fitting an exponential curve showed similar results with R^2 declining from 81% at 2003 to 52% at 2008.

Bicarbonate-extractable phosphorus

Pre-clearing, P(B) concentrations in the three catchments averaged 13.67 mg/kg (range 13.3–14 mg/kg). From 1981 to 2014, P(B) in C1 averaged 14.31 mg/kg and showed no significant linear or exponential trend ($P = 0.063$ and $P = 0.18$ respectively) (Fig. 11). Clearing and burning C2 and C3 increased P(B) by an average of 2.5 times pre-

clearing concentrations. After this initial increase a significant exponential decline occurred from 1982 to 2014 in both C2 ($P<0.001$, R^2 = 88%) (Eqn 12 in Table 4) and C3 ($P<0.001$, R^2 = 92%) (Eqn 13 in Table 4) (Fig. 11). Thirty-two years after the increase in P(B) concentrations as a result of burning, P(B) concentrations in C2 had declined to 15.9 mg/kg, equal to 114% of its pre-clearing concentration; P(B) concentrations in C3 had declined to 12.63 mg/kg, equal to 95% of its pre-clearing concentration. On a kg/ha basis, this was a decline of 18 kg/ha in C2 and 23 kg/ha in C3. During this 32-year period there was no significant correlation between P(B) and $pH_{(w)}$ in either C2 (P = 0.087) or C3 (P = 0.706).

Acid-extractable phosphorus

The behaviour of P(A) in all three catchments mirrored that of P(B). Pre-clearing, P(A) concentrations in the three catchments averaged 26 mg/kg (range 25–26.3 mg/kg). From 1981 to 2014, C1 P(A) averaged 23.48 mg/kg and showed no significant linear or exponential trend (P = 0.063 and P = 0.18 respectively) (Fig. 12). Clearing and burning C2 and C3 increased P(A) by an average of 2.2 times pre-clearing concentrations. After this initial increase a significant exponential decline occurred from 1982 to 2014 in both in C2 ($P<0.001$, R^2 = 91%) (Eqn 14 in Table 4) and C3 ($P<0.001$, R^2 = 97%) (Eqn 15 in Table 4) (Fig. 12). At 32 years post-burning, P(A) concentrations in C2 had declined to 24.63 mg/kg, equal to 94% of its pre-clearing concentration; P(A) concentrations in C3 had declined to 19.57 mg/kg, equal to 73% of its pre-clearing concentration. On a kg/ha basis, this was a decline of 36 kg/ha in C2 and 39 kg/ha in C3. During this 32-year period there was no significant correlation between P(A) and $pH_{(w)}$ in either C2 (P = 0.108) or C3 (P = 0.391).

Total sulfur

Pre-clearing, TS concentrations in the three catchments averaged 0.021% (range 0.02–0.023%). In C1, TS showed a significant linear and exponential (Eqn 16 in Table 4) increase of 9% from 0.021% in 1981 to 0.022% in 2014 (P = 0.002, R^2 = 55% and P = 0.008, R^2 = 51% respectively) (Fig. 13). As for TP, this increase was not constant over time with no significant linear trend occurring before 2000 (P = 0.058) or exponential trend before 2003 (P = 0.145).

Clearing and burning C2 and C3 increased TS by an average of 6%. Post-burning, TS in C2 showed a significant exponential decline of 49%, or 153 kg/ha, from 0.024% in 1982 to 0.012% in 2014 ($P<0.001$, R^2 = 90%) (Eqn 17 in Table 4) (Fig. 13). Data from C3 did not meet the assumptions for valid statistical testing so no statement of significance can be made about trends over the entire 32-year post-burning period. However, the calculated loss of TS was 23%, or 67 kg/ha, from 0.022% in 1982 to 0.017% in 2014. Visually, the increase in TS associated with clearing and burning declined rapidly from 1982 to 1984 followed by a gradual increase with a substantial spike in 2008 (Fig. 13). The initial decline during 1982–1987 was exponential (P = 0.009, R^2 = 93%). An exponential curve could be fitted to the data up to 2003 (P = 0.001, R^2 = 80%); however, inclusion of the 2008 data resulted in a nonsignificant regression (P = 0.286). No significant linear trend occurred from 1984 to 2000 (P = 0.211); however, incremental inclusion of data for 2003–2014 showed significant increases in TS (P = 0.005 to 0.037, R^2 = 35% to 60%).

Total potassium

Pre-clearing, TK concentrations in the three catchments averaged 0.483% (range 0.248–0.716%). In C1, TK averaged 0.716% and showed no significant linear or exponential trend from 1981 to 2014 (P = 0.084 and P = 0.119 respectively) (Fig. 14).

Clearing and burning C2 and C3 increased TK by an average of 5%. Post-burning, TK in C2 showed a significant exponential decline of 9% or 579 kg/ha, from 0.506% in 1982 to 0.461% in 2014 (P = 0.004, R^2 = 61%) (Eqn 18 in Table 4). Post-burning, TK in C3 showed a significant exponential decline of 10% or 364 kg/ha, from 0.264% in 1982 to 0.237% in 2014 ($P<0.001$, R^2 = 94%) (Eqn 19 in Table 4) (Fig. 14). At 32 years post-burning, TK concentrations in C2 had declined to 0.461%, equal to 95% of its pre-clearing concentration; TK concentrations in C3 had declined to 0.237%, equal to 96% of its pre-clearing concentration.

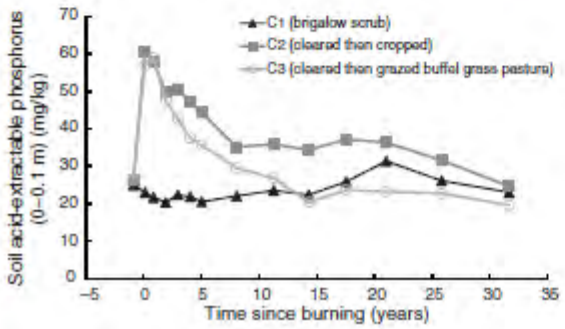

Fig. 12. Soil acid-extractable phosphorus (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

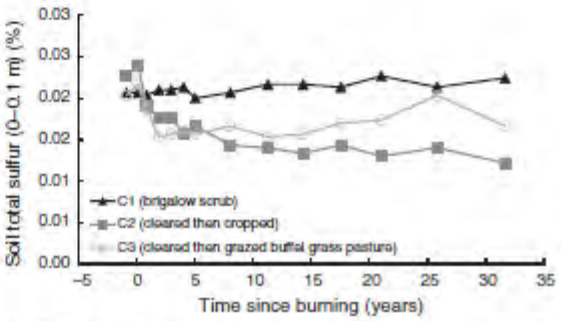

Fig. 13. Soil total sulfur (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

Exchangeable potassium

Pre-clearing, Exch. K concentrations in the three catchments averaged 0.46 $cmol_c$/kg (range 0.41–0.52 $cmol_c$/kg). From 1981 to 1990, Exch. K in C1 averaged 0.53 $cmol_c$/kg with no significant linear or exponential trend ($P = 0.729$ and $P = 0.731$ respectively) (Fig. 15). From 1990 to 2003, Exch. K increased, peaking at 0.77 $cmol_c$/kg, before declining to 0.63 $cmol_c$/kg in 2014 (Fig. 15). The Exch. K trend for the whole 32-year period was best described by a quadratic-by-quadratic curve ($P < 0.001$, $R^2 = 94\%$) (Eqn 20 in Table 4).

Clearing and burning C2 and C3 increased Exch. K by an average of 1.7 times pre-clearing concentrations. After this initial increase a significant exponential decline occurred from 1982 to 2014 in both C2 ($P < 0.001$, $R^2 = 80\%$) (Eqn 21 in Table 4) and C3 ($P < 0.001$, $R^2 = 89\%$) (Eqn 22 in Table 4) (Fig. 15). Thirty-two years after the increase in Exch. K concentrations as a result of burning, Exch. K concentrations in C2 had declined to 0.29 $cmol_c$/kg, equal to 65% of its pre-clearing concentration; Exch. K concentrations in C3 had declined to 0.28 $cmol_c$/kg, equal to 70% of its pre-clearing concentration.

Trends after accounting for natural fertility change

Organic carbon

Similar to the observed C2 OC data, the C2/C1 OC ratio also showed a significant exponential decline from 1981 to 2014 ($P < 0.001$, $R^2 = 91\%$) (Eqn 1 in Table 5). However, the 54% decline in the ratio was greater than the 46% decline in the observed C2 OC data. In contrast to the observed C3 OC data, the C3/C1 OC ratio showed a significant exponential decline of 21% ($P = 0.05$, $R^2 = 32\%$) from 1981 to 2014 (Eqn 2 in Table 5). The exponential decline of 24% ($P = 0.002$, $R^2 = 74\%$) in the C3/C1 OC ratio from 1981 to 2000 was similar to the observed data.

Total nitrogen

The C2/C1 TN ratio behaved similarly to the observed C2 TN data. The ratio showed a significant exponential decline of 53% from 1981 to 2014 ($P < 0.001$, $R^2 = 93\%$) (Eqn 3 in Table 5). Prior to the commencement of the adaptive land management phase the ratio showed a significant exponential decline of 58% from 1981 to 2014 ($P < 0.001$, $R^2 = 92\%$). From 2010 to 2014, the adaptive land management phase, the ratio

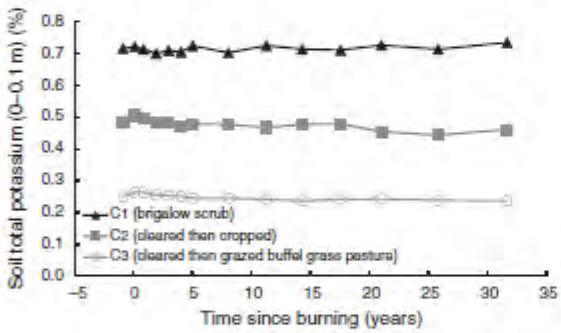

Fig. 14. Soil total potassium (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

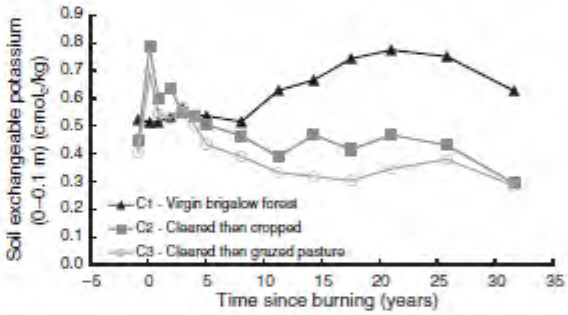

Fig. 15. Soil exchangeable potassium (0–0.1 m) over 32 years in C1 (brigalow scrub), C2 (cleared then cropped) and C3 (cleared then grazed buffel grass pasture).

Table 5. Equations describing the ratios of soil fertility over time in catchments two and three to the soil fertility in catchment 1, where *x* is years since burning

Parameter	Ratio	Period	Trend equation	*P*	R^2	Equation number
Organic carbon	C2/C1	1981–2014	C2/C1 OC = 0.5251 + 0.4332 × (0.8649^x)	<0.001	0.91	1
	C3/C1	1981–2012	C3/C1 OC = 0.7613 + 0.02445 × (0.1095^x)	0.05	0.32	2
Total nitrogen	C2/C1	1981–2014	C2/C1 TN = 0.5059 + 0.5222 × (0.8496^x)	<0.001	0.93	3
	C3/C1	1981–2014	C3/C1 TN = 0.7071 + 0.0681 × (0.290^x)	0.004	0.57	4
Total phosphorus	C2/C1	1982–2014	C2/C1 TP = 0.7334 + 0.5014 × (0.9406^x)	<0.001	0.95	5
	C3/C1	1982–2014	C3/C1 TP = 0.8621 + 0.2019 × (0.8091^x)	<0.001	0.75	6
Bicarbonate-extractable phosphorus	C2/C1	1982–2014	C2/C1 P(B) = 0.913 + 1.556 × (0.9216^x)	<0.001	0.86	7
	C3/C1	1982–2014	C3/C1 P(B) = 0.768 + 1.746 × (0.8197^x)	<0.001	0.91	8
Acid-extractable phosphorus	C2/C1	1982–2014	C2/C1 P(A) = 1.0516 + 1.6841 × (0.9018^x)	<0.001	0.97	9
	C3/C1	1982–2014	C3/C1 P(A) = 0.7736 + 1.952 × (0.8565^x)	<0.001	0.97	10
Total sulfur	C2/C1	1982–2014	C2/C1 TS = 0.6177 + 0.4874 × (0.756^x)	<0.001	0.87	11
	C3/C1	1982–2014	C3/C1 TS = 0.7736 + 0.337 × (0.245^x)	0.009	0.53	12
Total potassium	C2/C1	1982–2014	C2/C1 TK = 0.58 + 0.112 × (0.971^x)	0.001	0.68	13
	C3/C1	1982–2014	C3/C1 TK = 0.32862 + 0.04139 × (0.8752^x)	<0.001	0.85	14
Exchangeable potassium	C2/C1	1982–2014	C2/C1 Exch. K = 0.539 + 0.8672 × (0.8532^x)	<0.001	0.91	15
	C3/C1	1982–2014	C3/C1 Exch. K = 0.4269 + 0.8494 × (0.8556^x)	<0.001	0.94	16

increased by 13%. The C3/C1 TN data also behaved similarly to the observed C3 TN data. The ratio showed a significant exponential decline of 18% from 1981 to 2014 ($P = 0.004$, $R^2 = 57\%$) (Eqn 4 in Table 5). From 2010 to 2014, the adaptive land management phase, the ratio increased by 1%.

Total phosphorus

Compared with the observed TP data, both C2/C1 and C3/C1 TP ratios showed smaller increases with clearing and burning, averaging 2%, but greater declines over time. In C2, the C2/C1 TP ratio showed a significant exponential decline of 36% from 1982 to 2014 ($P<0.001$, $R^2 = 95\%$) (Eqn 5 in Table 5). In C3, the C3/C1 TP ratio showed a significant exponential decline of 23% from 1982 to 2014 ($P<0.001$, $R^2 = 75\%$) (Eqn 6 in Table 5).

Bicarbonate-extractable phosphorus

Compared with the observed P(B) data, both C2/C1 and C3/C1 P(B) ratios showed greater increases with clearing and burning, averaging 2.7 times the pre-clearing ratio, but similar declines over time from 1984 to 2014. The significant exponential decline in the C2/C1 ratio ($P<0.001$, $R^2 = 86\%$) (Eqn 7 in Table 5) to 114% of its pre-clearing ratio over 32 years post-burning, equalled the change in the observed data. The significant exponential decline in the C3/C1 ratio ($P<0.001$, $R^2 = 91\%$) (Eqn 8 in Table 5) to 95% of its pre-clearing ratio also equalled the change in the observed data.

Acid-extractable phosphorus

As for the P(B) ratios, both C2/C1 and C3/C1 P(A) ratios showed greater increases with clearing and burning compared with the observed P(A) data, averaging 2.4 times the pre-clearing ratio. However, over the 32 years post-burning, the P(A) ratios showed a smaller decline than the observed data. From 1982 to 2014, the C2/C1 P(A) ratio had a significant exponential decline ($P<0.001$, $R^2 = 97\%$) (Eqn 9 in Table 5) to 102% of its pre-clearing ratio while the C3/C1 P(A) ratio had a significant exponential decline ($P<0.001$, $R^2 = 97\%$) (Eqn 10 in Table 5) to 80% of its pre-clearing ratio.

Total sulfur

Clearing and burning C2 and C3 increased ratios of C2/C1 and C3/C1 TS by an average of 6%, equalling the average increase in the observed data. Post-burning, the C2/C1 TS ratio showed a significant exponential decline of 53% from 1982 to 2014 ($P<0.001$, $R^2 = 87\%$) (Eqn 11 in Table 5), similar to the observed data. In contrast to the observed C3 TS data, which did not meet the assumptions for valid statistical testing, the C3/C1 TS ratio could be fitted with a significant exponential decline curve ($P = 0.009$, $R^2 = 53\%$) for the whole post-burning period (Eqn 12 in Table 5). The decline in the C3/C1 TS ratio from 1982 to 2014 was 29%.

Total potassium

Clearing and burning C2 and C3 increased ratios of C2/C1 and C3/C1 TK by an average of 4%, similar to the observed data. Post-burning, the ratios for both catchments showed significant exponential declines, similar to the observed data. From 1982 to 2014, the C2/C1 TK ratio declined by 10% ($P = 0.001$, $R^2 = 68\%$) (Eqn 13 in Table 5) and the C3/C1 TK ratio declined by 12% ($P<0.001$, $R^2 = 85\%$) (Eqn 14 in Table 5).

Exchangeable potassium

Compared with the observed Exch. K data, both C2/C1 and C3/C1 Exch. K ratios showed greater increases with clearing and burning, averaging 1.8 times the pre-clearing ratio. The significant exponential decline in the C2/C1 ratio ($P<0.001$, $R^2 = 91\%$) (Eqn 15 in Table 5) to 55% of its pre-clearing ratio over 32 years post-burning, was greater than the decline in the observed data. The significant exponential decline in the C3/C1 ratio ($P<0.001$, $R^2 = 94\%$) (Eqn 16 in Table 5) to 59% of its pre-clearing ratio was also greater than the decline in the observed data.

Comparison of approaches for assessing fertility decline

All of the significant declines in observed soil fertility post-burning in both C2 and C3 (Table 4) were confirmed by the ratio analysis (Table 5). When the observed soil fertility data from C2 was adjusted for the natural variation in soil fertility in the control catchment, the R^2 of the exponential decline curves increased by an average of 3% with a maximum change of 12%. When this adjustment was made for C3, the R^2 of the exponential decline curves increased by an average of 9%; however, the maximum change was 42%. While observed C3 OC and TS data showed no significant change in the 32 years post-burning, adjusting for the natural variation in soil fertility in the control catchment revealed a significant decline, similar to C2.

Correlations between soil nitrogen and phosphorus decline and removal in produce

The sum of total nitrogen removed from C2 in grain between soil samplings showed an exponential relationship with soil TN ($P = 0.061$, $R^2 = 54\%$) (Eqn 5). The sum of total phosphorus removed showed an exponential relationship with TP ($P = 0.014$, $R^2 = 75\%$) (Eqn 6), P(A) ($P = 0.01$, $R^2 = 78\%$) (Eqn 7) and P(B) ($P = 0.061$, $R^2 = 54\%$) (Eqn 8).

$$\text{C2 TN}(\%) = 0.0811 + 0.0993 \times (0.997^{\text{TN removed in grain (kg/ha)}}) \quad (5)$$

$$\text{C2 TP}(\%) = 0.02739 + 0.0085 \times (0.970^{\text{TP removed in grain (kg/ha)}}) \quad (6)$$

$$\text{C2 P(A)}(\text{mg/kg}) = 34.26 + 37.1 \times (0.945^{\text{TP removed in grain (kg/ha)}}) \quad (7)$$

$$\text{C2 P(B)}(\text{mg/kg}) = 18.55 + 13.59 \times (0.971^{\text{TP removed in grain (kg/ha)}}) \quad (8)$$

The sum of total nitrogen and total phosphorus removed from C3 in beef showed no significant correlation with soil TN ($P = 0.907$) and soil TP ($P = 0.702$) respectively. The sum of

total phosphorus removed showed an exponential relationship with P(A) ($P < 0.001$, $R^2 = 97\%$) (Eqn 9) and P(B) ($P = 0.002$, $R^2 = 75\%$) (Eqn 10).

$$\text{C3 P(A)(mg/kg)} = 19.83 + 27.63 \times (0.781^{\text{TP removed in beef (kg/ha)}}) \quad (9)$$

$$\text{C3 P(B)(mg/kg)} = 12.26 + 12.63 \times (0.709^{\text{TP removed in beef (kg/ha)}}) \quad (10)$$

Discussion

Nutrient cycling in natural ecosystems was traditionally considered a steady-state, closed system, with nutrients being taken up from the soil by plant roots and being recycled back to the soil through leaf and litter fall and root decay (Murty *et al.* 2002; Radford *et al.* 2007). Under this hypothesis it is expected that no change in soil fertility would occur under brigalow scrub. This was generally supported by the study data, with no significant change in OC, TN, P(B), P (A) and TK. Radford *et al.*'s (2007) study of OC and TN at this site from 1981 to 2003 also supports the hypothesis. However, as rainfall patterns fluctuate over time, extended wet periods are likely to result in increased nutrient uptake from deeper down the soil profile by the extending root systems of actively growing plants, followed by increased leaf and litter fall and root decay. This may lead to measurable nutrient redistribution at particular timescales within an otherwise steady-state ecosystem. This redistribution may account for the increases noted in TP and TS. Alternative mechanisms for redistribution include the ability of plants to move water through the soil profile via hydraulic lift and downward siphoning, allowing access to nutrients otherwise unavailable due to inadequate soil moisture (Sardans and Peñuelas 2014). Rainfall also provides nutrient inputs. The rainfall nutrient concentrations reported by Packett (2017) indicate that from 1981 to 2014, an estimated 60 kg/ha of dissolved nitrogen, 0.5 kg/ha of dissolved phosphorus (in the form of phosphate) and 1070 kg/ha of dissolved sulfur (in the form of sulfate) have been supplied in rainfall. The magnitude of these inputs has increased over time as a result of anthropogenic activity which, for example, has increased atmospheric concentrations of carbon dioxide and nitrogen (Tipping *et al.* 2017; Schulte-Uebbing and de Vries 2018). These inputs are a counter to the natural loss of nutrients in runoff and may also explain fluctuations within what was traditionally considered a steady-state ecosystem. Feedback cycles between increasing deposition of carbon and nitrogen and increasing temperature may also contribute to fertility changes (Crowther *et al.* 2016; Tipping *et al.* 2017), which would affect all land uses, but would likely be easiest to detect in virgin ecosystems where no other treatment effects are present.

Irrespective of the analysis methodology, two distinct trends in soil fertility were observed as a result of land development and land use change. The first trend was for clearing and burning to release a flush of nutrients which subsequently declined over time to near, or below, pre-clearing concentrations. The clearest display of this trend was in mineral nitrogen and available phosphorus, with smaller increases in TP, TS and TK. The second trend was an ongoing decline in fertility commencing at clearing. This was observed in OC and TN. Both of these trends reflect predictions that clearing brigalow followed by subsequent exploitative land use would result in declining nutrient availability and landscape productivity (Dowling *et al.* 1986).

The effect of land clearing and burning on soil bulk density

Worldwide, an increase in bulk density as a result of land development and long-term cropping or grazing is commonplace (Dalal and Mayer 1986*b*; Murty *et al.* 2002; Dalal *et al.* 2005). The primary mechanism for increase is physical compaction by machinery and animal hoof traffic, and the degradation of soil structure and loss of organic matter in tilled soil. Conceptually, land use change followed by more than 30 years of either cropping or grazing should have increased bulk density in both the cropped and grazed catchments of this study. Although the significance of trends identified via regression analysis varied, all comparisons of pre-clearing bulk density with long-term averages under cropping and grazing showed an increase with land development. In the same period, bulk density under brigalow remained constant. Changes in the ratios of bulk density between the developed catchments and the control catchment also suggested an increase with land development.

