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Contrasting nutrient exports from a forested and an agricultural catchment in south-eastern Australia

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Abstract Dissolved organic carbon (DOC) and total and inorganic nitrogen and phosphorus concentrations were determined over 3 years in headwater streams draining two adjacent catchments. The catchments are currently under different land use; pasture/grazing vs plantation forestry. The objectives of the work were to quantify C and nutrient export from these landuses and elucidate the factors regulating export. In both catchments, stream water dissolved inorganic nutrient concentrations exhibited strong seasonal variations. Concentrations were highest during runoff events in late summer and autumn and rapidly declined as discharge increased during winter and spring. The annual variation of stream water N and P concentrations indicated that these nutrients accumulated in the catchments during dry summer periods and were flushed to the streams during autumn storm events. By contrast, stream water DOC concentrations did not exhibit seasonal variation.

Higher DOC and NO_3^- concentrations were observed in the stream of the forest catchment, reflecting greater input and subsequent breakdown of leaf-litter in the forest catchment. Annual export of DOC was lower from the forested catchment due to the reduced discharge from this catchment. In contrast however, annual export of nitrate was higher from the forest catchment suggesting that there was an additional NO_3^- source or reduction of a NO_3^- sink. We hypothesize that the denitrification capacity of the forested catchment has been significantly reduced as a consequence of increased evapotranspiration and subsequent decrease in streamflow and associated reduction in the near stream saturated area.

Keywords Nutrient export · Land use change · Paired catchments · Nitrogen · Dissolved organic carbon · Phosphorus

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Introduction

Nutrient export from catchments is governed by interactions between the hydrological cycle and a suite of geochemical and biological process occurring in the landscape and in the streams (Neal et al. 1997; Harris 2001; Meyer et al. 1988). The relative importance of the factors influencing export will vary depending on catchment features, including physical geography, geology and land use, as well as the biogeochemical environment.

Interactions between hydrology and biogeochemistry are complex and interdependent. Hydrology, specifically the quantity of water and flow path, plays two key roles: water availability controls plant nutrient uptake and microbial transformations within the soil profile and in-stream sediments (Welter et al. 2005; Belnap et al. 2005; Baldwin and Mitchell 2000); and the water flow transports the reactants and transformed products within the catchment and delivers them to the draining stream. The hydrological regime will determine whether nutrients are rapidly transported to the stream with little opportunity for transformations to occur or whether nutrients are translocated to areas with different biogeochemical environments within the catchment (e.g. groundwater vs. near-stream/riparian saturated areas) (Mulholland 1992; Hill et al. 2000; Schiff et al. 2002; Welter et al. 2005). Typically in these areas, biologically mediated reactions transform the nutrient species, altering the form and amount of nutrient delivered to the stream (Mulholland 1992; Welter et al. 2005; Belnap et al. 2005; Hill et al. 2000). Changes in climate or in land use that alter the hydrological regime will therefore have the potential to change the chemical composition of streams draining the area. While the absolute concentrations of bioavailable nutrients delivered to a stream from the catchment are critical factors determining downstream aquatic ecological function, the relative concentrations of nutrients and bioavailable carbon are also important. From an aquatic perspective, the stoichiometric departure of the stream nutrient and carbon deliveries from the Redfield ratio (C_{106}:N_{16}:P) is a good indicator of the possibility of nutrient limitation to phytoplankton downstream and the capacity of delivered organic matter to support higher trophic levels.

Considerable attention has been paid to determining nutrient export from agricultural land due to its potential for high anthropogenic nutrient losses and consequential ecological impacts in receiving water bodies (e.g. Jordan et al. 1997; Howarth et al. 1996; Johnson et al. 1997). Forested ecosystems have also been extensively investigated, particularly in North America with respect to impacts of disturbance such as clear felling, other forestry operations, and fire (Vitousek and Melillo 1979; Williams and Melack 1997). Many of the studies in forested ecosystems have focussed on nitrogen cycling due to the impacts of increased atmospheric deposition from anthropogenic sources and the general tendency for N-limitation in terrestrial forest systems (Holland et al. 1997; Vitousek and Melillo 1979; Stoddard 1994). Investigations of the relationship between landuse and catchment nutrient exports have typically been conducted in temperate high-rainfall areas (Campbell et al. 2004; Lewis et al. 1999; Hornbeck et al. 1997; Cirmo and McDonnell 1997). Few studies have been conducted in mesic temperate regions (Rassam et al. 2006) where the interdependence of hydrological regime and biogeochemical environment may become more critical in terms of the net retention or loss of nutrient input to the system (Belnap et al. 2005; Dahm et al. 2003).

The impetus for this work came from the recognition that in Australia, large areas of land originally cleared of native vegetation and now used for pasture/grazing are to be converted to plantation forestry (primarily *Pinus radiata*) in the coming decade. It is expected that the area of plantations will triple in the next 15 years (Department of Primary Industries and Energy, 1997). Most of the new plantations will occur in upland areas which are the primary sources of river flow in the Murray–Darling system, the largest catchment area in Australia. Extending the land area under plantation is expected to provide environmental benefits in terms of reduction of dry land salinisation, increased carbon sequestration and reduction of erosion (e.g. Jackson et al. 2005; Vertessy et al. 2003; Hairsine 1997; Hairsine and Van Dijk 2006). These benefits however must be balanced against the well-established decrease in water yield associated with increased evapotranspiration of forests (Zhang et al. 1999; Vertessey and Bessard 1999; Keenan et al. 2004; Hairsine and Van Dijk 2006). The impact of increasing plantation area on nutrient export, and particularly dissolved nutrient export, has not been well quantified. In a review of factors influencing nitrogen and phosphorus exports from Australian catchments, Harris (2001) noted that there was a paucity of published data. Further, most previous studies have focussed on total N and P and not the dissolved forms, which are the most readily available for uptake by aquatic primary producers (Bren and

Hopmans 2003; Smith and Nathan 2002). Dissolved organic carbon has not been investigated in headwater streams in Australia, although some work has been done in billabongs and wetlands of higher order floodplain rivers (Robertson et al. 1999).

We examined stream carbon and nutrient (N, P) dynamics in a pair of adjacent catchments in a low-medium rainfall environment over 3 annual cycles. The catchments have contrasting land uses: pasture/grazing and pine forestry. The plantation was established 16 years ago and is projected to be harvested in about 5 years. The primary objective of this work was to compare and quantify the amount, forms and ratios of carbon and nutrients exported via headwater streams draining catchments under plantation forestry and pasture/grazing landuses. The secondary objective was to elucidate the factors controlling dissolved carbon and nutrient export in each catchment and develop a conceptual model of the interactions between hydrological and biogeochemical processes that influence export at a catchment scale.

In this paper we give a detailed account of the time series of stream water nutrient concentration data and quantify the annual export of dissolved and particulate forms of the major nutrients and organic carbon from the two catchments. Using the time series data, we develop a conceptual model of the hydrological and biogeochemical processes currently affecting nutrient export from these catchments. We do not attempt to construct full nutrient budgets for these catchments. However we have estimated rainfall nutrient inputs and livestock exports to provide a comparative framework for evaluating the magnitude and composition of stream nutrient exports.

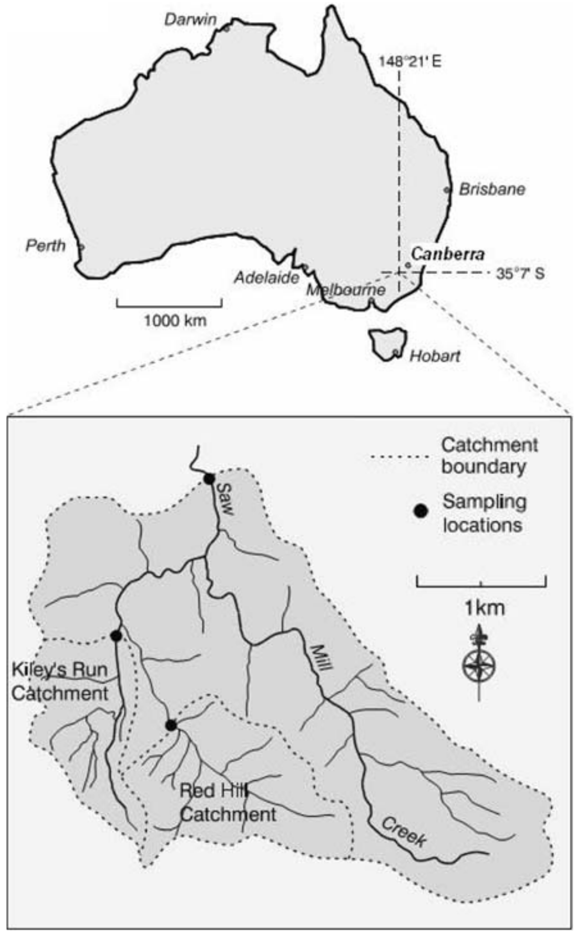


Fig. 1 Location of the study area. Kileys Run is the pasture catchment and Red Hill is the forested catchment