Determining change in bulk density was confounded due to it only being measured in seven of the 14 sampling events. In addition to limited data, other confounding issues include differing soil water content between samplings and the corresponding shrinking and swelling characteristics of Vertosols; and the ability of the chosen core diameter to obtain representative samples, particularly in heavily cracked dry soils, in wet soils prone to compaction or distortion and in soils prone to shattering (Berndt and Coughlan 1977; Coughlan *et al.* 1987; Al-Shammary *et al.* 2018).

Coughlan *et al.* (1987) stress the influence of soil water content on bulk density and note that the swelling of Vertosols with increasing soil water and the resultant reduction in bulk density complicates the comparison of measurements over time. On two occasions soil water was measured within two weeks of a soil sampling event that had measured bulk density. In both instances, soil water under cropping and grazing was substantially greater than under brigalow. However, despite likely reductions in observed bulk density due to increased soil water storage, bulk densities of the agricultural catchments continued to be similar or higher than that of the brigalow catchment. This provides additional evidence that an increase in bulk density has occurred with land development and long-term cropping or grazing. Other than variations in soil water content, the primary limitation to measuring bulk density in this study is likely to be sampling error associated with loss of sample and inaccurate core trimming in friable soils or due to shattering of dry soil during coring.

The effect of land clearing and burning on soil pH

Globally, the burning of forests as a result of land use change and the burning of crop residues in agricultural systems both result in increased soil pH (Ellis and Graley 1983; Roder *et al.* 1993; Guinto *et al.* 2001; Herpin *et al.* 2002; Fraser and Scott 2011). The mechanism of this increase has been attributed to the deposition of ash which releases basic cations (Raison 1979; Guinto *et al.* 2001; Castelli and Lazzari 2002; Herpin *et al.* 2002). Upon wetting, these cations hydrolyse to form alkaline residues which convert to hydroxides or carbonates (Fraser and Scott 2011). Increases in soil pH as a result of burning have been shown to persist for decades (Herpin *et al.* 2002; Fraser and Scott 2011).

The increases in soil pH as a result of clearing and burning brigalow scrub in this study, the mechanism of increase and the persistence of increased pH, clearly follow typical global responses. For example, Hunter and Cowie (1989) attributed the initial increase in soil pH at this site to soil heating and the release of basic cations as a result of organic matter combustion. Alkaline salts were then likely leached from strongly alkaline ash deposits, which had an average pH of 12.5 (Hunter and Cowie 1989), further raising soil pH. Thirty-two years after burning, soil pH in both agricultural catchments was greater than it was pre-clearing.

The effect of raised soil pH on nutrient availability

Changes in soil pH can have implications for nutrient availability. The preferred range of soil $pH_{(w)}$ for plant growth is 6 (slightly acid) to 8 (slightly or mildly alkaline), with nutrient availability optimised in the range 6–7 (Rayment and Lyons 2011). For example, maximum phosphorus availability is considered to occur near pH 6.5 (Penn and Camberato 2019). Pre-clearing, soil $pH_{(w)}$ in C1 and C2 was classified as neutral, while C3 was classified as slightly or mildly alkaline (Bruce and Rayment 1982; Rayment and Lyons 2011). As such, the pH of the surface soil in its pre-cleared state is unlikely to limit nutrient availability. The increases in soil pH as a result of clearing and burning at this site were not great enough to raise the soil pH classifications of the catchments, with C2 remaining neutral and C3 remaining slightly or mildly alkaline; both still within the preferred range for plant growth. Despite being above the optimum range for nutrient availability, average soil $pH_{(w)}$ in C2 and C3 post-clearing and burning was below the threshold of 7.9 where plant availability of nutrients such as phosphorus may be restricted (Rayment and Lyons 2011).

About 36% of Queensland soils have a neutral or alkaline surface pH. Within the Brigalow Belt bioregion these neutral or alkaline soils are dominated by Black and Grey Vertosols (Ahern *et al.* 1994). The Vertosols of the BCS are representative of these soils, with average soil $pH_{(w)}$ values within the range reported for other Vertosols developed for cropping and grazing within the bioregion (Dalal and Mayer 1986*b*; Allen *et al.* 2016). The limited field data in the literature suggest that the pH of these well-buffered Vertosols (Ahern *et al.* 1994; Page *et al.* 2018) is not easily changed, much less raised to a level likely to limit plant growth. For example, additions of gypsum to a moderately alkaline Vertosol had no significant effect on pH (Hulugalle *et al.* 2010). Similarly, the addition of biochar, a product of organic matter combustion, to a neutral Vertosol had no significant effect on pH or crop productivity (Macdonald *et al.* 2014). Land use change was reported to increase soil $pH_{(w)}$ and limit nutrient availability for plant growth on a grazed Vertosol (Sangha *et al.* 2005). However, the natural variability in soil $pH_{(w)}$ reported for the three catchments in this study before clearing and burning equalled many of the increases in soil $pH_{(w)}$ that Sangha *et al.* (2005) attributed to land use change. This suggests that Sangha *et al.* (2005) found limited evidence of pH increase and resultant decline in nutrient availability.

Additionally, declines in available nutrients have been reported in the neutral or alkaline Vertosols of the Brigalow Belt bioregion in the absence of soil pH change. For example, significant declines in available phosphorus were observed over seven years of cropping with no significant change in pH (Standley *et al.* 1990). Similarly, significant declines in available phosphorus occurred in this study during a nine-year period with no significant change in soil pH. Over the entire experimental period, there was no significant correlation of soil $pH_{(w)}$ with P(B) and P(A) under cropping or grazing. Subsoil acidity, and to a lesser extent alkalinity (Dang *et al.* 2006*a*, 2006*b*, 2008; Page *et al.* 2018), is a much greater concern to agricultural production on the neutral or alkaline Vertosols of the Brigalow Belt bioregion than any unlikely reduction in nutrient availability as a result of fire-induced increases in surface soil pH.

The effect of land clearing and burning on soil fertility

Increases in mineral nitrogen, TP, available phosphorus, TS and TK as a result of burning vegetation on the soil surface, as observed in this study, are well documented in both the Australian and international literature (Ellis and Graley 1983; Kyuma *et al.* 1985; Carreira and Niell 1995; Castelli and Lazzari 2002; Brennan *et al.* 2004; Fraser and Scott 2011; Butler *et al.* 2017; MacDermott *et al.* 2017). The increase has been attributed to nutrient release from plant material and deposition in ash, and is often referred to as the ash bed effect (Raison 1979; Kyuma *et al.* 1985; Roder *et al.* 1993; Castelli and Lazzari 2002; Herpin *et al.* 2002; May and Attiwill 2003; Cowie *et al.* 2007). These increases are typically restricted to the surface few centimetres of the soil profile and often persist for only one to two years (Raison 1979; Ellis and Graley 1983; Kyuma *et al.* 1985; Castelli and Lazzari 2002).

Decreases in soil OC and TN as a result of burning are also well documented in Australian and international literature (May and Attiwill 2003; Oyedeji *et al.* 2016). However, some studies, including a meta-analysis, have shown no change in TN as a result of burning (Guinto *et al.* 2001; Wan *et al.* 2001). Initial soil nitrogen level, soil clay content and fire intensity can account for these contrasting observations. Firstly, low-fertility soils may have already lost their most fire-susceptible nitrogen fractions. Secondly, clay particles within soil assist in physically protecting organic matter from the effects of fire, therefore soils with varying clay content are likely to display different responses to burning (Guinto *et al.* 2001). Finally, low-intensity fires have been

shown to increase TN whereas high-intensity fires decrease TN (Raison 1979). The fire intensity resulting from the burning of pulled brigalow scrub would be similar to that of slash fires and wildfires, providing intense heat for long periods (Johnson 1964). The loss of TN with burning observed in this study is consistent with that recorded from other sites subjected to high-intensity fires (Raison 1979).

The effect of land use change on soil OC

The decline in OC when brigalow scrub was developed for cropping supports the earlier findings of Radford *et al.* (2007) at this site, and mirrors the response of other pre-clearing Australian and international landscapes developed for, and managed as, long-term cropping (Murty *et al.* 2002; Collard and Zammit 2006). The decline is typically restricted to the surface soil layers no deeper than 1 m (Dalal *et al.* 2005). The mechanism is usually attributed to the removal of nutrients in harvested grain, reduced carbon inputs and the impacts of tillage on soil structure, chemical and biological processes including shattering, redistribution, oxidation and decomposition (Murty *et al.* 2002).

The finding of no significant change in observed OC when brigalow scrub was developed for grazing is in agreement with the findings of other studies conducted at this site (Radford *et al.* 2007; Dalal *et al.* 2011, 2013). The international review of Murty *et al.* (2002) concluded that on average, the conversion of forest to uncultivated grazing does not lead to a loss of OC; however, this does not hold for all specific sites. Within Australia, Harms *et al.* (2005) reported OC losses from coarse-textured soils such as Kandosols as a result of changing land use from native vegetation to grazing, but found no change in Sodosols and Vertosols, which reflect the soil types of this study. However, although no decline in OC was observed after clearing brigalow followed by grazing for 31 years, a significant decline was evident during the first 17 years of grazing – the period of continuous stocking before irregular spelling. When the observed OC data were adjusted for the natural variation in soil fertility in the control catchment, a statistically significant decline in the OC ratios between the catchments was found for the entire study period. These alternative approaches suggest that a decline in OC has occurred.

Change in OC cycling under grazing at this site is apparent in the observation that OC derived from the original brigalow vegetation comprised only 58% of measured OC while buffel grass-derived OC contributed the remaining 42% (Dalal *et al.* 2011). Without this replacement of carbon by buffel grass, a greater decline in total OC would have occurred. For example, declines in soil OC have been found at sites with low inputs of root biomass (Li *et al.* 2018), which is expected given that root biomass is the main source of carbon input to soil OC (Rasse *et al.* 2005). Indeed, long-term bare fallow sites with nil inputs of organic matter have been found to lose between 21% and 65% of initial soil OC over 36 and 80 years respectively (Barré *et al.* 2010). This may explain the observed increase in OC after the commencement of irregular spelling in 1996, undertaken specifically for the purpose of allowing regeneration of the buffel grass pasture. If grazing management over the 32 years since development had resulted in continual overgrazing, it is likely that the ability of the buffel grass pasture to sequester carbon and buffer fertility decline would have been reduced or negated (Conant and Paustian 2002).

Buffel grass growth is also highly responsive to seasonal rainfall trends, hence variation in the observed OC data could indicate changes in carbon inputs and nutrient redistribution within a steady-state ecosystem, as hypothesised could occur under brigalow scrub. The literature also shows that there is potential for increased OC sequestration with low precipitation and decreased sequestration with high precipitation. McSherry and Ritchie (2013) attribute this to greater, more active microbial biomass carbon and more labile organic matter pools in wetter environments, which may increase carbon turnover under grazing. This suggests that carbon sequestration at the study site is likely to vary temporally due to the variable semiarid climate, further explaining fluctuations in observed OC.

The effect of land use change on soil TN

As for OC, the decline in TN when brigalow scrub was developed for cropping supports the earlier findings of Radford *et al.* (2007) at this site. Significant loss of TN following the conversion of forest to cropping or multiple years of cultivated cropping alone was also found in other long-term studies (Dalal and Mayer 1986*b*; Dalal *et al.* 2005; Anaya and Huber-Sannwald 2015) and international reviews (Murty *et al.* 2002). Removal of nitrogen in grain has been identified as the primary mechanism of TN loss (Dalal and Mayer 1986*a*; Dalal *et al.* 2005) and was shown by Radford *et al.* (2007) to account for 39% of the TN lost from the surface 0.3 m of the soil profile at this site from 1981 to 2003. In agreement with these findings, regression analysis showed nitrogen removed from the cropped catchment as grain accounted for 54% of the variation in TN from 1981 to 2014. On a kg/ha basis, nitrogen removed from the catchment in grain accounted for 80% of the TN lost from the surface 0.1 m of the soil profile before planting of the legume ley pasture. In contrast, the equivalent of 8% of soil TN decline was lost in runoff (Elledge and Thornton 2017).

The increase in TN from 2008 to 2014 may be attributed to nitrogen fixation by the butterfly pea legume ley pasture planted in 2010. The ley pasture was planted in order to arrest the declining TN that was limiting the productivity of dryland farming in the catchment (Radford *et al.* 2007; Huth *et al.* 2010). The ability of butterfly pea to increase TN in a grazed ley pasture system is well documented in central Queensland (Collins and Grundy 2005). However, despite the addition of legumes into the cropping system, modelling suggests that fertility decline will continue (Huth *et al.* 2010).

With no pasture legumes to maintain fertility, developing brigalow scrub for grazing resulted in ongoing TN decline from 1981 to 2014. This supports the findings of Dalal *et al.* (2013), who found significant decline in TN at this site 23 years after clearing brigalow scrub for grazing. However, both of these studies contrast with the findings of Radford *et al.* (2007). This is likely due to differences in sampling strategies, analytical methods and the specific

comparisons made. This current study reports the longest period of record, used the most intensive sampling strategy, consistent analytical methodology and compared each catchment to its starting soil fertility, and so should be considered the most robust. Globally, the conversion of forest to uncultivated grazing generally does not lead to a loss of TN; however, this does not hold for all specific sites (Murty *et al.* 2002). This is reflected in the contrasting conclusions of Australian studies. For example, a single paired-site study by Dalal *et al.* (2005) found a decrease in TN when mulga forest was developed for grazed pasture, with the majority of loss occurring from the surface 0.1 m of the soil profile. Removal of TN in beef accounted for less than half of this loss, with additional potential losses via deep drainage. In contrast, Harms *et al.* (2005) found no significant loss of TN across multiple paired-sites encompassing the same soil and vegetation. Similar to Dalal *et al.* (2005), Pringle *et al.* (2016) found a 19% decline in TN where fire had been used to clear native vegetation for grazing across 11 locations in the Brigalow Belt bioregion. The similarity of the 11 locations with the monitoring sites of the BCS is undisputable, extending to having been historically subjected to the same land use change and similar subsequent management regime (Allen *et al.* 2016). This clearly demonstrates that the decline in TN observed when brigalow scrub was developed for grazing in this study is representative of decline processes under grazing in the wider Brigalow Belt bioregion. It is also likely representative of fertility decline across most of the extensively grazed landscapes of northern Australia, which can halve the productive capacity of the pasture (Peck *et al.* 2011). The incorporation of legumes, particularly leucaena, into grazing systems within the Brigalow Belt bioregion has been shown to increase both soil fertility and enterprise profitability (Bowen and Chudleigh 2017). However, broad-scale adoption within the grazing industry is still evolving (Burgis 2016).

In this study there was no significant correlation between the decline in TN and the amount of nitrogen removed in beef. However, removal of nitrogen in beef accounted for 32% of the TN lost from the surface 0.1 m of the soil profile. This is comparable to the equivalent of 25% of soil TN decline lost in runoff (Elledge and Thornton 2017). Losses of nitrogen through volatilisation from urine and faeces was estimated to remove 71 kg/ha of nitrogen, equivalent to 49% of TN loss. Annual buffel grass yields have been shown to be in the order of 3000 kg/ha (Myers and Robbins 1991). Previous work at this site has shown the standing aboveground biomass of buffel grass was 4601 kg/ha and contained the equivalent of 27.6 kg/ha of nitrogen, equivalent to 19% of TN loss (Thornton and Elledge 2013). Annual root growth biomass estimations at this site are similar to aboveground biomass (Dalal *et al.* 2013) and are likely to have similar nitrogen contents (Robertson *et al.* 1993), potentially accounting for a similar proportion of TN loss. The work of Graham *et al.* (1985), on similar vegetation and soil associations elsewhere within the Fitzroy Basin, suggests that this is likely an underestimation having measured 207 kg/ha of nitrogen in buffel grass roots to 0.3 m. The combination of annual aboveground and belowground plant growth and litter deposition over 32 years likely accounts for the majority of TN decline and immobilisation in plant biomass under grazing although substantial losses occur via removal in beef, volatilisation and runoff.

The effect of land use change on soil mineral nitrogen

The immediate, short-term increase in NH_4-N post-burning in C2 and C3, followed by a delayed and longer-lived increase in NO_3-N, clearly demonstrates the generalised pattern of available nitrogen response to fire, as documented in the meta-analyses of Boerner *et al.* (2009) and Wan *et al.* (2001). The mechanism of increase is attributed to NH_4-N liberation from organic matter followed by its nitrification to NO_3-N. This is supported by previous work at this site attributing many of the changes in soil chemistry after burning to the effects of soil heating (Hunter and Cowie 1989). Subsequent declines over time were attributed to runoff losses, plant uptake and microbial immobilisation (Hunter and Cowie 1989).

The extended period of elevated NO_3-N under cropping is likely to reflect the stimulating influence of fallow tillage on nitrogen mineralisation as described by Dalal and Mayer (1986*b*). This is supported by the observed decline in mineral nitrogen around 15 years post-burning that corresponds to a change in cropping management practices to minimum tillage and opportunity cropping. These practices reduce tillage and shorten fallows, leading to reduced mineralisation combined with increased nitrogen uptake due to increased cropping frequency. Declining TN is also likely to result in declining mineral nitrogen under continuous cropping. This is demonstrated elsewhere within the Dawson subcatchment of the Fitzroy Basin where mineral nitrogen levels of Vertosols after more than 30 years of cropping were 82% lower than adjacent Vertosols still supporting native brigalow scrub (Shrestha *et al.* 2015).

The rapid decline of NO_3-N in C3 is likely due to uptake by the newly planted buffel grass pasture. Similar pastures in central Queensland have been shown to be highly productive in the first two years after planting due to high levels of available nitrogen, with productivity declining over time as available nitrogen declines and nitrogen immobilisation occurs (Myers and Robbins 1991). Decline and immobilisation in the grazed catchment at this site is demonstrated after the first two to three years in the ongoing low concentrations and minimal fluctuation of TN and mineral nitrogen compared with that under cropping and brigalow. It is further demonstrated by the decline in pasture productivity and cattle liveweight gain over time at this site as described by Radford *et al.* (2007).

The effect of land use change on soil TP

Although the enrichment of surface soil with phosphorus as a result of burning was clear, in the absence of fertilisation, phosphorus depletion commenced immediately. Within four years, TP was depleted to near or below pre-clearing concentrations. Removal of phosphorus in grain was equivalent to 95% of TP lost under cropping; however, removal of phosphorus in beef was only equivalent to 22%

of the loss of TP under grazing. Removal of TP in runoff was equivalent to 12% of the total decline under cropping and 11% of the total decline under grazing (Elledge and Thornton 2017). Extraction of phosphorus from the soil profile below 0.1 m is clearly occurring under cropping given that TP removal in grain and runoff exceeded the measured TP decline in the top 0.1 m of the soil profile.

Other Queensland and international studies have also reported declines in TP under cropping (Bowman *et al.* 1990; Standley *et al.* 1990; Zhang *et al.* 2006; Song *et al.* 2011; Wang *et al.* 2012). Typically, the decline could be almost entirely accounted for in crop removal (Dalal 1997). However, changes in TP under grazing are typically less pronounced and the mechanism for change less obvious. Erosion and leaching losses are acknowledged to play some role in TP decline under grazing, but they are unlikely to be a key decline mechanism, particularly in flat landscapes with high clay content soils such as Vertosols (Townsend *et al.* 2002). Internationally, the removal of phosphorus in beef was poorly correlated with TP decline and hence was unlikely to be a key decline mechanism (McGrath *et al.* 2001; Townsend *et al.* 2002). These observations led Townsend *et al.* (2002) to conclude that the bulk of TP decline must be occurring by other mechanisms.

Previous work has shown the aboveground biomass of buffel grass in the grazed catchment contained the equivalent of 5.8 kg/ha of phosphorus (Thornton and Elledge 2013). Assuming the soil contribution to phosphorus in aboveground biomass is equal to one-third of the phosphorus content of the biomass grown each season, this transfer over 32 years is equivalent to the amount of TP removed from the soil. The cycling of phosphorus from soil to plant to animal waste is also likely to account for some of the phosphorus lost, given that phosphorus in dung can exceed that contained within both the aboveground plant and litter biomass (Dubeux *et al.* 2007), and its deposition on the soil surface increases its susceptibility to loss in runoff (McGrath *et al.* 2001). The key mechanisms of decline in TP under grazing in this study is likely to be redistribution into plant biomass and litter with additional smaller losses through runoff and removal in beef.

The effect of land use change on soil available phosphorus

Similar to TP, the enrichment of surface soil with available phosphorus as a result of burning was clear, and in the absence of fertilisation, depletion commenced immediately. Under cropping, P(B) was still above pre-clearing concentrations at 32 years post-burning while P(A) had declined below pre-clearing concentrations. Under grazing, both P(A) and P(B) declined below pre-clearing concentrations within 14 years post-burning.

Other long-term Queensland studies conducted at Chinchilla and Mt. Murchison on Vertosols that originally supported brigalow vegetation associations, also found declines in available phosphorus as a result of cropping (Thomas *et al.* 1990; Dalal 1997). The declines were attributed to removal of phosphorus in grain, transformation within soil, and runoff and erosion processes. However, at Mt. Murchison, it was noted that phosphorus removal by the crop and stubble could not be accounted for simply in terms of P(A) and P(B) (Thomas *et al.* 1990). Greater retention of P(B) in treatments with higher soil biomass and the replacement of depleted P(B) with phosphorus from other pools (Standley *et al.* 1990) further indicates that land use change alters the speciation and cycling of phosphorus in soil. Similar declines in available phosphorus are noted internationally (Nancy Mungai *et al.* 2011; Song *et al.* 2011). They are also attributed to cultivation and erosion-induced declines in soil structure leading to reductions in soil organic matter, promoting microbial cycling of available phosphorus (Zhang *et al.* 2006). Harvest losses were also noted as a decline mechanism. In this study, phosphorus removal in grain was better correlated with TP than with either measure of available phosphorus. Because TP accounts for losses from the organic pool, this suggests that both the inorganic and organic phosphorus pools are depleted by grain removal. The key mechanism of decline in available phosphorus under cropping in this study is likely to be removal in grain combined with cycling into other phosphorus pools.

The levels of phosphorus enrichment and decline following land use change for grazing in this study exceed that reported by Sangha *et al.* (2005) for grazing systems developed on similar vegetation and soil associations elsewhere within the Fitzroy Basin. Their study found no difference in P(B) under uncleared brigalow compared with sites cleared for grazing five, 12 and 33 years previously. This lack of difference in P(B) is likely due to the space-for-time paired site approach, which fails to guarantee the same starting condition for each pair; the impacts of grazing on the uncleared control plots; and the P(B) levels of their uncleared control being only 56% of the BCS brigalow scrub control in this study.

Internationally, changing land use from virgin forest to grazing has also resulted in an initial flush of available phosphorus followed by a decline (McGrath *et al.* 2001; Townsend *et al.* 2002). Pasture growth and aboveground biomass accounted for some of the decline; however, beef production was poorly correlated. While removal of phosphorus in beef showed no correlation with TP in this study, it explained 97% of the decline in P(A) and 75% of the decline in P(B). This suggests that any loss of phosphorus from the organic pool is likely being replaced from the inorganic pool (Garcia-Montiel *et al.* 2000; McGrath *et al.* 2001; Townsend *et al.* 2002; Fonte *et al.* 2014). The key mechanism of decline in available phosphorus under grazing in this study is likely to be removal in beef combined with cycling into other phosphorus pools. Additional losses are likely through the cycling of phosphorus from soil to plant to animal waste with smaller losses in runoff.

The effect of land use change on soil TS

As for phosphorus, surface soil was enriched with sulfur as a result of burning and, in the absence of fertilisation, depletion commenced immediately. Other studies, both in the Brigalow Belt bioregion and internationally, attribute sulfur decline under cropping to mineralisation associated with cultivation (Dalal and Mayer 1986*b*; Wang *et al.* 2006; Kopittke *et al.* 2016). Decline under grazing has also been attributed to

accelerated mineralisation with additional declines as a result of reduced inputs of plant residues, particularly in arid, low-fertility landscapes, and losses in runoff and leaching (Steffens *et al.* 2008; Wiesmeier *et al.* 2009).

Sulfur is a constituent of organic matter and has similar responses under agriculture as nitrogen (Williams 1962; Kopittke *et al.* 2016). The rapid decline in sulfur within two years of burning mirrors that of total and mineral nitrogen, suggesting its removal from soil by actively growing crops and pasture in response to the ash bed effect. Leaching losses are also likely during this time given deep drainage through the soil profile increased from <1 mm/year pre-clearing to 59 mm/year under development for cropping and 32 mm/year under development for grazing (Silburn *et al.* 2009). Some ongoing loss of easily leached sulfur fractions may have occurred under cropping where deep drainage averaged 19.8 mm/year; however, leaching losses under grazing are unlikely with deep drainage returning to near pre-clearing rates of <1 mm/year.

Although some of the continued sulfur decline under cropping can certainly be attributed to mineralisation associated with tillage, estimates of grain sulfur content combined with measured yield data indicate that 63% of the lost sulfur can be accounted for in crop removal. In contrast, estimates of the sulfur content of beef combined with measured liveweight gain data indicate that only 5% of the lost sulfur can be accounted for in beef removal. This is supported by the observed sulfur data showing continued decline under cropping but little change under grazing after the initial decline in the ash bed effect. Thus, removal of sulfur in agricultural products is a major pathway under cropping but is negligible under grazing.

The effect of land use change on soil TK

As for phosphorus and sulfur, surface soil was enriched with potassium as a result of burning, and in the absence of fertilisation, depletion commenced immediately. Both cropping and grazing land uses lost similar amounts of potassium over the 32 years post-burning. Potassium decline has been noted in cropping systems worldwide, particularly where crop residue removal was practiced in addition to grain removal (Chen *et al.* 2006; Karlen *et al.* 2013; Rezapour *et al.* 2013). Decline has also been noted under grazing systems, typically with erosion as the primary loss mechanism, while reafforestation of grazing lands has been shown to increase surface soil potassium (Sangha *et al.* 2005; Liu *et al.* 2010; Huth *et al.* 2012; Cheng *et al.* 2016).

Although some potassium is removed in grain, potassium in crop residues greatly exceeds that removed in grain (Chen *et al.* 2006). This implies that removal of potassium in beef is greatly exceeded by the potassium retained in pasture and litter. Despite similar percentage declines in potassium under both cropping and grazing, potassium removal in grain accounted for 39% of the total decline under cropping while removal in beef accounted for only 1% of the decline under grazing. This suggests that removal of potassium in agricultural produce is not the primary loss mechanism.

Potassium is relatively immobile in soil and prone to surface stratification, but can be leached slowly and lost in runoff (Drew and Saker 1980; Bertol *et al.* 2007). The return of crop residues and buffel grass litter to the soil surface promotes stratification in both the cropping and grazing systems of this study, leaving nutrients vulnerable to loss in runoff. Given that changing land use from brigalow scrub to cropping or grazing doubled runoff (Thornton *et al.* 2007), and similar potassium losses were found under both cropping and grazing, it is likely that loss in runoff is the primary loss mechanism at this site. Loss in runoff as a primary loss mechanism is supported by earlier analyses of study data and has been noted as a loss mechanism internationally (Hunter and Cowie 1989; Kayser and Isselstein 2005). Drainage is unlikely to be a primary loss mechanism given drainage under the two systems is two orders of magnitude apart and does not reflect the similar potassium losses from the surface soil of each system.

Natural fluctuations in soil exchangeable potassium

According to the criteria of Bruce and Rayment (1982), average exchangeable potassium concentrations in the catchments pre-clearing were medium. Fluctuations in exchangeable potassium concentrations in C1 are likely due to feedback mechanisms between variable climate cycles and biological processes, including uptake, recycling, maintenance of soil potassium pool equilibrium and the respective lags of each process. Comparison of exchangeable potassium concentrations with a five-year moving average of annual rainfall (Thornton *et al.* 2007) shows a general trend of lower exchangeable potassium in above-average rainfall periods and higher exchangeable potassium in below-average rainfall periods. Increased plant growth during wet periods could result in greater exchangeable potassium uptake than in dry periods, resulting in lower measured soil exchangeable potassium. This process is responsible for the low-rainfall and drought-induced accumulation of NO_3 (Liebig *et al.* 2014; Chen *et al.* 2015; Segoli *et al.* 2015) and is a likely driver of exchangeable potassium dynamics in this study. Increased return of potassium to the soil surface as a result of leaf drop (Tripler *et al.* 2006) in subsequent dry periods, combined with the requirement of the soil potassium pools to remain in equilibrium (Moody and Bell 2006), could then result in higher measured soil exchangeable potassium. Fluctuations in exchangeable potassium concentrations have been noted in other long-term studies of native forest, which concluded that the changes are real, informative of natural processes and should not be treated simply as statistical noise (Johnson *et al.* 2008).

The effect of land use change on soil exchangeable potassium

Post-burning, exchangeable potassium concentrations in C2 and C3 increased from medium to high. This increase may be attributed to soil biomass breakdown due to heating (Hunter and Cowie 1989), to exfoliation of mica from disturbed regolith (CSIRO 2006) or illite clay minerals in the soil profile exposing potassium in formerly contracted interlayers and to removal of organic coatings (Scott and

Smith 1968; Smith and Scott 1974; Sharpley and Smith 1988). In the absence of fertilisation, depletion commenced immediately, similar to the behaviour of available phosphorus. After 32 years of cropping or grazing, the concentrations of exchangeable potassium that had increased from medium to high with burning, declined to low.

Declines in exchangeable potassium over time under cropping have been reported both elsewhere in Australia and internationally, and are typically attributed to plant uptake followed by removal in harvested grain and stubble (Cope 1981; Sharpley and Smith 1988; Bell *et al.* 1995; Litvinovich *et al.* 2006; Curtin *et al.* 2015). Declines in exchangeable potassium over time under grazing have also been reported both elsewhere in Australia and internationally, with the primary loss occurring during potassium cycling, particularly from urine patches, which account for ~80% of the potassium cycled through the animal (Cox 1973; Williams and Haynes 1990; Haynes and Williams 1992; Prober *et al.* 2002; Kayser and Isselstein 2005; Sangha *et al.* 2005). Preferential flow of water-soluble urine potassium, which is deposited in concentrated patches, to beneath 0.1 m of the soil profile may also account for some of the measured decline in exchangeable potassium (Kayser and Isselstein 2005). Leaching of exchangeable potassium, particularly urine potassium, is often cited as a loss mechanism (Kayser and Isselstein 2005). However, as for TK, the similar decline in exchangeable potassium under both cropping and grazing at this site, despite the drainage under the two systems being two orders of magnitude apart, indicate that drainage is unlikely to be a primary loss mechanism. In addition, the feedback mechanisms between variable climate cycles and biological processes that drive exchangeable potassium fluctuations in native forests will also influence dynamics in agricultural systems. This will occur in parallel to loss via removal in agricultural products and loss from cycling pathways specific to either cropping or grazing.

Conclusion

Development of brigalow scrub for cropping or grazing significantly altered soil nutrient balances. Initial clearing and burning resulted in a temporary increase, or flush, of mineral nitrogen, total and available phosphorus, total potassium and total sulfur in the surface soil (0–0.1 m) as a result of soil heating and the ash bed effect. Bulk density was consistently higher post-clearing and burning than it was pre-clearing. Soil pH also increased, but did not peak immediately after burning. Increases in soil pH were unlikely to limit nutrient availability and plant growth.

Over the 32 years since changing land use from brigalow scrub to cropping, surface soil fertility has declined significantly. Specifically, organic carbon has declined by 46%, total nitrogen by 55%, total phosphorus by 29%, bicarbonate extractable phosphorus by 54%, acid extractable phosphorus by 59%, total sulfur by 49%, total potassium by 9% and exchangeable potassium by 63% from post-burn, pre-cropping concentrations. This decline in fertility has limited crop yields and would have had an economic impact on a commercial cropping enterprise. However, the planting and maintenance of a butterfly pea legume ley pasture increased total nitrogen by 15% within five years, consistent with other studies in the region. Nutrient removal from the catchment as beef following 173 days of grazing the ley pasture was substantially less than that removed in an average crop. Beef production would have provided some economic benefit to offset the foregone cropping opportunities.

Surface soil fertility has also declined under grazing over the same period but in a different pattern to that observed under cropping. Organic carbon showed clear fluctuation but it was not until the natural variation in soil fertility over time was separated from the anthropogenic effects of land use change that a significant decline was observed. Total nitrogen declined by 22% and in the absence of a legume in the pasture, no fertility restoration occurred. Total phosphorus declined by 14%, equating to only half of the decline under cropping. Bicarbonate extractable phosphorus declined by 64% and acid extractable phosphorus declined by 66%; both greater than the decline observed under cropping, possibly due to immobilisation as organic phosphorus. Total sulfur declined by 23%; less than half of the decline under cropping. A similar decline in total potassium was observed under both land uses, with a 10% decline under grazing. Exchangeable potassium declined by 59%. As for cropping, this fertility decline has limited pasture production and hence beef production. Despite these production limitations, the grazing system is representative of much of the extensive grazing undertaken in northern Australia. The incorporation of legumes into grazing systems within the Brigalow Belt bioregion has been shown to increase both soil fertility and enterprise profitability; however, broad-scale adoption within the grazing industry is still evolving.

The primary mechanism of nutrient loss depended on the land use and nutrient in question but included removal in grain and beef, mineralisation and oxidation, redistribution and stratification within the soil profile and nutrient pools due to plant growth and litter recycling, uptake and storage in above ground biomass, and loss in runoff and leaching. The addition of legumes into both the cropping and grazing systems would assist in fertility restoration; however, particularly in the case of cropping, may not enable continued production without fertility decline. In contrast to the fertility decline of the agricultural land uses, surface soil fertility of the brigalow scrub remained in relative equilibrium.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix 3

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Heavy grazing of buffel grass pasture in the Brigalow Belt bioregion of Queensland, Australia, more than tripled runoff and exports of total suspended solids compared to conservative grazing

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ABSTRACT

Loss of sediment and particulate nutrients in runoff from the extensive grazing lands of the Fitzroy Basin, central Queensland, continue to contribute to the declining health of the Great Barrier Reef. This study measured differences in hydrology and water quality from conservative and heavy grazing pressures on rundown improved grass pastures in the Fitzroy Basin. Conservative grazing pressure was defined as the safe long-term carrying capacity for rundown buffel grass pasture, whereas heavy grazing pressure was defined as the recommended stocking rate for newly established buffel grass pasture. Heavy grazing of rundown pasture resulted in 2.5 times more bare ground and only 8% of the pasture biomass compared to conservative grazing. Heavy grazing also resulted in 3.6 times more total runoff and 3.3 times the peak runoff rate compared to conservative grazing. Loads of total suspended solids, nitrogen and phosphorus in runoff were also greater from heavy than conservative grazing.

1. Introduction

The Fitzroy Basin is Queensland's largest coastal catchment and is almost entirely contained within the Brigalow Belt bioregion of Australia. Both the basin and the wider bioregion have experienced some of the highest rates of land clearing in the world, with up to 93% of vegetation communities dominated by brigalow (*Acacia harpophylla*) cleared for agriculture since European settlement (Butler and Fairfax, 2003; Cogger et al., 2003; Tulloch et al., 2016). Grazing is the dominant land use in the Fitzroy Basin, with more than 2.6 million cattle over 11.1 Mha (Australian Bureau of Statistics, 2009; Meat and Livestock Australia, 2017a). This is the largest cattle herd in any natural resource management region in both Queensland and Australia, accounting for 25% of the state herd and 11% of the national herd (Meat and Livestock Australia, 2017a).

The 2017 Scientific Consensus Statement for Great Barrier Reef water quality identified the Fitzroy Basin as a high priority area for reducing fine sediment and particulate nutrients. This is due to their ongoing contribution to marine water quality decline and resultant damage to seagrass and coral reefs (Waterhouse et al., 2017). Increased adoption of best management practices for agriculture was identified as a key strategy to reduce sediment and nutrient loads in runoff. Within the Grazing Water Quality Risk Framework for 2017 to 2022, the lowest risk to water quality from hillslope pasture management is achieved by practices such as forage budgeting to determine carrying capacity, ground cover monitoring and the adoption of wet season spelling (The State of Queensland, 2020b). These practices are commonly recommended to maintain or improve ground cover (Jones et al., 2016; Moravek et al., 2017; O'Reagain et al., 2011), as high cover is known to reduce runoff, and hence also sediment and nutrients exported in runoff (Murphy et al., 2008; Nelson et al., 1996; Schwarte et al., 2011; Silburn et al., 2011). For example, light and heavy stocking rates were compared in the Burdekin Basin with 20 to 25% and 40 to 50% pasture utilisation, respectively (O'Reagain et al., 2008). A safe long-term carrying capacity is defined as the capacity of the pasture to sustainably carry livestock in the long-term whereas a safe pasture utilisation rate is defined as the proportion of annual forage growth that can be consumed by domestic livestock without adversely affecting land condition in the long-term (McKeon et al., 2009; Walsh and Cowley, 2011).

In below average rainfall years, the heavy stocking rate had less ground cover, a greater frequency and intensity of runoff, and higher sediment concentrations in runoff. However, there was little difference between the two stocking rates in high rainfall years due to high ground cover (O'Reagain et al., 2008). This reflects international literature from

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at least the last 100 years that demonstrates heavy continuous grazing accelerates runoff and erosion (Hubbard et al., 2004). Multiple global meta-analyses have shown that grazing decreases ground cover and increases compaction, which consequently decreases protection from raindrop impact, aggregate stability and infiltration while increasing runoff. These impacts were greater from heavy grazing than conservative or rotational grazing (Byrnes et al., 2018; Eldridge et al., 2016; Lai and Kumar, 2020; McDonald et al., 2019; Sirimarco et al., 2018; Wang and Tang, 2019; Xu et al., 2018). Thus, erosion and sediment transport are primarily associated with high-density stocking and/or poor forage stands on grazed landscapes (Hubbard et al., 2004). Globally, degradation by overgrazing is estimated to effect 20 to 35% of permanent pastures, which total about half of the earths terrestrial surface (Byrnes et al., 2018; Lai and Kumar, 2020).

Although spelling pasture has been shown to increase biomass, seasonal conditions can actually have a stronger effect on ground cover and pasture biomass (Jones et al., 2016). This further highlights the importance of managing grazing pressure to maintain landscape resilience, particularly during periods of below average rainfall (Edwards, 2018). Managing grazing pressure is typically undertaken by varying stocking rate, as it is the most powerful management tool available to the grazier (Lawrence and French, 1992).

These interrelated land use and land management issues were a focus of the Reef 2050 Water Quality Improvement Plan (The State of Queensland, 2018). This plan seeks to improve Great Barrier Reef health and resilience by facilitating increased adoption of lower risk land management practices to achieve specific water quality targets. Progress towards these targets is measured via the Paddock to Reef Integrated Monitoring, Modelling and Reporting program (Paddock to Reef program) (Waterhouse et al., 2018). The Paddock to Reef program is underpinned by a modelling framework that ranges in scale from individual paddocks though to entire basins with real-world validation provided by numerous studies (Waterhouse et al., 2018). The Brigalow Catchment Study is a paddock scale study that is used to validate the effects of hillslope grazing management on water quality from the Fitzroy Basin. This long-term study has a paired catchment design where catchments are adjacent within a uniform landscape, whereas other paired catchment studies often have sites located further apart in the landscape which confounds interpretation due to inherent differences in soil, slope, vegetation and climatic sequences.

Despite the existence of about 200 paired catchment studies worldwide (Peel, 2009), only 13 of them are based in Australia and only three of these have any form of pasture treatment (Best et al., 2003). Two of the three pasture studies were based in Mediterranean climates (cool wet winters and hot dry summers) and are now both inactive (Best et al., 2003; Mein et al., 1988), whereas the third at the Brigalow Catchment Study was based in a semi-arid, subtropical climate (warm wet summers and cool dry winters) and remains active. Bartley et al. (2012) noted that there is a limited amount of Australian runoff and water quality data that is urgently required for modelling activities, such as determining progress towards achieving the Reef 2050 Water Quality Improvement Plan targets. This study provides empirical data from the Fitzroy Basin to determine the effects of grazing management practices on paddock scale water quality. More specifically the study aims to:

1) Quantify the impact of conservative and heavy cattle grazing pressures on hydrology and both event mean concentrations (EMCs) and loads of total suspended solids, nitrogen and phosphorus in hillslope runoff over four hydrological years (2015 to 2018);
2) Determine the anthropogenic impact of cattle grazing by comparing hydrology and both EMCs and loads of total suspended solids, nitrogen and phosphorus in hillslope runoff from a conservatively grazed pasture and virgin brigalow woodland which is representative of the pre-European landscape; and
3) Quantify the impact of conservative and heavy cattle grazing pressures on pasture biomass and ground cover over four hydrological years (2015 to 2018).

2. Methods

2.1. Site description

This study was undertaken at the Brigalow Catchment Study which is representative of both the Fitzroy Basin and the Brigalow Belt bioregion (Cowie et al., 2007) (Fig. 1). It is a paired, calibrated catchment study located near Theodore in central Queensland (24° 48′S and 149° 47′E), Australia, which was established in 1965 to quantify the impact of land development for agriculture on hydrology, productivity and resource condition (Cowie et al., 2007). The hydrological cycle of this study site is extensively documented (Silburn et al., 2009; Thornton et al., 2007; Thornton and Yu, 2016), as are the impacts of land clearing and land use change on runoff water quality (Elledge and Thornton, 2017; Thornton and Elledge, 2016; Thornton and Elledge, 2013). Data from this site is representative of hillslope runoff and erosion processes without any scalds, gullies, streams or streambanks.

In its native state, the study site was dominated by brigalow (*Acacia harpophylla*), either in a monoculture or in association with other species, such as belah (*Casuarina cristata*) and Dawson River blackbutt (*Eucalyptus cambageana*) (Johnson, 2004). This vegetation association is colloquially known as brigalow scrub (Cowie et al., 2007). The extant uncleared vegetation of the Brigalow Catchment Study is classified as regional ecosystems 11.4.8, *Eucalyptus cambageana* woodland to open forest with *Acacia harpophylla* or *Acacia argyrodendron* on Cainozoic clay plains, and 11.4.9, *Acacia harpophylla* shrubby woodland with *Terminalia oblongata* on Cainozoic clay plains (The State of Queensland, 2020e). Slope of the land averages 2.5% (range 1.8% to 3.5%) for Catchments 1 and 3 (Cowie et al., 2007), and based on an aerial LiDAR survey of the Brigalow Catchment Study in 2019, slope of Catchment 5 averages 5.7%. Soils are an association of Vertosols, Dermosols and Sodosols which are representative of 67% of the Fitzroy Basin under grazing; that is, 28% Vertosols, 28% Sodosols and 11% Dermosols (Roots, 2016). The region has a semi-arid, subtropical climate and mean annual hydrological year (October 1965 to September 2018) rainfall at the site was 648 mm.

2.2. Site history and monitoring period

The Brigalow Catchment Study can be separated into four experimental stages: Stage I, calibration of three catchments in an uncleared state from 1965 to 1982; Stage II, development of two catchments for agriculture from 1982 to 1983; Stage III, comparison of cropping and grazing land use to virgin brigalow scrub from 1984 to 2010; and Stage IV, a comparison of leguminous and non-leguminous pastures to virgin brigalow scrub during the adaptive land management phase from 2010 to 2018. Further details on these experimental phases are documented in other sources (Cowie et al., 2007; Radford et al., 2007; Thornton et al., 2007; Thornton and Elledge, 2013). Data in this study is from Catchments 1, 3 and 5 during the adaptive land management phase for the 2015 to 2018 hydrological years (01 October 2014 to 30 September 2018). Catchments 1 and 3 were established during Stage I and Catchment 5 was incorporated into the long-term Brigalow Catchment Study during Stage IV. Table 1 outlines the land use history of these catchments over the four experimental stages, Fig. 2 shows the location of these three catchments within the landscape, and Table 2 characterises the catchments and the treatments applied over this four year study.

Since the commencement of the Brigalow Catchment Study in 1965, Catchment 1 has been retained in a virgin uncleared state to provide a control treatment representative of the Brigalow Belt bioregion in its pre-European condition. Catchment 3 remained uncleared during Stage I. During Stage II it was cleared by bulldozer and chain in March 1982,

Fig. 1. Location of the Brigalow Catchment Study within the Brigalow Belt bioregion of central Queensland, Australia.

Table 1
Land use history of the three catchments monitored over the 2015 to 2018 hydrological years.

Catchment	Land use by experimental stage			
	Stage I	Stage II	Stage III	Stage IV
	Jan 1965 to Mar 1982	Mar 1982 to Sep 1983	Sep 1984 to Jan 2010	Jan 2010 to Oct 2018
Catchment 1	Brigalow scrub	Brigalow scrub	Brigalow scrub	Brigalow scrub
Catchment 3	Brigalow scrub	Development	Grass pasture	Grass pasture
Catchment 5	Not monitored	Not monitored	Not monitored	Grass pasture

the fallen timber burnt in October 1982 and then the catchment planted to buffel grass (*Cenchrus ciliaris*) pasture in November 1982.

Although all catchments reported in this study were previously part of the former Queensland Department of Primary Industries' Brigalow Research Station, Catchment 5 has a longer history of agricultural land use as it was not incorporated into the Department of Resources' Brigalow Catchment Study until 2014. Aerial photography shows that Catchment 5 was virgin brigalow scrub in 1965 but in a cleared state

Fig. 2. Aerial photograph of the Brigalow Catchment Study which shows catchment boundaries, topography and location of monitoring equipment.

Table 2
Description of the three catchments monitored over the 2015 to 2018 hydrological years.