Site description

The catchments are in the Red Hill State Forest located 100 km west of Canberra (Fig. 1). The forested Red Hill catchment is slightly larger, 1.95 km^2, than the pastured catchment, Kileys Run, 1.35 km^2. The catchments range in altitude between 590–835 m above sea level with a gently undulating to rolling landscape (Major et al. 1998). Both catchments were originally cleared of native forest more than 100 years ago. Since then the catchments were used for pasture/grazing until 1988 when *Pinus radiata* planting began in the Red Hill catchment. The plantation was completed in April 1989. Trees planted near the stream did not grow due to waterlogging and this area, occupying ~20% of the catchment, is now vegetated with grasses. First thinning of the forest was completed during this study (October 2003–February 2004). No fertilizer applications have been made to the plantation.

The Kileys Run catchment has continued to be maintained as grazing/pasture, which is primarily native grasses with small amounts of clover and does not receive fertilizer applications. The near stream area of the pasture catchment is vegetated with sedges and occasional stands of emergent reeds (*Phragmites* sp.).

Hydrological monitoring began immediately after the plantation was established in 1989. Drought conditions existed over south eastern Australia during this investigation (2002–2004). Average annual rainfall during this study was 715 mm, approx 300 mm lower than the long term average (Major et al. 1998), although the typical pattern of higher winter and spring rainfall was maintained. Annual average potential evapotranspiration estimated at the nearby Tumut weather station between 2002–2004 is 1218 mm (http://www.nrme.qld.gov.au/silo).

The streams of both catchments were reported to be perennial prior to forestry operations. Major et al. (1998) and Hickel (2001) showed that the catchments had a similar water yield during the first 2 years after forestry planting. Thereafter water use by the growing pine plantation has reduced water yield in the Red Hill catchment (Major et al. 1998; Hickel 2001; Brown et al. 2005). Brown et al. (2005) showed that 8 years after planting the decrease in annual flow was due to a significant decrease in both baseflow and peak flows in the forested catchment. Baseflow in the pasture catchment, Kileys Run, continues to be maintained via small springs.

Methods

Water sampling

Each site has a V-notch weir set in a 2 m wide concrete flume. Each flume has a 300 mm diameter stilling well with a float attached to a Unidata (Model 6509A) shaft encoder for measuring stage height. Stage height was continuously monitored, but only recorded every 2 h if the value remained constant, and more frequently if the value changed by more than 0.5 mm. Discharge was determined from a rating table (Major et al. 1998). The rating table was determined from the theoretical rating equation based on the weir geometry and verified during this work using RBC flume measurements. Rainfall was measured at each site using an Environdata FR4 tipping bucket rain gauge, calibrated at least annually. Water temperature, conductivity and pH are continuously monitored using a Hydrolab™ sonde.

Water chemistry monitoring in this study was conducted between 2002–2004, 13–15 years after planting was completed. Sampling began in mid 2002 and included a combination of routine monthly low-flow samples and more frequent sampling during discharge events. Water sampling during discharge events was conducted using a refrigerated (4°C) ISCO™ sampler, triggered to sample based on change in stage height. Trigger values were changed throughout the year depending on expected rainfall and runoff so that samples were obtained throughout the event hydrograph. These water samples were collected from the field within 1–2 days after the initial event sample was triggered and vacuum filtered in the lab through 0.45 um cellulose acetate filters.

Routine water samples were collected in HDPE bottles from the weir outlet during routine calibration/maintenance visits to the stations. Sub-samples collected for measurement of dissolved nutrients during routine visits were filtered in the field through 0.45 um cellulose acetate syringe filters. All samples were held on ice during transport and stored frozen (−20°C) prior to analysis (Australian Standard AS/NZS 5667.1-1998).

Soil samples (0–5 cm) were collected in 2004 on a stratified random grid with 20 samples taken from each catchment. These samples were dried at 85°C and ground to a fine powder prior to analysis.