Parameter	Brigalow scrub	Conservative grazing	Heavy grazing
Alternative catchment name	Catchment 1	Catchment 3	Catchment 5
Soil type (% of catchment)	Vertosols and Dermosols (70%), Sodosols (30%)	Vertosols and Dermosols (70%), Sodosols (30%)	Vertosols and Dermosols (93%), Sodosols (7%)
Slope	2.5%	2.5%	5.7%
Land use	Virgin brigalow scrub	Improved grass pasture	Improved grass pasture
Cattle stocking philosophy	Ungrazed control	Conservative stocking rate	Heavy stocking rate
Catchment area (ha)	16.8	12.7	12.0
Total grazed area (ha)	Not applicable	17.0	25.0
Pasture spelling philosophy	Ungrazed control	Wet season spell	Limited spelling
Pasture biomass philosophy	Not applicable	Minimum 1000 kg/ha	No minimum limit
Photo			

planted to pasture in 1969, 1977 and 1984 (Commonwealth of Australia, 1969; The State of Queensland, 1965, 1977, 1984). It was a common management practice to have a period of cropping following the initial development of improved pasture on brigalow lands to physically control regrowth of brigalow suckers (Johnson, 1968; Johnson and Back, 1974). Use of this strategy at the Brigalow Research Station was demonstrated by land use maps in annual reports and program reviews which classify Catchment 5 as cultivation in 1988 and

1989, in addition to written records for the planting of forage sorghum in 1989 and barley in both 1990 and 1991 (Queensland Department of Primary Industries, 1988, 1989, 1990, 1991). Aerial photography in 1991 shows the catchment in a tilled state which supports the written records (The State of Queensland, 1991). Catchment 5 was then planted to buffel grass (*Cenchrus ciliaris*) and purple pigeon grass (*Setaria incrassata*) in January 1992 which remains today (Queensland Department of Primary Industries, 1992).

Beef cattle commenced grazing Catchment 3 in December 1983 at a stocking rate of 0.45 adult equivalent (AE)/ha/yr which decreased to 0.26 AE/ha/yr over the next 21 years (Radford et al., 2007). An adult equivalent is considered to be a non-lactating animal of 450 kg live weight (McLean and Blakeley, 2014). Stocking rates varied between 0.06 and 0.23 AE/ha/yr from February 2005 to September 2011, averaging 0.14 AE/ha/yr. The catchment was spelled from September 2011 to December 2013, and then grazed at 0.19 AE/ha/yr from December 2013 to February 2014.

While not incorporated into the Brigalow Catchment Study until 2014, management of Catchment 5 was taken over by the Department of Resources in 2008. Although exact stocking rates prior to this period were unknown, cattle stocking philosophies for the broader Brigalow Research Station can be used as a surrogate. In 1965 it was stated that the Brigalow Research Station could carry 800 head of cattle once cleared and developed (Queensland Department of Primary Industries, 1965). This was later revised to an aspirational range from 800 to 1000 head of grown cattle in 1976 (Stringer, 1976) which remained until 1989 while land development was still in progress (Nasser, 1986; Queensland Department of Primary Industries, 1987, 1988, 1989). Carrying capacities were not published in annual reports from 1990 to 1995; however, from 1996 to the final technical report in 2004 it was stated that the station had a sustainable carrying capacity of 1200 adult equivalents (Jeffery and Loxton, 1998, 1999; Loxton et al., 1994; Loxton and Boadle, 1995, 1996, 1997; Loxton and Forster, 2000; Queensland Department of Primary Industries, 1990, 1991, 1992; Sinclair and White, 2004).

Early carrying capacities expressed as grown cattle can be converted to adult equivalents using carcase specifications for the brigalow lands of Queensland combined with dressing percentages. Carcase weights averaged 269 kg (range 250 to 300 kg) (Strachan, 1976) and an appropriate dressing percentage to convert live weight to carcase weight is 53% (Meat and Livestock Australia, 2017b). The average dressing percentage of 53% for heavy steers with a fat score of three was selected, as Strachan (1976) states that steers with a low fat carcass were the most common animal produced for slaughter. For example, a carcase weight of 269 kg and a dressing percentage of 53% suggests that the live weight of a grown animal was about 508 kg, equal to 1.13 adult equivalents. Thus, the aspiration to carry 800 to 1000 head of grown cattle equates to carrying capacities of 896 and 1120 adult equivalents, respectively, which were both lower than the 1200 adult equivalent carrying capacities reported from 1996 to 2004. These carrying capacities translate into surrogate stocking rates of 0.33 AE/ha/yr, 0.41 AE/ha/yr and 0.45 AE/ha/yr, respectively (Fig. 3).

Although these calculated stocking rates can be used as a surrogate for Catchment 5 over one or more decades, they are less suited to estimate annual stocking rates. Brigalow Research Station documents from 1990 to 2004 noted an increase in both area of pasture and annual livestock returns over time (Jeffery and Loxton, 1998, 1999; Loxton et al., 1994; Loxton and Boadle, 1995, 1996, 1997; Loxton and Forster, 2000; Queensland Department of Primary Industries, 1990, 1991, 1992; Sinclair and White, 2004). Thus, a surrogate annual stocking rate for Catchment 5 can be calculated as the number of cattle on the entire station during the year divided by the total area of available pasture to yield an AE/ha/yr (Fig. 3). Annual livestock returns for the station reported both young cattle less than one adult equivalent and older cattle greater than one adult equivalent, so it is reasonable to assume that the total number of cattle reported could be expressed as adult equivalents.

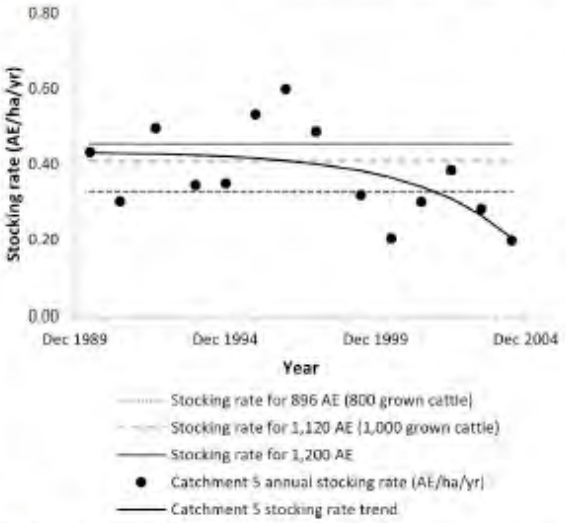

Fig. 3. Aspirational and actual stocking rates for the Brigalow Research Station used to estimate stocking rates from Catchment 5 prior to the commencement on this study in 2014.

Annual calculations suggest that stocking rates for Catchment 5 decreased from 0.43 AE/ha/yr in 1990 to 0.20 AE/ha/yr in 2004 (Fig. 3). Limited grazing occurred in Catchment 5 from 2004 until discussions to close the Brigalow Research Station in 2008. The catchment was spelled from June 2008 to July 2012 when it was grazed at 0.45 AE/ha/yr until September 2012, then grazed at 0.11 AE/ha/yr until December 2012.

2.3. Treatments

Over the four hydrological years of this study, Catchment 1 was retained in its virgin uncleared condition supporting brigalow scrub. Vertosols and Dermosols (clay soils) occupy approximately 70% of the catchment and Sodosols occupy the remaining 30% (Cowie et al., 2007; Isbell, 1996). Catchment 3 continued as a conservatively grazed catchment with a buffel grass (*Cenchrus ciliaris* cv. Biloela) pasture. Vertosols and Dermosols (clay soils) occupy approximately 58% of the catchment and Sodosols occupy the remaining 42% (Cowie et al., 2007; Isbell, 1996). Catchment 5 commenced as a heavily grazed catchment with an existing buffel grass (*Chenchrus ciliaris*) and purple pigeon grass (*Setaria incrassata*) pasture. Vertosols occupy approximately 93% of the catchment and Sodosols occupy the remaining 7% (Isbell, 1996). The Australian Soil Classification for Catchment 5 was determined by Land Resource Officers from the Department of Resources based on the soil survey of Webb (1971), the soil chemistry of Webb et al. (1977) and soil descriptions undertaken in 2013 which were extracted from the Soil And Land Information (SALI) system (Biggs et al., 2000).

The two pastures were spelled prior to the commencement of this study in October 2014. The conservatively grazed pasture was spelled from February 2014, while the heavily grazed pasture was spelled from December 2012. Conservative grazing pressure reflected the safe long-term carrying capacity for rundown buffel grass pasture, whereas heavy grazing pressure reflected stocking rates recommended for newly established buffel grass pasture. The Brigalow Catchment Study has been managed to maintain good (A) land condition and the estimated long-term carrying capacity was 0.22 AE/ha/yr (range 0.19 to0.27 AE/ha/yr). This estimate was obtained from the Long Paddock FORAGE system which provides a property specific report based on climate data, satellite imagery and modelled pasture growth (The State of

Queensland, 2021). Whereas published recommended stocking rates are about 0.50 AE/ha/yr for newly established buffel grass pasture and about 0.33 AE/ha/yr for rundown buffel grass pasture, which can occur in as little as five to ten years after establishment (Noble et al., 2000; Peck et al., 2011).

Stocking rates during this study were set based on measured pasture biomass, with pasture utilisation targets of less than 30% in the conservatively grazed pasture and greater than 50% in the heavily grazed pasture. Dietary intake was considered to be 2.2% of animal live weight (Minson and McDonald, 1987). Actual stocking rates for this study have been presented as adult equivalents per hectare per year (AE/ha/yr) to account for differences in the size of cattle and the length of time the pastures were grazed (Table 3). Spelling was defined as the number of days annually that pasture wasn't grazed (Table 4). Overall, the conservatively grazed pasture had lower stocking rates and greater periods of spelling.

2.4. Hydrology

Rainfall and runoff were monitored over four hydrological years from October 2014 to September 2018. Rainfall was measured using a 0.5 mm tipping bucket rain gauge located at the head point of the three long-term catchments (Thornton et al., 2007). Each catchment was instrumented to measure runoff using a 1.2 m HL flume with a 3.9 × 6.1 m approach box (Brakensiek et al., 1979). Water heights through the flume were recorded using a pressure transducer with a mechanical float recorder backup. Stage heights were converted to discharge using a rating table (Brakensiek et al., 1979), while peak runoff rate was calculated on an event basis from instantaneous peak height. A runoff event commenced when stage height exceeded zero and finished when it returned to zero. Further details on calculating total runoff and peak runoff rates are documented in other sources (Thornton et al., 2007; Thornton and Yu, 2016).

The 18 year calibration period for the three long-term catchments in Stage 1 meant that runoff from Catchment 3 can be estimated from measured runoff from Catchment 1 (Thornton et al., 2007). A calibration period for Catchment 5 was not possible as it had been developed for agriculture sometime between 1965 and 1969, which was at least 40 years prior to its inclusion in the study. Thus, although Catchment 5 has its own unique hydrological characteristics, its relationship to Catchments 1 and 3 in an uncleared state is unknown.

2.5. Water quality

Discrete water quality samples were obtained over four hydrological years (October 2014 to September 2018) using an auto-sampler located at the flume of each catchment. Auto-samplers were programmed to sample every 0.1 m change in stage height. Laboratory analyses of runoff samples were undertaken by Queensland Health Forensic and Scientific Services (Table 5), with some parameters calculated by difference (Table 6).

Event based water quality loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the resulting loads from all intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Total annual load was calculated by summing all the event-based water quality loads, and load in kg/ha was calculated by accounting for catchment area.

Event based EMCs were calculated by dividing total event load by total event flow, and mean annual EMCs were calculated by averaging the event-based EMCs within each year. Mean annual EMCs from 2000 to 2018 were used to calculate a long-term site EMC for each catchment using the method of Elledge and Thornton (2017). Where water quality data was not captured due to flows being too small to trigger auto-samplers, load estimations were obtained by multiplying the long-term EMC by observed flow. This method was applied to all events from brigalow scrub as flows were too small to trigger auto-samplers. Only observed (measured) event-based EMCs were included in the calculation of mean annual EMCs.

Dominant pathways of nitrogen and phosphorus loss in runoff were determined by the proportion of particulate and total dissolved fractions. That is, if total dissolved nitrogen was greater than 60% of total nitrogen it was considered to be transported primarily in a dissolved phase, and if less than 40% it was transported primarily in a particulate phase. If the value was between 40% and 60%, it was considered to have no dominant pathway of loss. The same method was applied to total phosphorus and total dissolved phosphorus.

Table 3
Annual stocking rates in adult equivalents (AE) per hectare per year for the two pasture treatments.

Year	Stocking rate (AE/ha/yr)	
	Conservative grazing	Heavy grazing
2013	Destocked	0.09
2014	0.19	Destocked
2015	0.20	0.83
2016	0.13	0.20
2017	0.19	0.26
2018	Destocked	0.86

Table 4
Annual number of non-grazed days (spelling) for the two pasture treatments.

Year	Pasture spelled (days/yr)	
	Conservative grazing	Heavy grazing
2013	365	303
2014	320	365
2015	80	33
2016	297	286
2017	76	180
2018	365	146

Table 5
Methods used by Queensland Health Forensic and Scientific Services for total suspended solids and nutrient analyses of runoff samples.

Parameter	Method
Total suspended solids	Method 18211 based on gravimetric quantification of solids in water
Total nitrogen and total dissolved nitrogen	Method 13802 by simultaneous persulfate digestion
Oxidised nitrogen	Method 13798 based on flow injection analysis of nitrogen as oxides
Ammonium-nitrogen	Method 13796 based on flow injection analysis of nitrogen as ammonia
Total phosphorus and total dissolved phosphorus	Method 13800 by simultaneous persulfate or Kjeldahl digestion
Dissolved inorganic phosphorus	Method 13799 by flow injection analysis

Table 6
Equations used to estimate nutrient parameters that were not directly measured.

Parameter	Equation
Particulate nitrogen	Total nitrogen minus total dissolved nitrogen
Dissolved inorganic nitrogen	Oxidised nitrogen plus ammonium-nitrogen
Dissolved organic nitrogen	Total dissolved nitrogen minus dissolved inorganic nitrogen
Particulate phosphorus	Total phosphorus minus total dissolved phosphorus
Dissolved organic phosphorus	Total dissolved phosphorus minus dissolved inorganic phosphorus

2.6. Pasture biomass

The BOTANAL method of Tothill et al. (1978) was used to estimate pasture biomass one to two times per year over the total grazed area of the two pasture catchments, excluding the shade lines. Pasture assessments occurred in the late wet and/or the late dry season. The late wet season is typically the end of the pasture growing season, and the late dry season provides an indicator of the remaining pasture available for cattle grazing until suitable conditions for growth occur. Pasture biomass was visually estimated for up to 300 0.16 m^2 quadrats in each catchment at each sampling period. Visual estimates were calibrated against a set of 10 quadrats which were cut, dried and weighed.

2.7. Ground cover

Ground cover from the total grazed area of the two pasture catchments was compared from October 2012 to October 2018 using VegMachine® (Fitzroy Basin Association, 2018). VegMachine is a simple tool for interrogating large raster time series ground cover datasets derived from Landsat satellite imagery (Beutel et al., 2019; Terrestrial Ecosystem Research Network, 2010). The analysis of ground cover at or near ground level, which excludes taller cover such as tree and shrub canopies, required individual spatial polygons to define each catchment (Beutel et al., 2019). Polygons for the conservatively and heavily grazed catchments were defined as the fence line boundary for each paddock, which was identified via satellite imagery. Both catchment polygons were then manually imported into VegMachine and the "*Polygon Comparison*" tool used to perform a ground cover analysis of the conservatively and heavily grazed catchments. Seasonal deciles were also reported for total (green and non-green) cover, where total cover and bare ground equal 100%. These were calculated automatically within VegMachine using quarterly data from Autumn (March to May) 1988 to Summer (December to February) 2012/2013 as a baseline, with every season ranked (expressed as a decile) against all corresponding values for that season in the baseline period (Trevithick, 2017). For example, total cover from spring (September to November) 2015 was ranked against total cover from all the spring images from the baseline period.

2.8. Benchmarking ground cover to the Fitzroy Basin

VegMachine was also used to determine how representative ground cover from the Brigalow Catchment Study was to the wider Fitzroy Basin. This was achieved by comparing the conservatively and heavily grazed catchments to the six sub-basins of the Fitzroy Basin; that is, the Dawson, Comet, Nogoa, Isaac, Mackenzie and Fitzroy. Sub-basin comparisons were undertaken to better represent the range of covers within the Fitzroy Basin. Spatial layers for VegMachine analysis were prepared using a multi-step process in ArcGIS (Environmental Systems Research Institute, 2020):

1) Boundaries for the six sub-basins were obtained from the "*Basin sub areas - Queensland*" spatial layer, accessed via the Queensland Spatial Catalogue (QSpatial) (The State of Queensland, 2020c).
2) Landscapes that were comparable to the Brigalow Catchment Study were identified by interrogating the Regional Ecosystem Description Database to return Regional Ecosystems that contained the term "harpophylla" in the description (The State of Queensland, 2019). These landscapes historically supported brigalow (*Acacia harpophylla*) vegetation communities on predominantly clay soils.
3) The "*Grazing land management land types V5*" spatial layer (accessed via QSpatial) was clipped to the six sub-basin boundaries defined in step one. This layer was used by VegMachine to determine the appropriate ground cover data for polygon comparisons.
4) The layer produced in step three was further clipped to the Regional Ecosystems identified in step two by using a definition query for "harpophylla" within the attribute table.
5) The "*Land use mapping – 1999 to 2017*" spatial layer (accessed via QSpatial) was clipped to landscapes with a secondary land use of "grazing" in the 2017 data to provide a relevant comparison to the grazed pasture catchments in this study. This layer was further clipped to six sub-basin boundaries defined in step one.
6) The Regional Ecosystem layer created in step four was further clipped to the grazing layer produced in step five. The result was a spatial layer for each sub-basin that had multiple polygons displaying only grazing land supporting Regional Ecosystems containing *Acacia harpophylla*.
7) The layer produced in step 6 retained Regional Ecosystem classifications within the attribute table under the identifier "stratum". This stratum identifier is required by VegMachine to determine the appropriate ground cover data for polygon comparison and was listed as "FT05" or brigalow with melonholes for the Brigalow Catchment Study (Fitzroy Basin Association, 2018; The State of Queensland, 2021). For each sub-basin, the stratum identifier FT05 was assigned to every polygon and then all polygons dissolved into a single polygon. The final result was a single polygon for each sub-basin displaying only grazing land supporting Regional Ecosystems containing *Acacia harpophylla* with the stratum identifier FT05.

Polygons for the conservatively and heavily grazed catchments in addition to polygons for all six sub-basins of the Fitzroy Basin were manually imported into VegMachine and the "*Polygon Comparison*" tool was used to perform ground cover analyses. Comparative ground cover analyses only considered time periods where ground cover observations, including deciles, occurred for all polygons.

3. Results

3.1. Hydrology

Total annual rainfall at the study site was below the long-term mean annual rainfall of 648 mm (October 1965 to September 2018) in all four hydrological years (Fig. 4). Rainfall was in the 31st percentile in 2015 (563 mm), the 29th percentile in 2016 (562 mm), the lowest on record in 2017 (272 mm) and in the 40th percentile in 2018 (584 mm).

Similar to rainfall, runoff for the four hydrological years was below the long-term mean annual runoff (1985 to 2018) for the brigalow scrub and conservatively grazed catchment (Fig. 5). The heavily grazed catchment was only instrumented in 2014, at the commencement of this study, and mean annual runoff was based on four years (2015 to 2018) data. Runoff from brigalow scrub was in the 32nd percentile in 2015, no runoff occurred in 2016 and 2017, and in 2018 was in the 29th percentile. Runoff from the conservatively grazed catchment was in the 35th percentile in 2015, the 30th percentile in 2016, no runoff occurred

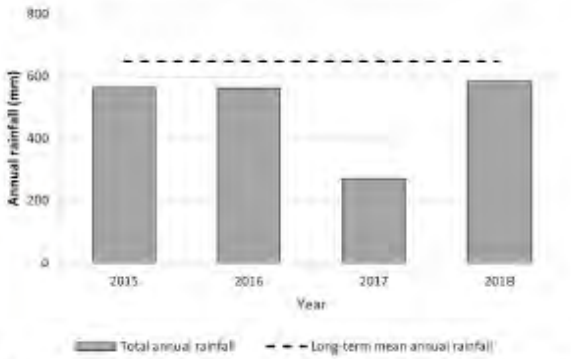

Fig. 4. Total annual hydrological year rainfall for 2015 to 2018 relative to the long-term mean annual rainfall for the Brigalow Catchment Study.

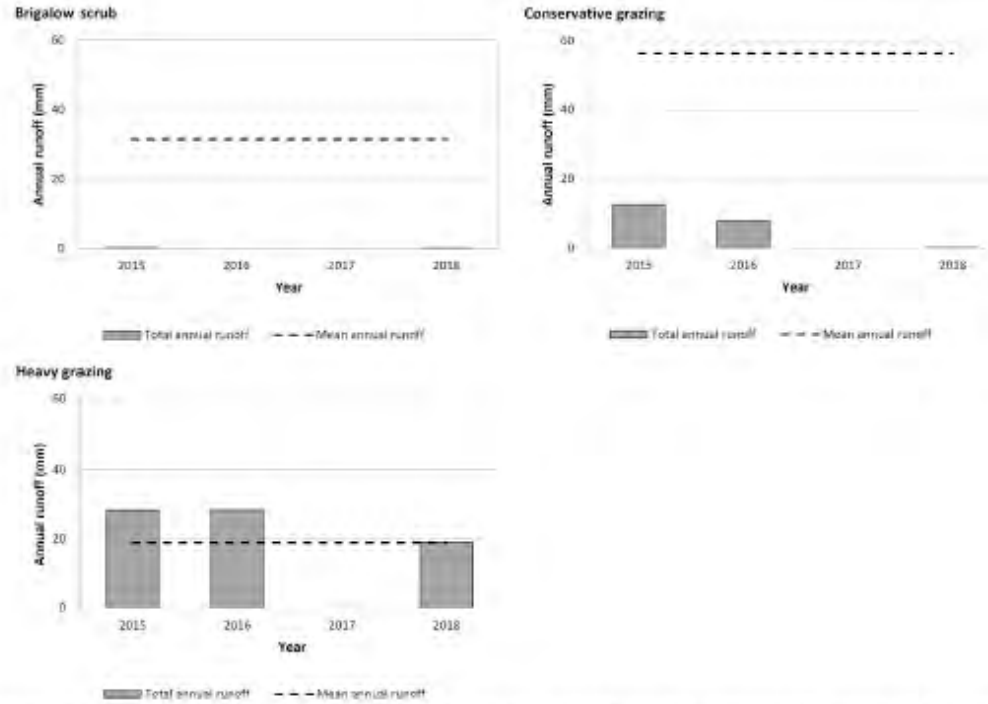

Fig. 5. Total annual hydrological year runoff for 2015 to 2018 relative to mean annual runoff for the three catchments. Mean annual runoff for the brigalow scrub and conservatively grazed catchments were based on 34 years (1985 to 2018) data, but only four years data (2015 to 2018) for the heavily grazed catchment.

Table 7
Observed annual hydrological year summaries of runoff and sampling effort for three catchments.

Parameter	Year	Brigalow scrub	Conservative grazing	Heavy grazing
Number of events	2015	1	2	2
	2016	0	1	1
	2017	0	0	0
	2018	1	1	2
Number of samples	2015	0	3	21
	2016	0	2	6
	2017	0	0	0
	2018	0	0	4
Total runoff (mm)	2015	0.2	13	28
	2016	0	8	28
	2017	0	0	0
	2018	0.1	0.1	19
Average peak runoff rate (mm/h)	2015	0.1	2.6	6.4
	2016	0	1.0	2.6
	2017	0	0	0
	2018	0.1	0.1	2.6
Maximum peak runoff rate (mm/h)	2015	0.1	3.1	6.5
	2016	0	1.0	2.6
	2017	0	0	0
	2018	0.1	0.1	4.7

in 2017, and in 2018 was in the 15th percentile.

Hydrological data and water quality sampling effort for 2015 to 2018 are summarised in Table 7. Although the number of events and total runoff was low in these below average rainfall years, when runoff did occur, the heavily grazed catchment had at least double the runoff of the conservatively grazed catchment. A similar trend was also observed for peak runoff rates with both average and maximum values greatest from the heavily grazed pasture.

Table 8
Predicted annual hydrological year summaries of runoff from the conservatively grazed pasture catchment had it remained uncleared brigalow scrub.

Parameter	Year	Catchment 3
Estimated uncleared runoff (mm)	2015	0.2
	2016	0
	2017	0
	2018	0.1
Increase in runoff under pasture (mm)	2015	12
	2016	8
	2017	0
	2018	0
Estimated uncleared average peak runoff rate (mm/h)	2015	0.2
	2016	0
	2017	0
	2018	0.4
Increase in average peak runoff rate under pasture (mm/h)	2015	2.4
	2016	1.0
	2017	0
	2018	0

Using the hydrological calibration developed during Stage I (1965 to 1982), runoff characteristics for the conservatively grazed pasture (Catchment 3) can be estimated had it remained brigalow scrub (Table 8).

3.2. Water quality

3.2.1. Total suspended solids

Mean annual EMC for total suspended solids was greater from conservatively than heavily grazed pasture (Table 9). Mean annual load of total suspended solids from the heavily grazed pasture was 3.2 times greater than from the conservatively grazed pasture (Fig. 6, Table 10). Brigalow scrub had no EMCs as flows were too small to collect runoff

Table 9
Event mean concentrations of total suspended solid, nitrogen and phosphorus parameters in runoff from 2015 to 2018.

Parameter	Event mean concentration (mg/L)		
	Brigalow scrub	Conservative grazing	Heavy grazing
Total suspended solids	No data	278	235
Total nitrogen	No data	6.49	2.39
Particulate nitrogen	No data	3.40	1.14
Total dissolved nitrogen	No data	3.08	1.25
Dissolved organic nitrogen	No data	1.28	0.66
Dissolved inorganic nitrogen	No data	1.81	0.59
Total phosphorus	No data	0.81	0.49
Particulate phosphorus	No data	0.50	0.22
Total dissolved phosphorus	No data	0.31	0.27
Dissolved organic phosphorus	No data	0.05	0.04
Dissolved inorganic phosphorus	No data	0.26	0.23

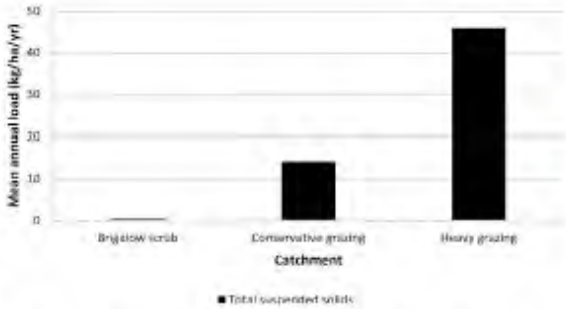

Fig. 6. Mean annual load of total suspended solids in runoff from 2015 to 2018.

Table 10
Mean annual loads of total suspended solid, nitrogen and phosphorus parameters in runoff from 2015 to 2018.

Parameter	Mean annual load (kg/ha)		
	Brigalow scrub	Conservative grazing	Heavy grazing
Total suspended solids	0.4	14.2	46.0
Total nitrogen	0.01	0.29	0.46
Particulate nitrogen	<0.01	0.14	0.21
Total dissolved nitrogen	0.01	0.15	0.26
Dissolved organic nitrogen	<0.01	0.07	0.13
Dissolved inorganic nitrogen	<0.01	0.08	0.12
Total phosphorus	<0.01	0.04	0.10
Particulate phosphorus	<0.01	0.02	0.04
Total dissolved phosphorus	<0.01	0.02	0.06
Dissolved organic phosphorus	<0.01	0.00	0.01
Dissolved inorganic phosphorus	<0.01	0.01	0.05

samples whereas loads were estimated by multiplying the long-term site EMC by observed flow.

3.2.2. Nitrogen

Mean annual EMC for total, particulate and total dissolved nitrogen were greater from conservatively than heavily grazed pasture (Table 9). Mean annual load of total nitrogen from the heavily grazed pasture was 1.6 times greater than from the conservatively grazed pasture (Fig. 7, Table 10). Total nitrogen was composed of similar amounts of

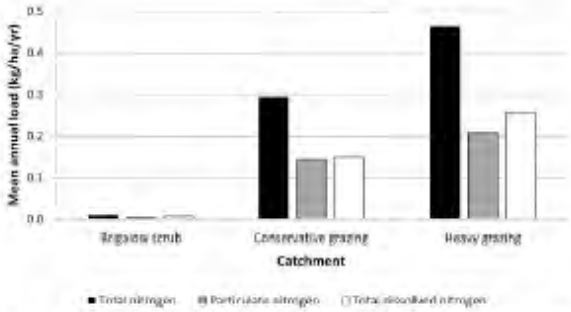

Fig. 7. Mean annual load of total, particulate and dissolved nitrogen in runoff from 2015 to 2018.

particulate and total dissolved nitrogen irrespective of grazing pressure; 49% and 51% for conservatively grazed pasture and 45% and 55% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of total dissolved nitrogen (64%) than particulate nitrogen (36%) towards total nitrogen. The dominant pathway of nitrogen loss was in a dissolved form from brigalow scrub but was unclear for the two pasture catchments (Table 11).

The mean annual EMC for dissolved organic and inorganic nitrogen were greater from conservatively grazed pasture than heavily grazed pasture (Table 9). Mean annual load of total dissolved nitrogen from the heavily grazed pasture was 1.7 times greater than from conservatively grazed pasture (Fig. 8, Table 10). Dissolved organic and inorganic fractions contributed similar amounts towards total dissolved nitrogen from the two pasture catchments; 47% and 53% for conservatively grazed pasture and 53% and 47% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of dissolved inorganic nitrogen (66%) than dissolved organic nitrogen (34%) towards total dissolved nitrogen. Oxidised nitrogen was the greatest fraction of dissolved inorganic nitrogen from all catchments; 99% for brigalow scrub, 94% for conservatively grazed pasture and 88% for heavily grazed pasture.

3.2.3. Phosphorus

The mean annual EMC for total, particulate and total dissolved phosphorus were greater from conservatively than heavily grazed pasture (Table 9). Mean annual load of total phosphorus from the heavily grazed pasture was 2.6 times greater than from conservatively grazed pasture (Fig. 9, Table 10). Total phosphorus was composed of similar amounts of particulate and total dissolved phosphorus irrespective of grazing pressure; 59% and 41% for conservatively grazed pasture and 43% and 57% for heavily grazed pasture, respectively. Although there was limited data from brigalow scrub, estimations indicate a greater contribution of particulate phosphorus (72%) than total dissolved phosphorus (28%) towards total phosphorus. The dominant pathway of phosphorus loss was in a particulate form from brigalow scrub but was unclear for the two pastures (Table 12).

The mean annual EMC for dissolved inorganic and organic phosphorus was greater from conservatively grazed pasture than heavily grazed pasture (Table 9). Mean annual load of total dissolved

Table 11
Dominant pathway of nitrogen loss in runoff from 2015 to 2018.

Year	Brigalow scrub	Conservative grazing	Heavy grazing
2015	Dissolved	No dominant	No dominant
2016	No runoff	No dominant	Dissolved
2017	No runoff	No runoff	No runoff
2018	Dissolved	Dissolved	Particulate

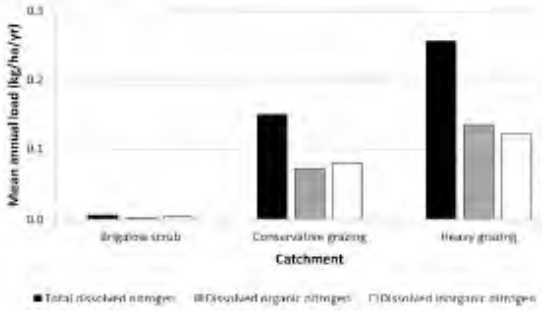

Fig. 8. Mean annual load of dissolved nitrogen fractions in runoff from 2015 to 2018.

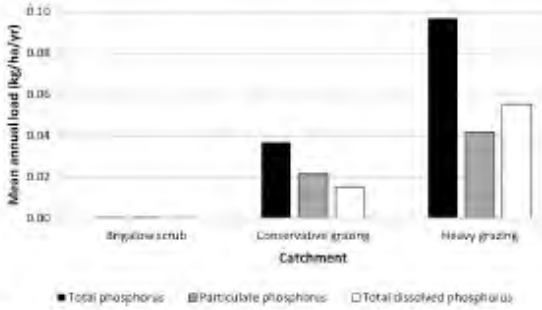

Fig. 9. Mean annual load of total, particulate and dissolved phosphorus in runoff from 2015 to 2018.

Table 12
Dominant pathway of phosphorus loss in runoff from 2015 to 2018.

Year	Brigalow scrub	Conservative grazing	Heavy grazing
2015	Particulate	Particulate	No dominant
2016	No runoff	No dominant	Dissolved
2017	No runoff	No runoff	No runoff
2018	Particulate	No dominant	Particulate

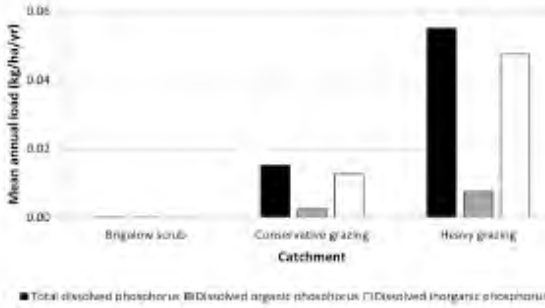

Fig. 10. Mean annual load of dissolved phosphorus fractions in runoff from 2015 to 2018.

phosphorus from the heavily grazed pasture was 3.6 times greater than from conservatively grazed pasture (Fig. 10, Table 10). Dissolved inorganic phosphorus was the greatest fraction of total dissolved phosphorus from all catchments; 78% from brigalow scrub, 84% from conservatively grazed pasture and 86% from heavily grazed pasture.

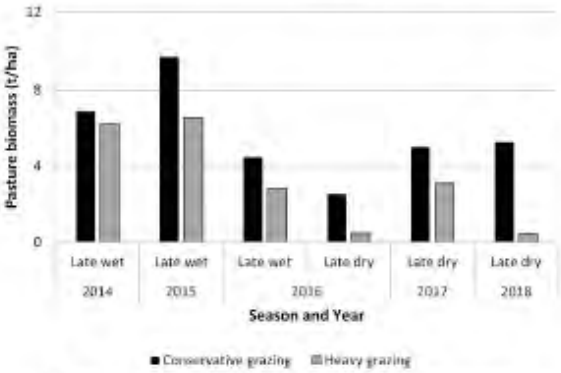

Fig. 11. Pasture biomass in the two pastures from 2015 to 2018.

3.3. Pasture biomass

Overall, the heavily grazed catchment had lower pasture biomass than the conservatively grazed catchment (Fig. 11). In the 2014 late wet season, prior to the commencement of the study, there was similar biomass in both the conservatively (6.9 t/ha) and heavily grazed pastures (6.2 t/ha). Biomass in the 2015 late wet season had increased 2.7 t/ha in the conservatively grazed pasture (9.6 t/ha) with little change in the heavily grazed pasture (6.5 t/ha). Biomass in the heavily grazed pasture went from 90% of the biomass in the conservatively grazed pasture in 2014 to 68% in 2015.

In the 2016 late wet season, biomass had reduced 53% under conservative grazing (4.5 t/ha) and 57% under heavy grazing (2.8 t/ha) compared to the previous year (Fig. 11). The difference in biomass between the two pastures was 63%, similar to the previous year. Biomass continued to decline in both pastures over the next six months, with a 43% reduction in the conservatively grazed pasture to 2.5 t/ha and a much greater 83% reduction in the heavily grazed pasture to 0.5 t/ha. Biomass in the heavily grazed pasture during the 2016 late dry season was reduced to 19% of that from the conservatively grazed pasture.

In the 2017 late dry season, biomass had increased to 5.0 t/ha under conservative grazing and 3.1 t/ha under heavy grazing (Fig. 11). Pasture biomass in the heavily grazed catchment increased to 62% of that from the conservatively grazed catchment, similar to the 2015 and 2016 late wet seasons. In the 2018 late dry season, biomass had increased 5% under conservative grazing (5.3 t/ha) whereas biomass under heavy grazing (0.4 t/ha) had declined 86% compared to the previous year. Biomass in the heavily grazed pasture during the 2018 late dry season was reduced to 8% of that from the conservatively grazed pasture.

Table 13 provides a visual comparison of the conservatively and heavily grazed pastures during the late wet and late dry seasons over the 2015 to 2018 hydrological years. In each instance the photographs show that the heavily grazed pasture had less pasture biomass and ground cover than the conservatively grazed pasture.

3.4. Ground cover

In the two years prior to the commencement of this study, the two pastures were extensively spelled with less than nine weeks of grazing at conservative stocking rates. During this time, the effect of season on cover can be observed with both pastures having higher proportions of bare ground in the late dry season (Fig. 12). At the commencement of this study in October 2014, the proportion of bare ground was similar in the conservatively (12.3%) and heavily grazed pastures (13.4%). At this time, 95% of the conservatively grazed pasture had cover levels of 78% or higher and 95% of the heavily grazed pasture had similar cover levels of 73% or higher. In October 2018, the amount of bare ground in the

Table 13
Photographic comparison of ground cover and pasture biomass from the two pastures in the late wet and late dry seasons from 2015 to 2018.

Year	Late wet season		Late dry season	
	Conservative grazing	Heavy grazing	Conservative grazing	Heavy grazing
2015				
2016				
2017				
2018				

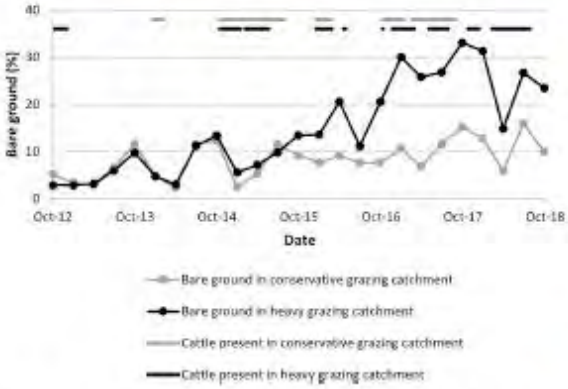

Fig. 12. Measurements of bare ground in the two pastures related to periods of cattle stocking.

heavily grazed pasture (23.5%) was 2.4 times greater than in the conservatively grazed pasture (9.9%). Ground cover in the conservatively grazed pasture remained relatively constant during the study with 95% of the pasture having cover levels of 80% or higher in October 2018. However, cover levels across 95% of the heavily grazed pasture decreased to 57% or higher by January 2018 before increasing to 69% or higher in October 2018, which was slightly lower than the distribution of cover at the commencement of the study. This analysis showed that the conservatively and heavily grazed pastures started in a similar condition, but an increase in bare ground and a corresponding decrease in ground cover were observed over time in the heavily grazed pasture.

3.5. Benchmarking ground cover to the Fitzroy Basin

Regional Ecosystems that contain brigalow (*Acacia harpophylla*) account for 32% of the Fitzroy Basin. Grazing is the predominant land use in these Regional Ecosystems, as it occurs on 86% of land that historically supported *Acacia harpophylla* in the Fitzroy Basin (Fig. 13).

VegMachine ground cover analysis provides outputs from May 1990. Since then, median VegMachine derived ground cover for the conservatively grazed catchment exceeded the lowest 80th percentile for the six Fitzroy sub-basins 95% of the time and exceeded the lowest 95th percentile 85% of the time (Fig. 14). Since the heavy grazing treatment was planted to the current pasture in 1992 until commencement of this study in 2014, median ground cover in the catchment equalled or exceeded the conservatively grazed catchment 40% of the time. During this period, ground cover exceeded the lowest 80th percentile for the six Fitzroy sub-basins 89% of the time and exceeded the lowest 95th percentile 70% of the time. Within five years of heavy grazing commencing, ground cover in that catchment was within the 5th percentile range of covers for the six Fitzroy sub-basins 44% of the time (Fig. 14).

4. Discussion

4.1. Stocking rates and safe long-term carrying capacity

Published recommended stocking rates for buffel grass pastures on brigalow lands vary from 0.1 AE/ha/yr to 0.5 AE/ha/yr (Lawrence and French, 1992), with observed stocking rates reported to be in the same range (Graham et al., 1991; Lawrence and French, 1992; Noble et al., 2000; Partridge et al., 1994; Paton et al., 2011; Peck et al., 2011). Some authors acknowledge that stocking rates should be adjusted for landscape and seasonal variability (Graham et al., 1991; Lawrence and French, 1992; Paton et al., 2011), while others note that stocking rates should be reduced over time as pasture productivity declines (Noble et al., 2000; Partridge et al., 1994; Peck et al., 2011). For example, Noble et al. (2000) recommends 0.5 AE/ha/yr on newly established buffel grass pastures and 0.33 AE/ha/yr on rundown buffel grass pastures. Daily live weight gains of 0.5 kg/head are considered possible from newly established pastures (Lawrence and French, 1992; Radford et al.,

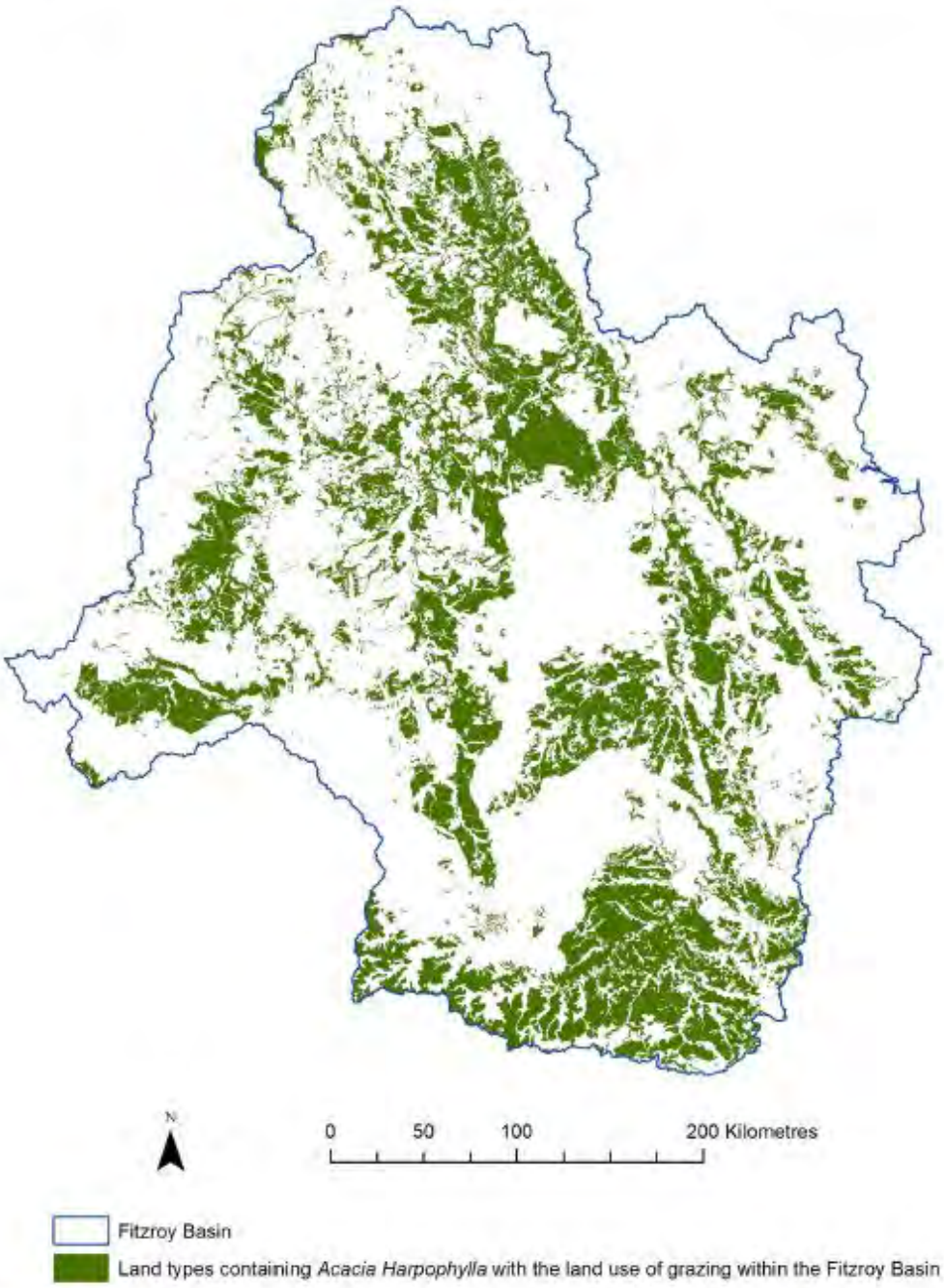

Fig. 13. Land types containing brigalow (*Acacia harpophylla*) with the land use of grazing (green) within the Fitzroy Basin (blue outline). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2007); however, Partridge et al. (1994) states that stocking rates should be adjusted to achieve daily weight gains of 0.4 kg/head on rundown pastures as the plants are more likely to be damaged at higher stocking rates.

In line with these recommendations and to maintain industry relevance, the average stocking rate of the conservatively grazed pasture during this study was 0.17 AE/ha/yr. Historically, stocking rates for this pasture were 0.45 AE/ha/yr on newly established buffel grass pasture when the study commenced, which decreased to 0.26 AE/ha/yr over the next 21 years (Radford et al., 2007). The average long-term (1984 to 2017) stocking rate was 0.30 AE/ha/yr (unpublished data). Daily weight gains in the order of 0.5 kg/head were achieved initially and have been

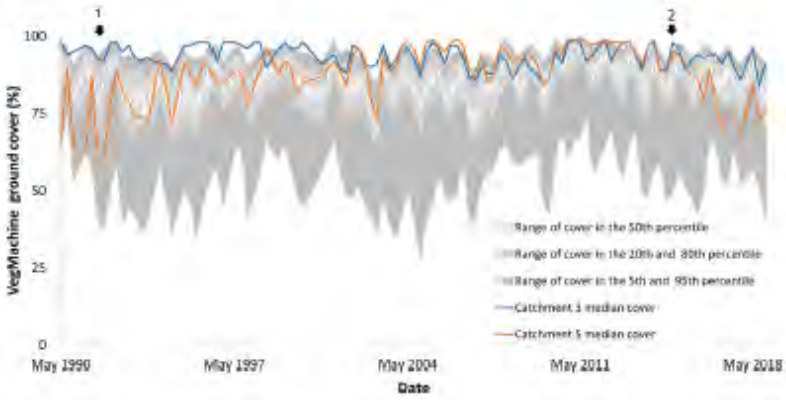

Fig. 14. Median satellite derived ground cover for the conservatively (blue line) and heavily (orange line) grazed catchments of the Brigalow Catchment Study compared to the range of cover percentiles for the Fitzroy Basin. Arrow 1 indicates planting of pasture in Catchment 5 following three years of cropping and arrow 2 indicates the commencement of heavy grazing in Catchment 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obtained periodically since (Radford and Thornton, 2011; Radford et al., 2007). However, maintaining the 0.45 AE/ha/yr stocking rate during the first 11 years following pasture establishment saw daily weight gains decline to about 0.3 kg/head (Radford et al., 2007).