Analytical methods

Dissolved nutrient concentrations (NO_3^- + NO_2^-, PO_4^{3-}, NH_4^+) were measured using standard Alpkem autoanalyser techniques (Alpkem 1992). Nitrite concentrations measured periodically on selected water samples were always below detection. Consequently results from analysis of NO_2^- + NO_3^- will be referred to in this paper as representing nitrate concentrations. Throughout the following discussion measurements of PO_4^{3-} will be referred to as dissolved inorganic phosphorus (DIP), and the sum of NO_3^- and NH_4^+ will be referred to as dissolved inorganic nitrogen (DIN).

Total nitrogen (TN) and phosphorus (TP) were measured on unfiltered samples using acid-persulphate oxidation (Lachat 1994; Hosomi and Sudo 1986). Total and dissolved organic carbon (TOC and DOC) were measured on unfiltered and filtered (0.45 μm cellulose acetate syringe filters) samples respectively using persulphate-UV oxidation according to APHA method #5310C (APHA 1992). Frozen samples were vigorously mixed after melting immediately before analysis. Total N, TP, TOC and DOC concentrations were measured on samples from only a few discharge events in 2003, but more frequently in 2004.

Stream water dissolved organic nitrogen concentrations (DON) were not measured directly, but calculated (DON = TN-PN-DIN) from the measured concentrations of other forms of nitrogen. Particulate nitrogen (PN) concentrations were calculated from suspended solids concentration and the nitrogen content of the suspended solids. Suspended solids concentrations (TSS) were measured by filtering a measured volume (at least 200 ml) of well-mixed sample through a pre-weighed 0.2 μm polysulfone membrane filter which was dried to constant weight at 85°C and reweighed.

Soil samples and a range of suspended solids samples were analysed for C and N using a Elementar VarioMax CNS analyser. Each sample (approximately 250 mg) was mixed with 250 mg WO_3 as accelerant.

Calculation of nutrient exports and budgets

Two methods were used to estimate the stream water nutrient exports: the regression approach (Richards 1998; Degens et al. 2002) and the integration approach (Richards 1998). Using the regression approach, the relationship between the log transformed instantaneous discharge and each nutrient concentration was derived. Because both flow and nutrient concentrations showed marked seasonal variations, separate relationships were derived for summer/autumn period and winter/spring period. These relationships were used to estimate nutrient concentrations for times when chemical measurements were not made, and the annual load was calculated by summing the product of the estimated concentration and measured instantaneous flow over a year. In the integration approach, the annual load was calculated by summing the product of the cumulative discharge between successive nutrient concentration observations and the average concentration calculated from these observations. Both methods yielded similar results on an annual basis, only annual loads calculated using the regression approach are reported.

We did not determine rainfall nutrient concentrations during this study. Rainwater NO_3^- and NH_4^+ concentrations were taken to be 137 μg N l^{-1} and 182 μg N l^{-1} respectively, as determined by Ayers and Manton (1991) at Wagga Wagga, located ca. 50 km from our study site. Rainfall Total N concentrations determined at Green Hills and Bondo State forests (Turner et al. 1996), respectively located ca. 40 km and 15 km from our study catchments and at the same altitude, are in good agreement with the Wagga Wagga data. Rainwater phosphate concentrations (11 μg P l^{-1}) were calculated from Turner et al. (1996). Note that this concentration is considerably less than the rainwater phosphate concentration determined by Flinn et al. (1979) for a site located several hundred kilometres to the south of our site. Since rainfall DOC concentrations have not been determined in Australia, we assumed the concentration to be 1.9 mg C l^{-1}, the world average for continental rain (Willey et al. 2000). Annual net dissolved fluxes were calculated as the difference between rainwater flux and stream water export flux (Bormann and Likens 1980). Carbon and nutrient losses via deep groundwater recharge (Bormann and Likens 1980) have not been included in this analysis.

Nutrient export from the catchment due to the removal of cattle and wool were calculated from estimates of changes in stock numbers and wool production combined with the standard values of the N and P content of livestock (Domberg et al 2000) and of wool (Jarvis et al 2002).