The average stocking rate in the heavily grazed pasture was 0.54 AE/ha/yr. Despite the age of the pasture (40 to 50 years old), this stocking rate was similar to recommended stocking rates for newly established buffel grass pastures. For three decades post-clearing but prior to the inclusion of Catchment 5 into the Brigalow Catchment Study, historical stocking rates were about 0.40 AE/ha/yr. These stocking rates decreased over the next decade to less than 0.25 AE/ha/yr, followed by extensive spelling over the next eight years. This management history is in line with published recommended and observed industry stocking rates for brigalow lands, which suggests that sustained heavy grazing prior to inclusion in this study was unlikely.

Given the difficulties encountered in changing the traditional paradigm of "more cattle means more money" towards lighter stocking rates, despite equal or greater economic return (Moravek et al., 2017; O'Reagain et al., 2011; Stockwell et al., 1991), it is likely that high stocking rates are still used within the industry. This is supported by the VegMachine ground cover analysis, which shows that while ground cover in the heavily grazed pasture of the Brigalow Catchment Study was often in the 5th percentile for grazed *Acacia harpophylla* landscapes in the Fitzroy Basin, ground cover was still higher than some properties within similar landscapes. Thus, the heavily grazed pasture in this study may overestimate pasture biomass and ground cover and underestimate hydrology and water quality compared to some properties.

The concept of a safe long-term carrying capacity for sustainable grazing management benefits productivity, land condition and runoff water quality by balancing pasture utilisation with pasture growth (O'Reagain et al., 2014). A pasture utilisation rate between 15 and 30% of pasture growth has been considered a safe long-term carrying capacity (O'Reagain et al., 2011; Peck et al., 2011). A safe long-term carrying capacity can be estimated using pasture biomass, dietary intake requirements of cattle and pasture utilisation rates. For the conservatively grazed pasture, a safe long-term carrying capacity was 0.29 AE/ha/yr based on a long-term pasture biomass of 3500 kg/ha (Radford et al., 2007), an estimated dietary intake of 2.2% bodyweight per day (Minson and McDonald, 1987) and a high but still economically viable utilisation rate of 30% (Bowen and Chudleigh, 2017). This was similar to the lower estimate of long-term carrying capacity of 0.27 AE/ha/yr for the Brigalow Catchment Study determined by the FORAGE system (The State of Queensland, 2021). This was expected given the Aussie GRASS model (Carter et al., 2000) used in the FORAGE system is based on the GRASP pasture simulation model (Rickert et al., 2000), and both models have been informed by long-term BOTANAL pasture assessments, stocking rate and animal production data from the Brigalow Catchment Study (Dalal et al., 2021). GRASP pasture simulation modelling for Catchment 3 shows that in order to maintain a long-term pasture biomass of 3500 kg/ha, an average of about 7400 kg/ha of pasture biomass needs to be grown each year (Dalal et al., 2021). Although a safe long-term carrying capacity can be calculated, stocking rates should still be adjusted annually at the end of the summer growing period to account for pasture biomass. This reduces environmental damage, workload and management stress while benefiting long-term financial viability for the grazing enterprises (Lawrence and French, 1992).

4.2. Effect of grazing pressure on hydrology

The climatic sequence experienced in this study should not be considered atypical. Long-term records for the Brigalow Catchment Study show four consecutive below average rainfall years have occurred previously from 2006 to 2009 (Elledge and Thornton, 2017; Thornton et al., 2007; Thornton and Elledge, 2013, 2014). While the lowest total annual rainfall in the history of the Brigalow Catchment Study occurred in 2017, resulting in no runoff from any catchment, there have been four years between 1965 and 2014 when there was also no runoff from both Catchments 1 and 3 (Elledge and Thornton, 2017; Thornton et al., 2007; Thornton and Elledge, 2013, 2014). This highlights the need for long-term studies in semi-arid landscapes to capture both seasonal and annual rainfall variability, which is the key driver of most landscape processes (Cowie et al., 2007).

From first principles, heavy grazing pressure should decrease ground cover compared to conservative grazing pressure in the same landscape due to increased pasture utilisation and cattle trampling. It was hypothesised that a decline in ground cover combined with the deleterious effects of grazing on soil physical characteristics, such as structure and infiltration rate, would lead to increased runoff. This trend was demonstrated by the findings of Silburn et al. (2011) and Silcock et al. (2005) in the Fitzroy Basin, Bartley et al. (2014) and McIvor et al. (1995) in the Burdekin Basin, and internationally in reviews such as those of van Oudenhoven et al. (2015). Increased runoff is noted as a driver for both increased erosion and nutrient loads in runoff by both Australia studies (Koci et al., 2020; Thornton et al., 2017) and international long-term paired catchment studies, such as those of the Santa Rita Experimental Watershed (Polyakov et al., 2010). For example, the long-term Santa Rita study determined that runoff was the best predictor of sediment yield and explained up to 90% of its variability. As runoff is known to increase with a decline in ground cover and/or biomass (Bartley et al., 2010; Koci et al., 2020; McIvor et al., 1995; Silburn et al., 2011), an increase in runoff from the heavily grazed catchment was expected. This reflects numerous other studies that have reported greater runoff from grazed than ungrazed areas and/or pastures with higher stocking rates (Duniway et al., 2018; Filet and Osten, 1996; Mapfumo et al., 2002;

O'Reagain, 2011; Silcock et al., 2005; van Oudenhoven et al., 2015). This body of evidence suggested that the heavy grazing pressure in this study would ultimately lead to increased loads of sediment and nutrients in hillslope runoff compared to conservative grazing. Hillslope erosion of particular concern, as it accounts for 22% of sediment loss from Great Barrier Reef catchments (McCloskey et al., 2021).

Changing land use from virgin brigalow scrub to conservatively grazed pasture at the long-term Brigalow Catchment Study doubled total runoff (Thornton et al., 2007) and increased both average and maximum peak runoff rates by 1.5 times and 3.0 times, respectively, when runoff occurred from both catchments (Thornton and Yu, 2016). Over the four below average rainfall years of this study, heavy grazing of rundown pasture at stocking rates recommended for newly established pasture resulted in 3.6 times more total runoff and 3.3 times greater average peak runoff rate than the conservatively grazed pasture. At the end of this four-year study, the heavily grazed pasture had 2.4 times more bare ground and only 8% of the pasture biomass compared to the conservatively grazed pasture. In years when no runoff occurred from brigalow scrub, total runoff from the conservatively grazed pasture represents an absolute anthropogenic increase attributable to land use change.

Although Catchment 5 had a prior history of grazing before its inclusion in the Brigalow Catchment Study, both pasture catchments were managed according to recommended stocking rates. Satellite derived ground cover from VegMachine reflects this cattle stocking philosophy with similar cover for both the conservatively and heavily grazed pastures following the establishment of the current pasture in Catchment 5. Both Catchments 3 and 5 were dominated by clay soils (Vertosols and Dermosols) with a low slope (<6%), so inherent geomorphological differences are unlikely to override the grazing treatment effects on runoff and water quality. Furthermore, evidence that the runoff response from Catchment 5 is a treatment effect was supported by runoff responses from other catchments of the Brigalow Catchment Study.

For example, Catchment 4 of the Brigalow Catchment Study (Thornton and Elledge, 2013) had the same land use history as Catchment 5 until 1998 when it was planted to a leucaena and grass pasture. If the runoff response to the heavy grazing treatment in Catchment 5 during this study was a legacy response to historical land use, then a similar runoff response was expected from Catchment 4. That is, Catchment 4, a conservatively grazed leucaena and grass pasture, would have about triple the runoff of Catchment 3, the conservatively grazed grass pasture. However, Catchment 4 had only 94% of the total runoff from Catchment 3 from 2010 to 2013 (Thornton and Elledge, 2013, 2014); 464 mm and 496 mm, respectively. Similarly, the calibration of the long-term catchments in Stage I showed that the greatest difference in pre-clearing runoff was 28% (Thornton et al., 2007). This is an order of magnitude less than the difference in runoff between Catchments 3 and 5 during this study. Thus, the impacts of heavy grazing pressure on hydrology and water quality were considered to be related to the treatment imposed in Catchment 5 rather than a legacy response to historical sustained heavy grazing.

While increases in runoff are commonly attributed to or observed in partnership with declining ground cover, the landscape response is more complex. For example, Thornton et al. (2007) showed that changed water use patterns was the primary driver of increased runoff when native vegetation was replaced with improved grass pasture, and that increased compaction and reduced ground cover, soil structure and infiltration rate were secondary drivers. It is also known that the effects of cover on runoff and erosion are more complicated than a simple presence or absence relationship, with additional drivers including the type, distribution and mass of cover (Bartley et al., 2014; Koci et al., 2020). Increased runoff, and subsequently increased loads of nutrients in runoff, were effectively a reduction in plant available water capacity and soil fertility which leads to reduced pasture growth.

Persistent heavy grazing is also known to change the composition of pasture species over time, which leads to a decline in desirable (perennial, palatable and productive) species and an increase in less desirable (annual, unpalatable and less productive) species. For example, studies in the Burdekin Basin have attributed the transition of productive native grass species, such as black speargrass (*Heteropogon contortus*) and desert bluegrass (*Bothriochloa ewartiana*), to the less productive and less drought tolerant Indian couch (*Bothriochloa pertusa*) to a combination of drought and heavy grazing (Bartley et al., 2014; Spiegel, 2016). Thus, runoff, plant available water capacity, soil fertility, pasture growth and changes in pasture species composition are all intrinsically linked by the management of grazing pressure.

Intervention to break the cycle of declining land condition can be achieved with the adoption of improved management practices; however, the time required to restore healthy eco-hydrological function may vary from years to decades (Bartley et al., 2014; Hawdon et al., 2008; Roth, 2004; Silcock et al., 2005). For example, a landholder in the Burdekin Basin reported improved land condition with the adoption of a safe long-term carrying capacity and pasture spelling (Landsberg et al., 1998). The property had reduced income during the three-year transition phase, but became profitable with less cattle once the perennial grasses recovered. Other research in the Burdekin Basin indicates that sustainable grazing management is profitable over extended time periods and varying climatic cycles (O'Reagain et al., 2011). Nonetheless, from both an environmental and economic perspective, it is better to improve grazing management before a dramatic decline in land condition occurs (Rolfe et al., 2020).

4.3. *Effect of grazing pressure on water quality*

Heavily grazed pasture had higher loads and lower EMCs for all water quality parameters compared to the conservatively grazed pasture. In years when no runoff occurred from brigalow scrub, total runoff and subsequent loads of total suspended solids and all nutrients from the conservatively grazed pasture represent an absolute anthropogenic increase attributable to land use change. Over four below average rainfall years, this study typically had lower loads and higher EMCs than previously reported for the conservatively grazed pasture during wetter periods and over longer timeframes (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014). These trends indicate that increased hillslope runoff, whether from above average rainfall or a treatment (grazing pressure) effect, results in dilution of total suspended solids and nutrients leading to lower EMCs. However, the dilution effect was not strong enough to result in reduced loads. Dilution effects have been reported for sediment and nutrient concentrations within events (Schepers and Francis, 1982), within seasons (Hay et al., 2006; Schepers et al., 1982), in the transition from dry to wet seasons (Vink et al., 2007), and also on an annual basis over multiple years (Bartley et al., 2014; Miller et al., 2017). This study reflects other publications that have reported increased loads with increased flow (Hay et al., 2006; Schepers et al., 1982). It also reflects previous observations that high EMCs at this site do not necessarily equate to high loads (Thornton and Elledge, 2013).

4.3.1. *Total suspended solids*

Runoff from heavily grazed pasture had 3.2 times greater loads of total suspended solids than the conservatively grazed pasture. An increase in suspended solids with a decrease in ground cover reflected the trend observed between runoff and cover in this study, which is a relationship often cited in the literature (Bartley et al., 2010; McIvor et al., 1995; Silburn et al., 2011). VegMachine® analysis in this study also showed that ground cover decreased with increased grazing pressure. Despite similar cover levels in the two pastures initially, there was 2.4 times more bare ground in the heavily grazed pasture (23.5%) after four years compared to the conservatively grazed pasture (9.9%). Mean annual loads for both the conservatively (14 kg/ha/yr) and heavily grazed pastures (46 kg/ha/yr) during the four below average rainfall years were considerably lower than observed from the conservatively grazed pasture during an extremely wet period from 2010 to 2013

(Thornton and Elledge, 2013), a return to average conditions from 2013 to 2014 (Thornton and Elledge, 2014), and also modelled loads for the period 1984 to 2010 (Elledge and Thornton, 2017). Mean annual load from the three previously reported periods was 258 kg/ha/yr (range 20 to 468 kg/ha/yr). Loads from this study were also lower than more erosive landscapes on shallower soils elsewhere in the Fitzroy Basin (Silburn et al., 2011) and also in the nearby Burdekin Basin (Bartley et al., 2014; Hawdon et al., 2008).

Mean annual EMCs of total suspended solids from both the conservatively (278 mg/L) and heavily grazed pastures (235 mg/L) were similar to those previously reported for the conservatively grazed pasture during wetter periods and over longer timeframes (301 mg/L; range 95 to 916 mg/L) (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014). These values also fit within the ranges reported for grazing on both improved and native pastures dominated (>90%) by a single land use (Bartley et al., 2012). Bartley et al. (2012) reviewed water quality data from across Australia and found that EMCs of total suspended solids were lower from forests than improved pasture, and both these land uses were lower than from native pastures. In contrast, EMCs from brigalow scrub of the Brigalow Catchment Study were generally higher than from conservatively grazed pasture when runoff occurred from both catchments (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014). This highlights the importance that hydrological characteristics, vegetation type and landscape condition (i.e., ground cover) have on the resulting total suspended solids concentrations and loads. Data from the Brigalow Catchment Study can fill the knowledge gap of water quality from brigalow lands in the Fitzroy Basin to further refine estimations of the impact of grazing land management on Great Barrier Reef water quality.

4.3.2. Nitrogen

Similar to total suspended solids, loads of all nitrogen parameters during the four below average rainfall years were greater from heavily than conservatively grazed pasture while EMCs were lower from the heavily grazed pasture. This reflects other studies that have reported greater loads of nitrogen from grazed than ungrazed areas and from heavier than lighter grazing pressures (Daniel et al., 2006; Park et al., 2017). Mean annual loads of total nitrogen (0.29 kg/ha/yr) and dissolved inorganic nitrogen (0.08 kg/ha/yr) from the conservatively grazed pasture in this study were lower than previously reported during wetter periods (Thornton and Elledge, 2013, 2014) and over longer timeframes (Elledge and Thornton, 2017); 2.6 kg/ha/yr (range 0.6 to 5.1 kg/ha/yr) and 0.37 kg/ha/yr (range 0.06 to 0.81 kg/ha/yr), respectively.

In contrast, EMCs of total nitrogen (6.49 mg/L) and dissolved inorganic nitrogen (1.81 mg/L) from the conservatively grazed pasture in this study were higher than previously reported; 2.4 mg/L (range 2.0 to 3.2 mg/L) and 0.41 mg/L (range 0.11 to 0.80 mg/L), respectively (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014). EMCs for these two nitrogen parameters were within the range for improved pastures in Australia, but exceeded the range for native pastures when the majority of the upstream area was under a single land use (Bartley et al., 2012). However, under the more rigorous criteria of upstream area dominated (>90%) by a single land use, the total nitrogen EMC in this study exceeded the ranges for both improved and native pastures. Comparable data was not available for dissolved inorganic nitrogen.

These high EMCs are likely a reflection of the high soil fertility of brigalow lands compared to the rangeland, savannah and woodland landscapes from which comparable data was available. This is supported by long-term total nitrogen (14.4 mg/L; range 9.9 to 20.2 mg/L) and dissolved inorganic nitrogen (4.82 mg/L; range 1.94 to 7.01 mg/L) EMCs from brigalow scrub (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014) which greatly exceed the ranges given for forest in Bartley et al. (2012). Furthermore, modelling of long-term water quality indicates that brigalow scrub has higher loads and concentrations of nitrogen (total and dissolved) compared to conservatively grazed pasture (Elledge and Thornton, 2017). This contrasts with a number of Australian and international studies that have noted higher loads of nitrogen from pasture than forest (Quinn and Stroud, 2002; Udawatta et al., 2011; Vink et al., 2007). This highlights the uniqueness of brigalow lands where nitrogen fixation by brigalow (*Acacia harpophylla*) leads to high soil fertility, and hence higher losses of nitrogen in runoff, compared to other landscapes (Thornton and Elledge, 2013; Webb et al., 1982; Yule, 1989).

The limited data collected during this study showed that nitrogen lost in runoff from brigalow scrub was predominately in the dissolved phase. This phase was dominated by dissolved inorganic nitrogen which in turn was dominated by oxidised nitrogen. In contrast, nitrogen from the two pastures was lost in both particulate and dissolved phases. Both dissolved organic and inorganic nitrogen made substantial contributions to the dissolved phase. Oxidised nitrogen dominated the dissolved inorganic nitrogen fraction. This reflects numerous authors that have highlighted the importance of dissolved organic nitrogen when considering nitrogen losses (Alfaro et al., 2008; Robertson and Nash, 2008; Van Kessel et al., 2009). This is certainly the case for grazed landscapes, as dissolved organic nitrogen is known to increase with the application of cattle urine and dung (Van Kessel et al., 2009; Wachendorf et al., 2005), and concentrations have also been shown to increase with increased grazing pressure (Owens et al., 1989).

4.3.3. Phosphorus

Similar to total suspended solids and nitrogen, loads of all phosphorus parameters during the four below average rainfall years were greater from heavily than conservatively grazed pastures while EMCs were lower from the heavily grazed pasture. This reflects other studies that have reported greater loads of phosphorus from grazed than ungrazed areas and from heavier than lighter grazing pressures (Butler et al., 2008; Daniel et al., 2006; Park et al., 2017; Vink et al., 2007). Mean annual loads of total phosphorus (0.04 kg/ha/yr) and dissolved inorganic phosphorus (0.01 kg/ha/yr) from the conservatively grazed pasture in this study were lower than previously reported during wetter periods (Thornton and Elledge, 2013, 2014) and over longer timeframes (Elledge and Thornton, 2017); 0.38 kg/ha/yr (range 0.07 to 0.76 kg/ha/yr) and 0.20 kg/ha/yr (range 0.04 to 0.42 kg/ha/yr), respectively.

In contrast, EMCs of total phosphorus (0.81 mg/L) and dissolved inorganic phosphorus (0.26 mg/L) from the conservatively grazed pasture were higher than previously reported; 0.32 mg/L (range 0.23 to 0.41 mg/L) and 0.17 mg/L (range 0.10 to 0.22 mg/L), respectively (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014). The total phosphorus EMC fits within the range for both improved and native pastures within Australia (Bartley et al., 2012). Although the EMC for dissolved inorganic phosphorus was just above the range for improved pastures, it greatly exceeded the range for native pastures (Bartley et al., 2012). Similarly, the EMC for dissolved organic phosphorus in this study (0.05 mg/L) greatly exceeded both the improved and native pasture ranges of Bartley et al. (2012).

Similar to the response for nitrogen, these high EMCs are likely a reflection of the high soil fertility of brigalow lands. This is supported by long-term EMCs of total phosphorus (0.79 mg/L; range 0.32 to 2.19 mg/L) and dissolved inorganic phosphorus (0.16 mg/L; range 0.10 to 0.29 mg/L) from brigalow scrub (Elledge and Thornton, 2017; Thornton and Elledge, 2013, 2014) which greatly exceed the ranges given for forest in Bartley et al. (2012). Furthermore, soil phosphorus levels prior to land development at the Brigalow Catchment Study were considered moderate (13.7 mg/kg; range 13.3 to 14.0 mg/kg) based on the classification of Ahern et al. (1994). Levels increased rapidly becoming high to very high (34.7 mg/kg; range 24 to 44 mg/kg) following clearing and burning due to the resulting ash bed. However, soil phosphorus levels under grazing then declined back to a moderate level (12.6 mg/kg; range 11.0 to 14.6 mg/kg) over the next 32 years (Thornton and Shrestha, 2021). This is in stark contrast to the low, deficient (very low) and acute (extremely low) status of soil phosphorus given to 72% of the central and

north-east Queensland grazing lands (Ahern et al., 1994) and the deficient and acute status given to 60% of northern Australian soils (McCosker and Winks, 1994).

Phosphorus loss from uncultivated fields and grazed pasture is typically in the dissolved phase, which is dominated by dissolved inorganic phosphorus (Alfaro et al., 2008; Gillingham and Gray, 2006; Potter et al., 2006; Robertson and Nash, 2008). The limited data collected during this study showed that phosphorus loss from brigalow scrub may be dominated by particulate phosphorus while the grass pastures lost phosphorus in both particulate and dissolved phases. Higher EMCs of dissolved inorganic phosphorus from conservatively grazed pasture compared to brigalow scrub has previously been attributed to the presence of grazing animals and their dung (Elledge and Thornton, 2017), which is in agreement with the literature (Schepers et al., 1982; Vadas et al., 2011).

4.4. Implications for the grazing industry

This study shows that grazing land management based on a safe long-term carrying capacity has a lower risk to water quality than heavily grazed pastures. This is essential knowledge for the grazing industry given the recent introduction of minimum practice agricultural standards for beef cattle grazing under the Reef protection regulation (Office of the Great Barrier Reef, 2020; The State of Queensland, 2020d). As per the regulation, where land has ground cover less than 50% at September 30 each year, measures must be undertaken to move land towards good (A) or fair (B) condition; that is, ground cover greater than 50%. This became enforceable under the Environmental Protection Act 1994 (The State of Queensland, 2020a) in December 2020 for the Burdekin region, and will commence in December 2021 for the Fitzroy region followed by the Wet Tropics, Mackay Whitsunday and Burnett Mary regions in December 2022. This is in addition to minimum standard record keeping requirements that commenced for most graziers in December 2019.

Adoption of a safe long-term carrying capacity can assist landholders to demonstrate compliance with this legislation. For example, the Grazing Water Quality Risk Framework shows that hillslope pasture management has seven performance indicators where each indicator is weighted based on its relative influence on water quality leaving farms (McCosker and Northey, 2015; The State of Queensland, 2020b). Hillslope management based on a safe long-term carrying capacity combined with seasonal forage budgeting to ensure pasture utilisation rates are not exceeded accounts for 45% of the relative influence. Ground cover monitoring and pasture management decisions to achieve ground cover thresholds account for a further 30% of the relative influence.

5. Conclusion

Long-term data from the Brigalow Catchment Study suggests that a stocking rate of 0.29 AE/ha/yr is a safe long-term carrying capacity for well-managed, rundown (30 to 40 years old) buffel grass pasture established on predominantly clay soils previously dominated by brigalow woodland. This recommendation is based on long-term pasture biomass and cattle live weight gains from the study site; however, stocking rates may need to be reduced at other locations unable to maintain similar amounts of pasture biomass under grazing (average 3500 kg/ha). Failure to reduce stocking rates on rundown pastures to match safe long-term carrying capacity led to increased hillslope runoff, and subsequently increased loads of total suspended solids, nitrogen and phosphorus in runoff. While limited water quality data was collected during the four below average rainfall years of this study, loads of total nitrogen and phosphorus both had substantial contributions of particulate and dissolved fractions. Although heavily grazed pasture had the highest runoff and greatest loads of total suspended solids and all nutrient parameters, it had the lowest EMCs. Heavy grazing pressure reduced ground cover which demonstrates the value of this indicator for assessing land condition. Continued monitoring would increase confidence in these findings by capturing more average and above average rainfall years, as wet years may produce different catchment responses. Continued monitoring to increase the dataset would enable statistical analyses of cover, hydrology and water quality interactions.

This study compliments other studies that have reported improved land condition and reduced economic risk by transitioning from heavy to conservative grazing pressures. Studies such as these underpin broader economic analyses that demonstrate long-term financial benefits for graziers who adopt improved management practices. This body of evidence demonstrates that reducing grazing pressure is a realistic economic option for landholders that will also have benefits for runoff water quality.

CRediT authorship contribution statement

C.M. Thornton: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **A. E. Elledge:** Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix 4

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Tebuthiuron Movement via Leaching and Runoff from Grazed Vertisol and Alfisol Soils in the Brigalow Belt Bioregion of Central Queensland, Australia

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ABSTRACT: Tebuthiuron is one of five priority herbicides identified as a water pollutant entering the Great Barrier Reef. A review of tebuthiuron research in Australia found 13 papers, 6 of which focused on water quality at the basin scale (>10,000 km^2) with little focus on process understanding. This study examined the movement of tebuthiuron in soil and runoff at the plot (1.7 m^2) and small catchment (12.7 ha) scales. The greatest concentration and mass in soil occurred from 0 to 0.05 m depth 30−57 days after application. Concentrations at all depths tended to decrease after 55−104 days. Runoff at the small catchment scale contained high concentrations of tebuthiuron (average = 103 μg/L) 100 days after application, being 0.05% of the amount applied. Tebuthiuron concentrations in runoff declined over time with the majority of the chemical in the dissolved phase.

KEYWORDS: *tebuthiuron, leaching, runoff, soil, pesticide, herbicide, brigalow, Brigalow Catchment Study, grazing*

INTRODUCTION

In 2009, the Australian and Queensland governments enacted the Reef Water Quality Protection Plan to reduce the risk of declining water quality entering the Great Barrier Reef (GBR). Five photosystem II (PSII) herbicides are targeted in the Reef Plan: ametryn, atrazine, diuron, hexazinone, and tebuthiuron.[1] The first four are registered for use in sugar cane, whereas tebuthiuron is registered for use in grazing.[2] Tebuthiuron is a substituted urea herbicide, chemical name *N*-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-*N*,*N'*-dimethylurea and chemical formula $C_9H_{16}N_4OS$.[3] Internationally, tebuthiuron is registered for use in grasslands and grazing systems in South Africa and the United States[3,4] and in sugar cane in Brazil.[5,6] It is not approved or known to be used in European countries.[6,7] Granular tebuthiuron has been registered in Australia since the 1980s and is used to control regrowth of brigalow (*Acacia harpophylla*), tea tree (*Melaleuca* spp.), and other problem woody weeds on grazing lands in Queensland.[8−10]

Tebuthiuron has been detected in GBR flood plumes from the Wet Tropics, Burdekin, Mackay-Whitsunday, and Fitzroy catchments. The greatest concentrations of tebuthiuron found in flood plumes were 0.014 μg/L from the Fitzroy basin and 0.006 μg/L from the Burdekin basin.[11] Kennedy et al.[12] reported tebuthiuron concentrations exceeding the ANZECC trigger value of 0.02 μg/L for 99% ecological protection at sites 3−11 km from the mouth of the Burdekin River and up to 240 km from the mouth of the Fitzroy River. Despite regular detections of tebuthiuron in the catchments of the GBR, there is a paucity of information on how this herbicide behaves in soil and water in the Australian environment. A literature review using "tebuthiuron" and "Australia" in 2015 found 13 journal papers. Six of these studies focused on freshwater and/or marine water quality at the reef catchment scale;[11−16] five studies determined the impacts and toxicity of herbicides to a range of organisms, including plants, fish, algal, coral, and seagrass;[17−21] one study assessed the role of herbicides on sustainability and water quality of forest ecosystems;[22] and another study considered the use of chemically reactive barriers for the treatment of runoff and drainage containing herbicides.[23] Some of these studies focus on PSII herbicides as a group rather than quantifying the concentration and effects of tebuthiuron as an individual herbicide. Most of the papers, particularly those relating to water quality, have monitored large areas containing multiple land uses with interpretation of tebuthiuron data from grazing inferred rather than measured directly. Furthermore, the literature review found no Australian data relevant to the movement of tebuthiuron in soil or in runoff from grazed pastures at the small catchment scale. Review of the international literature indicates that rainfall and soil organic matter and clay contents are linked to tebuthiuron dynamics.[24−26] The current lack of data relating to tebuthiuron movements in the Australian grazing landscape, including loss in runoff, is a knowledge gap.

The objective of this study was to better understand the persistence and movement of tebuthiuron in grazing systems in GBR catchments by investigating (1) the persistence of tebuthiuron in Vertisol and Alfisol soils under natural rainfall conditions, (2) the movement of granular and dry flowable tebuthiuron in runoff from both soil types at the plot scale (1.7 m^2) under simulated rainfall conditions, and (3) the movement of granular tebuthiuron in runoff at the small catchment scale (12.7 ha) under natural rainfall conditions.

MATERIALS AND METHODS

Site Description. This research was conducted at the Brigalow Catchment Study (BCS), which is a long-term (50 years) paired

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calibrated catchment study located in the Dawson subcatchment of the Fitzroy basin, central Queensland, Australia (24°48′29″ S, 149°47′50″ E using the Geodetic Datum Australia[27]). An overview of the BCS is presented in Cowie et al.;[28] rainfall and runoff results are presented in Thornton et al.[29] and Thornton and Yu;[30] agronomic and soil fertility results are presented in Radford et al.;[31] and the deep drainage component of the water balance is presented in Silburn et al.[32] The region has a semiarid, subtropical climate. Annual average rainfall (October−September) from 1965 to 2014 was 661 mm. Summers are wet with 70% of the annual rainfall falling between October and March, whereas winter rainfall is low.[33]

Soil Descriptions. The soils of the BCS are predominantly Vertisols and Alfisols with an average slope of 2.5%. In its virgin state the site was vegetated with brigalow scrub vegetation communities.[34] Tebuthiuron persistence in soil and its movement under simulated rainfall were investigated on two soil types, a Sodic Calciusterts Vertisol (Vertisol) and a Typic Natrustalfs Alfisol (Alfisol). The small catchment area of the natural rainfall study was 58% Vertisols and 42% Alfisols. In their virgin state, the Vertisols had an acid reaction trend with clay content increasing from 36% in the surface soil to 54% at 1.8 m.[35] In contrast, the Alfisols had an alkaline reaction trend with clay content of 18% in the surface soil, 31% at 0.2−0.3 m, and then decreasing with depth.[35] The physiochemical characteristics of the Vertsiols and Alfisols at this site are given in Table 1.

Movement in Soil under Natural Rainfall. The vertical movement of tebuthiuron was monitored in a Vertisol and an Alfisol under natural rainfall. On each soil type a row of 1.0 × 1.7 m adjacent unbounded plots was established. Graslan (200 g active ingredient (ai)/kg) is a tebuthiuron product registered for commercial application in Australia;[10] however, as soil concentrations of tebuthiuron decrease with distance from the site where granular pellets are placed, results can be biased by the choice of sampling locations within a plot.[36] To account for this sampling challenge, Spike 80DF (800 g ai/kg),[37] a dry flowable formulation of tebuthiuron, was applied to the plots at a rate of 3000 g/ha of ai instead of the granular product. Spike 80DF is not registered for commercial application in Australia but was approved for experimental use under a small-scale trial permit. Each plot was used for only one sampling interval with no plot sampled twice. Six soil cores were taken randomly from each plot using a hydraulic coring rig. Each core was divided into depth increments of 0−0.025, 0.025−0.05, and 0.05−0.1 m and then 0.1 m increments until a maximum of 0.4 m before the cores were combined to make a composite sample for analysis. Tebuthiuron concentration was determined by liquid chromatography−mass spectrometry (LC-MS/MS) method KEP14D.[38] In this method, the soil was shaken with acetone using a tabletop shaker for approximately 12 h. The herbicide was then extracted using a QuEChERS procedure. The final extract was analyzed by LC-MS/MS. The limits of detection, quantification, and reporting for this method are 0.2, 0.5, and 1 μg/kg, respectively. The concentration of tebuthiuron in soil was converted into mass per sampling depth using measured soil bulk density. Dissipation of tebuthiuron was represented using a first-order equation.[39] Half-lives of tebuthiuron in soil to 0.4 m were calculated by taking the natural log of soil tebuthiuron concentration at each sampling time, fitting a linear regression to the data, and then estimating the half-life by dividing the natural log of 0.5 by the slope of the regression line.

Sampling commenced in October 2011 with soil samples taken at 57, 104, 197, and 314 days after tebuthiuron application. This sampling strategy was chosen based on half-lives of 1−2 years reported in the literature.[3,40,41] Sampling was repeated in October 2012 with soil samples taken at 1, 16, 30, 55, and 104 days after tebuthiuron application. More intensive sampling was conducted to obtain data at shorter time intervals, particularly within the first 50 days after tebuthiuron application, to more accurately reflect the half-lives observed in the first sampling.

Movement in Runoff at the Plot Scale under Simulated Rainfall. Simulated rainfall was used to investigate tebuthiuron concentrations in runoff from a Vertisol and an Alfisol. In October 2011, six plots 1.0 × 1.7 m on each soil type were treated with 3000 g ai/ha of tebuthiuron, three with granular tebuthiuron (Graslan) (200 g ai/kg) and three with dry flowable tebuthiuron (Spike 80DF) (800 g ai/kg). Tebuthiuron was applied to the plots immediately before simulated rainfall. Rainfall was then applied to each plot at a target intensity of 80 mm/h. Once runoff commenced, rainfall continued on the plot for a further 30 min, during which time 1 L runoff samples were collected at 5 min intervals (0, 5, 10, 15, 20, 25, and 30 min) for the determination of runoff rate. Within each 5 min interval, runoff was sampled for a set time to generate one 0.75 L composite flow weighted-average sample for the determination of tebuthiuron concentration. Samples of the water used to simulate rainfall were also analyzed for tebuthiuron to allow the calculation of a corrected runoff result if necessary.

Details on the rainfall simulation setup are given in Thornton and Elledge.[34] Each plot was encapsulated by a three-sided sheet metal edge (0.15 m high) placed approximately 0.05−0.07 m into the ground to achieve a hydraulic barrier. The short, downslope side of the plot had a separate metal plot end with a trough and spout for collecting runoff; the plot end was pushed into the ground until the top edge was level with the soil surface. The rainfall simulator used was in an A-frame configuration. Three downward-facing oscillating nozzles delivered a flat spray pattern of water across the plot with a fan angle of 80°. A metal shroud positioned below each nozzle limited the lateral and longitudinal spray delivery and also collected excess water, which was returned to the pump delivery unit for recycling. The assembly was adjusted at each plot for adequate magnitude of nozzle sweep and symmetry of sweep relative to the simulator frame. Total runoff was calculated by a linear interpolation of the runoff rate of the seven 1 L samples integrated for the duration of the event using Water Quality Analyzer v2.1.2.4.[42] Tebuthiuron concentration was determined by liquid chromatography−mass spectrometry (LC-MS) method QLS 29937.[38] In this method an aliquot of water sample is extracted on a solid phase extraction cartridge prior to determination of herbicides by LC-MS/MS. The limits of detection, quantification, and reporting for this method are 0.003, 0.01, and 0.01 μg/kg, respectively. Tebuthiuron loads in runoff were then calculated as follows:

$$\text{load (g ai/ha)} = \left[\frac{[\text{concn in runoff } (\mu\text{g/L}) \times \text{runoff vol (L)}]/1000}{\text{plot length (m)} \times \text{plot width (m)}}\right] \times 10000/1000$$

Comparison of tebuthiuron load losses for the two formulations was made for each soil type using analysis of variance in Genstat v14.1.[43] The replicate and residual variances for soil types were then compared, determining that it was appropriate to pool variances and, thus, allowing soil types to be compared.

Movement in Runoff at the Small Catchment Scale under Natural Rainfall. Tebuthiuron movement in runoff was investigated at the small catchment scale (12.7 ha) in a buffel grass pasture (*Cenchrus ciliaris* cv. Biloela) under natural rainfall conditions. Pasture cover is consistently >80%. There had been no control of regrowth vegetation since clearing in 1982. Granular tebuthiuron (Graslan Aerial 200 g ai/kg) was applied by plane on November 15, 2011, by Dow AgroSciences at a rate of 12.5 kg/ha (2.5 kg ai/ha), reflecting commercial practice.[10,44] The catchment was instrumented to measure runoff using a 1.2 m steel HL flume with a 3.9 × 6.1 m concrete approach box. Water height through the flume was recorded using a mechanical float recorder. Rainfall was recorded at the head of the catchment.[29] A runoff event was defined as the period when water was flowing through the flume. Event-based water quality samples were collected by automated samplers between November 2011 and January 2015 with a maximum of 12 samples per an event. Samples were collected every 0.1 m change in absolute flow height. Tebuthiuron concentration was determined by LC-MS method QLS 29937 (as for the plot scale analysis), whereas total suspended solids was determined by gravimetric quantification of solids in water method 18211.[38] In this method a well-mixed sample is filtered through a predried and preweighed glass fiber filter. The residue on the filter is washed to remove soluble salts and then dried to a constant

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Table 1. Average Physiochemical Values for a Vertisol and Alfisol in Their Virgin State (After Cowie et al.[28])

depth (m)	pH	EC[a] (dS/m)	Cl[b] (μg/g)	OC[c] (%)	P[d] ($NaHCO_3$) (μg/g)	NO_3-N[e] (KCl) (μg/g)	TKN[f] (%)	TP[g] (%)	TK[g] (%)	TS[g] (%)	CEC (cmol/kg)	exchangeable Ca^{2+} (cmol/kg)	exchangeable Mg^{2+} (cmol/kg)	exchangeable Na^{+} (cmol/kg)	exchangeable K^{+} (cmol/kg)	clay (%)
Vertisol Soil																
0.0–0.1	6.56	0.16	75	1.58	12	2.7	0.16	0.03	0.15	0.03	34	12	11.1	1.4	0.4	36
0.1–0.2	7.54	0.48	450	0.95	8	1.2	0.11	0.04	0.15	0.02	36	12	14.6	3.2	0.2	40
0.2–0.3	8.14	0.68	730	0.52	4	0.5	0.06	0.02	0.14	0.02	35	10.0	15.4	4.1	0.2	44
0.5–0.6	5.70	0.77	1040		3	0.2		0.01	0.14	0.01	32	5.9	14.6	4.6	0.2	45
0.8–0.9	4.76	0.83	1145		1	0.2		0.01	0.14	0.01	32	4.1	13.7	4.9	0.1	46
1.1–1.2	4.64	0.83	1170		1	0.2		0.01	0.14	0	34	3.4	13.4	5.4	0.1	46
1.4–1.5	4.52	0.92	1320		2	0.1		0.01	0.14	0	38	3.4	15.0	6.6	0.2	50
1.7–1.8	4.48	0.98	1385		2	0.1		0.01	0.15	0	39	3.3	15.7	6.9	0.3	54
Alfisol Soil																
0.0–0.1	6.80	0.10	20	2.09	8	4	0.18	0.03	1.05	0.02	21	9.5	4.1	0.3	0.5	18
0.1–0.2	7.16	0.17	130	0.73	4	1.1	0.08	0.02	0.84	0.01	25	6.4	9.2	2.3	0.2	31
0.2–0.3	7.52	0.22	220	0.58	3	0.5	0.06	0.01	0.88	0.01	23	5.6	9.3	2.9	0.1	28
0.5–0.6	8.83	0.40	400			0.2					24	6.3	9.9	4.7	0.2	
0.8–0.9	9.20	0.47	470			0.2					16	2.8	6.8	4.1	0.1	

[a]Electrical conductivity. [b]Chloride. [c]Organic carbon (Walkley and Black). [d]Bicarbonate-extractable phosphorus (Colwell). [e]Potassium chloride-extractable nitrate-nitrogen. [f]Total Kjeldahl nitrogen. [g]Total by X-ray fluorescence.

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weight at 105 ± 2 °C. The increase in weight represents the total suspended solids. The limit of reporting for this method is 2 mg/L.

Event-based tebuthiuron load and event mean concentration (EMC) for each event are presented. Event loads were calculated by dividing the hydrograph into sampling intervals, multiplying the discharge in each interval by the sample concentration, and summing the loads over all of the intervals. The intervals were defined as the start of flow to the midpoint of sample one and sample two, the midpoint of sample one and sample two to the midpoint of sample two and sample three, and so on. Event-based EMC was calculated by dividing total event load by total event flow. Regressions were undertaken using Genstat v14.1.[43]

Comparing Tebuthiuron Movement from Simulated and Natural Rain Studies. To explore if the data collected using rainfall simulation is representative of tebuthiuron movement under natural rainfall, the small catchment scale data were combined with the plot scale rainfall simulation data for analysis. The EMC of each plot from the rainfall simulation trial was treated as a separate "event". Additionally, data from related plot scale rainfall simulation studies described by Cowie et al.[45] in the Wet Tropics, Burdekin, Fitzroy, and Burnett-Mary basins were included, with average tebuthiuron concentration in runoff calculated for each of the study sites, irrespective of tebuthiuron formulation or plot treatments. A time series of data from the various studies was combined to explore tebuthiuron movement in runoff relative to time after application.

RESULTS

Movement in Soil under Natural Rainfall. A total of 174 mm of rain fell during the 104 days of the short sampling interval study, with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 30 days after application for both soils (Figure 1). The greatest concentration from 0.05 to 0.4 m was measured 104 days after application in the Vertisol and 55 days in the Alfisol (Figure 1). The greatest mass of tebuthiuron from 0 to 0.4 m in both soils was also measured on day 30 (Figure 2). After 30 days, the mass of tebuthiuron from 0 to 0.4 m tended to decline over time in both soils (Figure 2).

A total of 710 mm of rain fell during the long sampling interval study, again with rainfall occurring between all sampling intervals. The greatest concentration of tebuthiuron from 0 to 0.05 m was measured 57 days after application for both soils. Tebuthiuron concentration tended to decline with time and depth in both soils (Figure 3). Tebuthiuron mass from 0 to 0.4 m declined over time in both soils (Figure 4). The change in tebuthiuron mass to 0.4 m equated to a half-life of 71 days in the Vertisol and 129 days in the Alfisol.

Movement in Runoff at the Plot Scale under Simulated Rainfall. Although the target intensity of simulated rainfall was 80 mm/h, actual intensities varied between 59 and 81 mm/h. When simulated rainfall was applied immediately after tebuthiuron application to Vertisols, 748 g/ha of granular formulation was lost in runoff (25% of applied tebuthiuron), significantly more than the 352 g/ha of dry flowable formulation lost in runoff (12% of applied tebuthiuron) ($P < 0.05$) (Figure 5). Average tebuthiuron loss in runoff from Alfisols was 373 g/ha (12.5% of applied tebuthiuron) with no significant difference in runoff loss due to formulation (Figure 5). Runoff from Vertisols averaged 123% of runoff from Alfisols, whereas tebuthiuron concentration in runoff was 125%, hence a significant trend for greater tebuthiuron loss from Vertisols compared to Alfisols ($P < 0.10$).

Movement in Runoff at the Small Catchment Scale under Natural Rainfall. Tebuthiuron samples were collected from 10 runoff events ranging from 100 to 1170 days after application (Table 2). These events accounted for >90% of the runoff events with >1 mm of runoff that occurred in this period with the sampling pattern reflecting the seasonality of rainfall and runoff in this climate. Tebuthiuron EMC declined exponentially with time (eq 1, $R^2 = 0.998$, $P < 0.001$), rainfall (eq 2, $R^2 = 0.999$, $P < 0.001$), and runoff (eq 3, $R^2 = 0.985$, $P < 0.001$) since application.

$$\text{EMC (mg/L)} = 2.556 + 265.4 \times 0.99^{x\ (\text{time in days})} \quad (1)$$

$$\text{EMC (mg/L)} = 2.482 + 573.3 \times 0.995^{x\ (\text{rainfall in mm})} \quad (2)$$

$$\text{EMC (mg/L)} = 4.54 + 109.49 \times 0.289^{x\ (\text{runoff in mm})} \quad (3)$$

The greatest decline occurred between the first two events, 100 and 224 days after application (Figure 6). The concentration of tebuthiuron in individual runoff samples within an event showed little variation; thus, event EMC was almost identical to the average of the individual sample concentrations. At 1170 days after application, a total of 2426 mm of rainfall and 274 mm of runoff had occurred, and a total of 1.07% of the applied tebuthiuron had been exported in runoff (Table 2). Tebuthiuron loss during each event was <0.45% of the total applied to the catchment. No relationship was detected between tebuthiuron concentration and the total suspended solids concentration of individual runoff samples ($P = 0.57$) (Figure 7).

Comparing Tebuthiuron Movement from Simulated and Natural Rain Studies. The combined data set of tebuthiuron EMCs in runoff from the small catchment scale under natural rainfall (section above) and tebuthiuron EMCs in runoff from 13 simulated rainfall studies at the plot scale (data presented under Movement in Runoff at the Plot Scale under Simulated Rainfall combined with the data of Cowie et al.[45]) showed an exponential decline over time since application (eq 4, $R^2 = 0.776$, $P < 0.001$) (Figure 8). The shortest time between tebuthiuron application and runoff was 5 min (the rainfall simulation studies), whereas the longest was 1170 days (the small catchment scale study). However, the relationship developed at the small catchment scale substantially underestimated EMCs from the combined data set prior to 30 days after application. When the time series of data was limited to events occurring >30 days after tebuthiuron application, a significant exponential decline over time was found (eq 5, $R^2 = 0.916$, $P < 0.001$).

$$\text{EMC (mg/L)} = 3.08 + 2349 \times 0.9432^{x\ (\text{time in days})} \quad (4)$$

$$\text{EMC (mg/L)} = 4.32 + 314.94 \times 0.9849^{x\ (\text{time in days})} \quad (5)$$

DISCUSSION

Tebuthiuron was found to be mobile to depths of 0.4 m in both Vertisols and Alfisols. The greatest concentrations and greatest mass of tebuthiuron in both soils was measured 30−57 days after application to the soil surface. Movement down the soil profile is consistent with international literature, which has reported tebuthiuron at depths of 0.15−0.6 m.[3,5,24,46] Movement of tebuthiuron to 1.8 m has been found in soil composed of 92% sand.[3] Emmerich et al.[47] reported that tebuthiuron adsorbed to clay and organic matter in soil and that movement decreased as clay and organic matter content increased. This may explain the movement of tebuthiuron to 1.8 m in soil with an extremely high sand content. In contrast, Matallo et al.[48]

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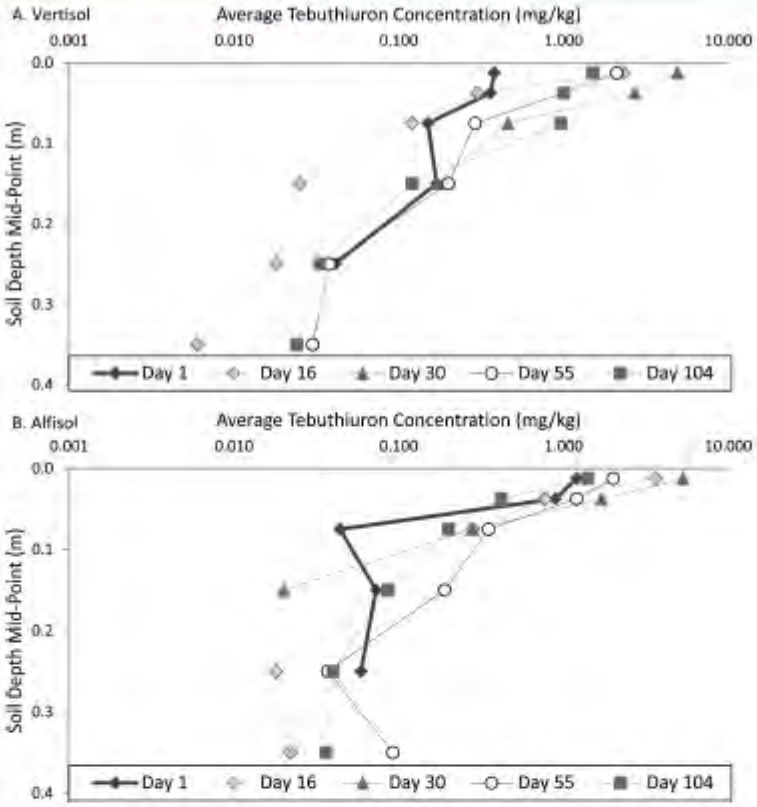

Figure 1. Tebuthiuron concentration (mg/kg) in the 0–0.4 m profile of the Vertisol (A) and Alfisol (B) at 1, 16, 30, 55, and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

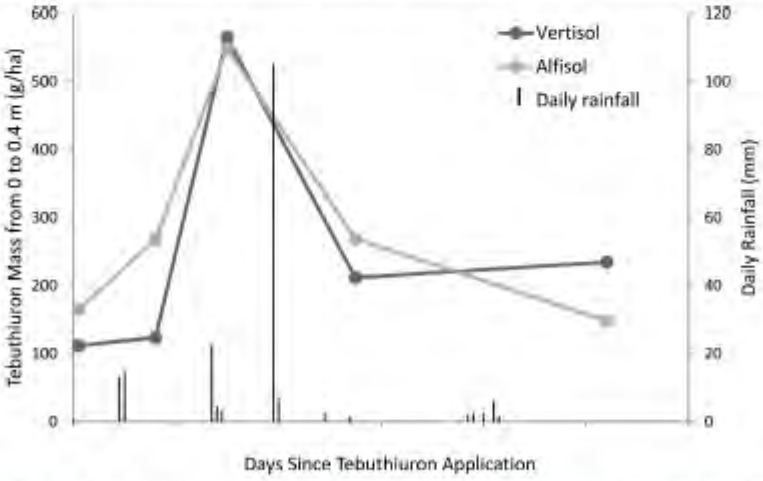

Figure 2. Tebuthiuron mass (g/ha) in the 0–0.4 m profile of the Vertisol and Alfisol at 1, 16, 30, 55, and 104 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

noted that tebuthiuron was poorly sorbed to soil but, similar to the results of Emmerich et al.,[47] found less leaching from clayey soil than from sandy soil. Given that tebuthiuron is highly soluble in water, its movement to depth in soil is likely a function of soil water-holding capacity and hydraulic conductivity, both of which are heavily influenced by clay and organic matter content.[3,36,49] This is supported by the redistribution of tebuthiuron in the soil profile after rainfall,

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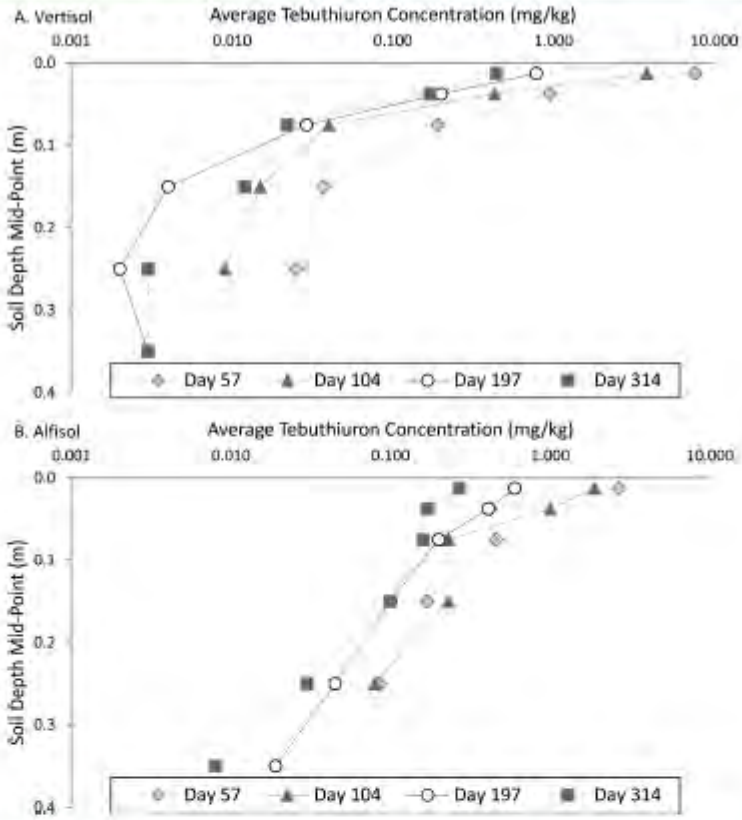

Figure 3. Tebuthiuron concentration (mg/kg) in the 0–0.4 m profile of the Vertisol (A) and Alfisol (B) at 57, 104, 197, and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

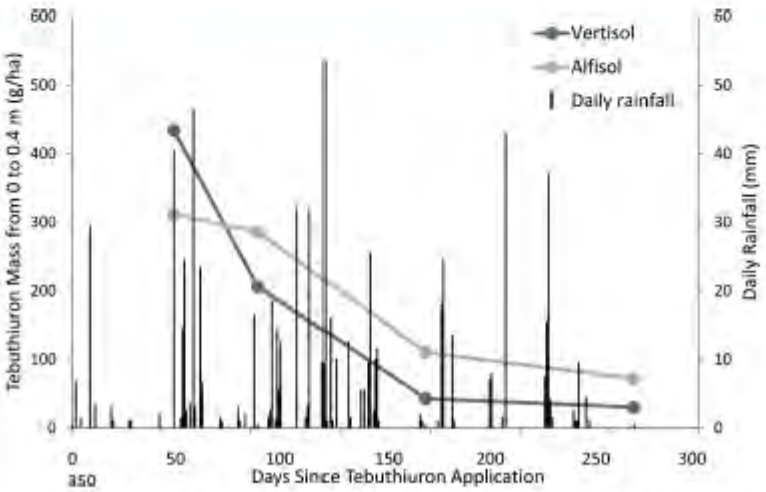

Figure 4. Tebuthiuron mass (g/ha) in the 0–0.4 m profile of the Vertisol and Alfisol at 57, 104, 197, and 314 days after application to the soil surface. Tebuthiuron was applied at a rate of 3000 g ai/ha.

which was observed in this study and was earlier noted by Parry and Batterham,[56] and by the observation that the pattern of tebuthiuron redistribution differed between the two soils, which have differing clay and organic matter contents.

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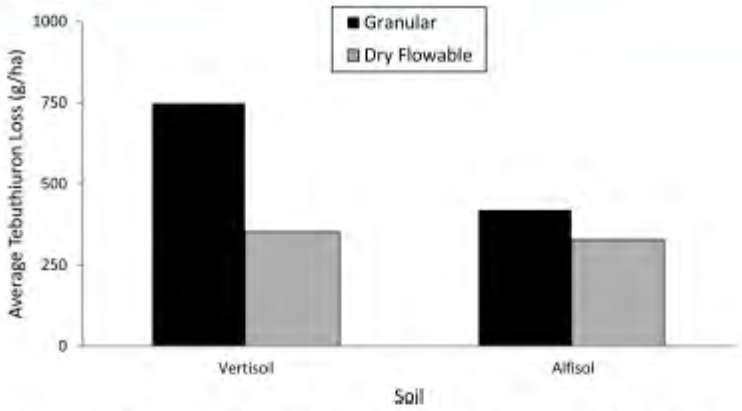

Figure 5. Average tebuthiuron loss (g/ha) in runoff from Vertisol and Alfisol soils under simulated rainfall immediately after application. Tebuthiuron was applied at a rate of 3000 g ai/ha.

Table 2. Event-Based Loads and Concentrations of Tebuthiuron and Total Suspended Solids in Runoff at the Small Catchment Scale under Natural Rainfall Conditions[a]

					tebuthiuron				total suspended solids	
runoff event date	days since tebuthiuron application	cumulative rainfall since tebuthiuron application (mm)	total event discharge (mm)	no. of samples	event load (g/ha)	av sample concn (μg/L)	event EMC (μg/L)	loss (% of applied)	event load (kg/ha)	event EMC (mg/L)
Feb 23, 2012	100	360	12	6	1.29	102.6	104.6	0.051	1.3	105.2
June 26, 2012	224	615	17.0	5	5.39	31.0	31.6	0.215	14.4	84.8
Nov 10, 2012	360	829	47.6	11	6.37	13.5	13.4	0.255	71.2	149.6
Jan 25, 2103	437	1006	138.1	2	11.30	8.0	8.2	0.450		
March 1, 2013	472	1239	25.7	11	1.30	6.0	5.2	0.050	57.2	222.7
Nov 23, 2013	739	1581	21.1	12	0.67	3.0	3.2	0.027	40.5	191.8
Dec 12, 2013	758	1680	10.4	4	0.26	3.0	2.5	0.011	170.8	1640.3
March 31, 2014	867	1994	0.2	3	0.01	2.8	2.8	0.000	0.5	
Dec 17, 2014	1128	2253	5.0	3	0.08	1.5	1.5	0.003	9.4	
Jan 28, 2015	1170	2426	7.7	3	0.08	1.0	1.0	0.003	7.6	99.5
total	1170	2426	274.1		26.7			1.1	372.9	
av			27.4		2.7	17.3	17.4	0.1	41.4	356.3

[a]Tebuthiuron was applied on Nov 15, 2011, at a rate of 12.5 kg/ha (200 g ai/kg).

Redistribution of tebuthiuron by rainfall is also likely responsible for two of the tebuthiuron dynamics observed in soil. First, the maximum concentration of tebuthiuron in the soil at 0−0.05 m occurred at day 30 rather than at day 1 in the short sampling interval study and, second, the concentrations of tebuthiuron fluctuated at depth in both studies. These dynamics are attributed to the interception of dry flowable tebuthiuron by plant residues during application and its subsequent wash-off and hence delayed transport into the soil profile. Herbicide interception by trash and subsequent wash-off into soil is a well-documented process with significant amounts of herbicide able to be intercepted.[50,51] It is likely that this behavior was absent from the long sampling interval study as the wash-off process had already occurred with the 85 mm of rainfall prior to the first sampling. This is supported by the apparent completion of the wash-off process in the short sampling interval study with the 53 mm of rainfall that occurred prior to the maximum soil concentration at 0−0.05 m.

Tebuthiuron half-lives in soil from this study were 71 and 129 days. This is considerably shorter than the 1−2 year half-lives reported in the United States, but not as short as the 16−20 days found in Brazil.[3,5,40,41] The half-lives from this study account for mass change of tebuthiuron in the soil profile irrespective of the change being attributed to breakdown, movement, or uptake by vegetation.

Simulated rainfall at the plot scale showed a greater loss of tebuthiuron in runoff from Vertisols compared with Alfisols. This is consistent with the theory that tebuthiuron movement is a function of soil water-holding capacity and hydraulic conductivity. Infiltration on Vertisols is expected to be lower than that of Alfisols due to higher clay content, which results in a shorter time to runoff and an increase in runoff volume.[29,52] A greater proportion of rainfall onto Vertisols interacts with highly soluble tebuthiuron that has not leached deeper into the soil prior to runoff, resulting in greater losses than from Alfisols.

The literature shows that pesticide decay after application generally exhibits a first-order decay pattern; however, no reference to the pattern of tebuthiuron decay in runoff over time could be found in the literature under natural rainfall conditions at the small catchment scale.[53] This study appears to be the first to demonstrate this pattern. A common trend of an exponential decline in tebuthiuron EMC over time when

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undertaking combined analysis of small catchment scale and simulated rainfall data from this study gives confidence that the data obtained using simulated rainfall reflect those collected under natural conditions. Silburn and Kennedy[54] presented the same conclusion when considering the suitability of simulated rainfall for pesticide research. Analysis of other simulated rainfall data from the Wet Tropics, Burdekin, Fitzroy, and Burnett-Mary basins with results obtained in this study also gives confidence that the exponential trend of declining tebuthiuron EMC over time is not just site-specific, but rather that it is indicative of the behavior of tebuthiuron in the broader landscape.

It is clear that tebuthiuron concentrations in both soil and runoff are a function of time and rainfall since application; however, as this study did not consider the decay of tebuthiuron in the absence of rainfall, it is difficult to separate the effect of each driver. Despite this limitation, the drivers can be inferred from the behavior of tebuthiuron in soil at the plot scale and in runoff at both the plot and small catchment scale. It is likely that time since application is the greater driver of the exponential decay of tebuthiuron EMC in runoff given that cumulative rainfall tends to be linear. This is supported by the combined analysis of this study with the simulated rainfall studies of Cowie et al.,[45] which showed good correlation of EMC with time when runoff occurred >30 days after tebuthiuron application. The first 30 days after application, when EMC in runoff was not well correlated with time since application, corresponds to the timing of peak soil tebuthiuron concentration in the surface layer and the greatest total mass in the profile for both soil sampling regimens. If time since application was the key driver in the first 30 days since application, it would be expected that the mass of tebuthiuron in soil at day 55 would have been similar for both samplings. This was not the case, with greater mass at day 55 in the long sampling interval study for both soils. Rainfall to day 55 during the long sampling interval study was 85 mm, only 51% of the 165 mm of rainfall to day 55 in the short sampling interval study. This suggests that rainfall rather than time is the main driver of tebuthiuron mass in soil for at least the first 8 weeks after application. From day 55 to day 104, rainfall in the long sampling interval study was 143 mm, whereas rainfall in the short sampling interval study was 9 mm. Despite the marked difference in rainfall totals during this 50 day period, a clearly proportional response in tebuthiuron mass was not found for either sampling. This suggests that rainfall is no longer the key driver of tebuthiuron mass in soil after about 55 days.

There are conflicting opinions on whether tebuthiuron is transported in dissolved phase in water or adsorbed to soil particles that are then lost from the catchment via erosion processes.[36,55] The lack of relationship observed between tebuthiuron and total suspended solids in this study indicates that the movement of tebuthiuron in runoff at the small catchment scale is occurring in a dissolved phase. This is consistent with the U.S. Environmental Protection Agency, which stated that the principal route of dissipation is mobilization in water, which includes loss by solubilization in runoff.[3] The lack of variability in tebuthiuron concentrations in runoff samples within an event suggests that high-frequency sampling may not be necessary to gain an accurate measure of tebuthiuron concentration in runoff.

It has been suggested that 0.5% of water-soluble, soil-applied herbicides will be lost in runoff.[56] The maximum tebuthiuron loss for an event at the small catchment scale in this study is

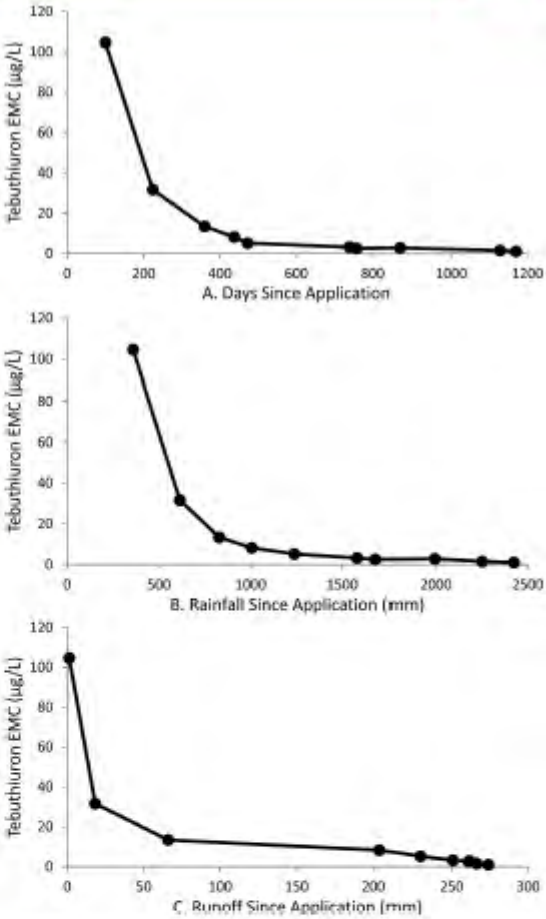

Figure 6. Event mean concentration (EMC) of tebuthiuron in runoff at the small catchment scale up to 1170 days (A), 2426 mm of rainfall (B), and 274 mm of runoff (C) following aerial application of 2500 g ai/ha of tebuthiuron to the soil surface.

similar to this figure, being 0.45% and averaging 0.1% of the amount applied. Despite the relatively small losses compared to application amounts, high solubility and low adsorption to soil can result in detectable levels of tebuthiuron downstream.[56] Strategies to minimize the risk of tebuthiuron loss in runoff are already in place under Queensland legislation, which currently does not permit broad-scale applications between November 1 and March 31 to minimize losses in runoff during the high-rainfall months.

Recommendations for tebuthiuron management in grazing lands to minimize water quality impacts should be based on the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ) water quality guidelines.[57] The ANZECC and ARMCANZ freshwater guideline value for tebuthiuron concentrations at which 99% of species are protected is 0.02 µg/L. This value has also been adopted in the Great Barrier Reef Marine Park Authority Water Quality Guidelines for protection of the Great Barrier Reef.[57,58] However, the trigger value for tebuthiuron is considered to have low reliability. Lewis et al. state that if using the 0.02 µg/L

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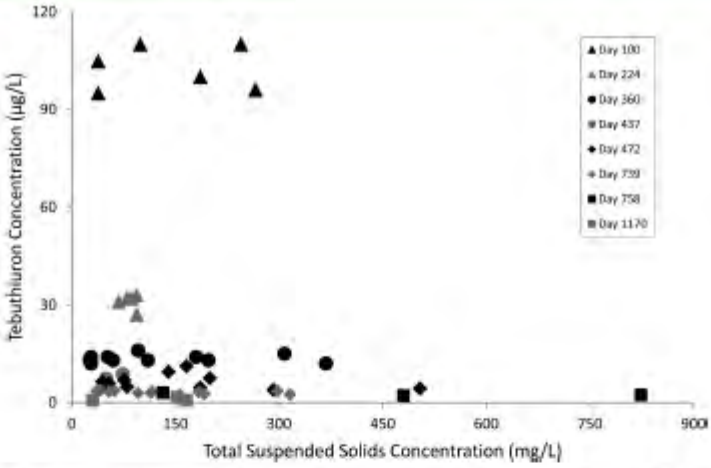

Figure 7. Comparison of total suspended sediment and tebuthiuron concentrations in individual runoff samples at the small catchment scale up to 1170 days after aerial application of tebuthiuron to the soil surface.

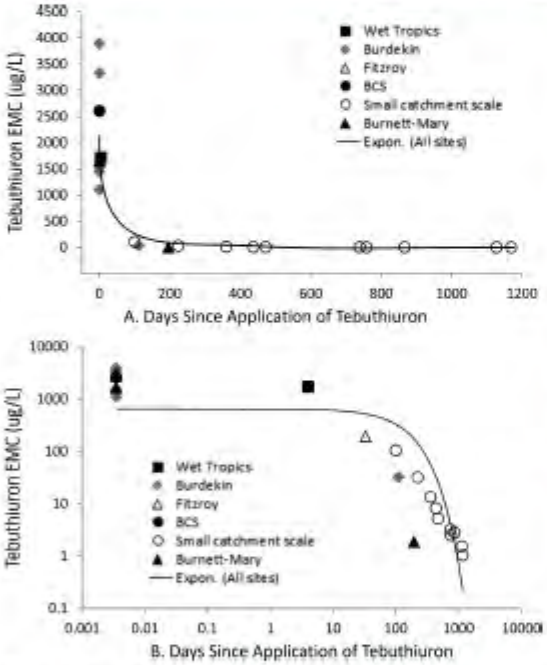

Figure 8. Linear (A) and logarithmic (B) plots of tebuthiuron event mean concentration in runoff from the small catchment scale and in runoff from 13 simulated rainfall studies across five catchments. Note the fitted line is an exponential.

guideline, tebuthiuron use in the Fitzroy basin would require immediate management action.[13] In contrast, photosystem inhibition data indicate that tebuthiuron is of much lower concern than other PSII herbicides used in the GBR, suggesting that additional toxicity data are required to provide further direction on the management of this herbicide.[13] This study supports the need for further ecotoxicology data given that tebuthiuron EMC in runoff at the small catchment scale was 5.2 µg/L 472 days after application. This exceeds the current freshwater guideline of 0.02 µg/L by a factor of 260, indicating that 260 ML of receiving water would be required to dilute 1 ML of runoff containing 5.2 µg/L of tebuthiuron to a concentration of 0.02 µg/L.[57]

Recent synthesis of pesticide research in Great Barrier Reef catchments has clearly shown that ecosystems are simultaneously exposed to multiple pesticides with toxicity effects that may be additive, synergistic, or antagonistic.[59] Simultaneous exposure is less applicable in upland catchments where grazing is the predominant, if not the sole, land use and where tebuthiuron is the most commonly used PSII herbicide. However, the risk of simultaneous exposure increases in the downstream transition from upland single land use catchments to multiple land use catchments and the marine environment. The stability of tebuthiuron in saltwater results in long residence times, which increase the risk of simultaneous exposure.[60]

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Notes

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