Results

Annual rainfall and runoff

Annual rain and runoff from both monitoring sites are summarised in Table 1. As expected given the close proximity of the catchments, total annual rainfall is similar in both catchments. The relatively small differences in annual rainfall between the sites can be

Table 1 Total annual rainfalls and discharges in Kileys Run and Red Hill catchments

	Kileys Run		Red Hill	
	Rainfall (mm)	Discharge (mm)	Rainfall (mm)	Discharge (mm)
2002	640	41	610	8
2003	815	47	853	16
2004	641	70	664	12

mostly attributed to the patchiness of summer thunderstorms. Snowfall is negligible in this area. Each catchment received approximately 200 mm more rain in 2003 compared to 2002 and 2004. While slightly more rainfall was recorded during January 2004 compared to January 2002 and 2003, the first 6 months of that year was exceedingly dry with only 100 mm of rain falling between January 1st and June 1st 2004.

At Kileys Run between 6–11% of rainfall is discharged while only 1–2% of total annual rainfall is discharged from the forested Red Hill catchment (Table 1). Specific daily discharges at both sites are shown in Figs. 2 and 3 and shows that discharge from both catchments predominantly occurs in winter and spring in accordance with the rainfall pattern. Note change in scale of y-axis between the figures indicating lower peak flows observed in the forested catchment. As noted above, the stream in the forested catchment is dry between October and June each year and continuous flow is only observed after several hundred mm of rain has fallen in the catchment (Fig. 3). Streamflow commences in the forest catchment as a series of intermittent, short duration, low flow pulses. Depending on rainfall frequency, baseflow gradually increases after each rainfall event. Once the stream in the forest catchment is flowing continuously, the discharge response to rainfall

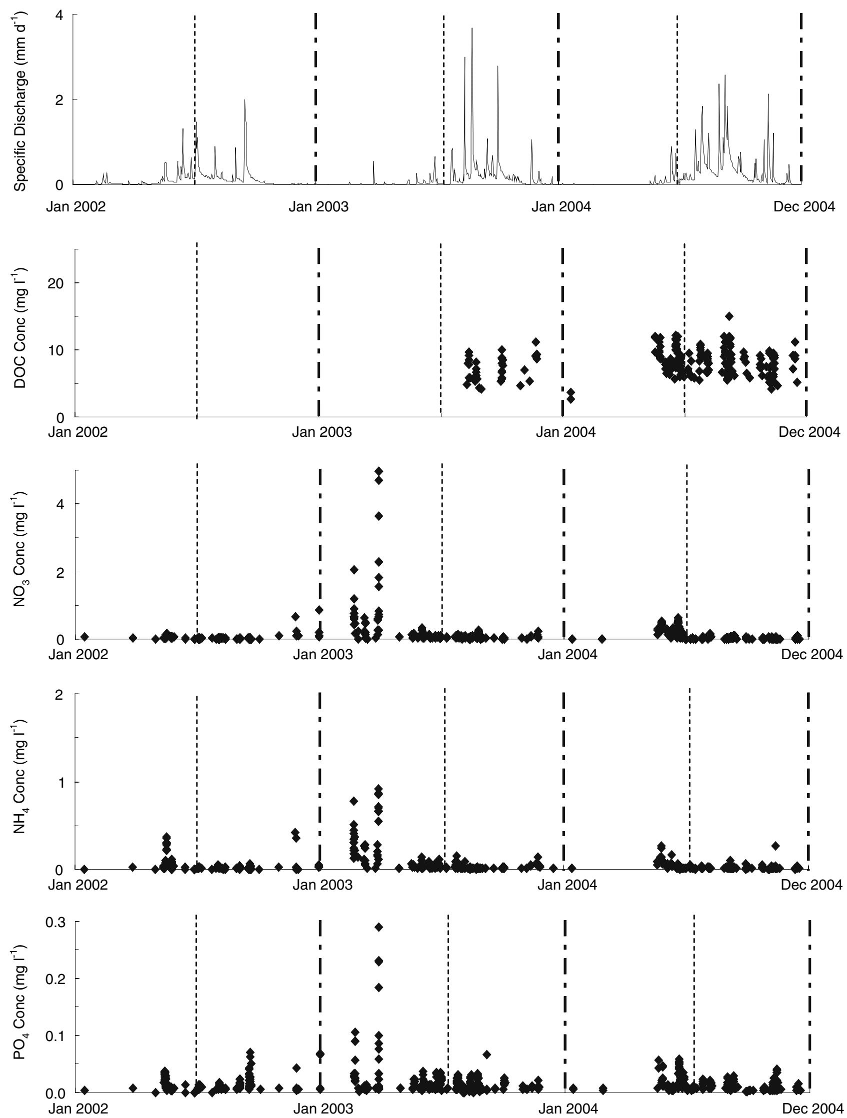
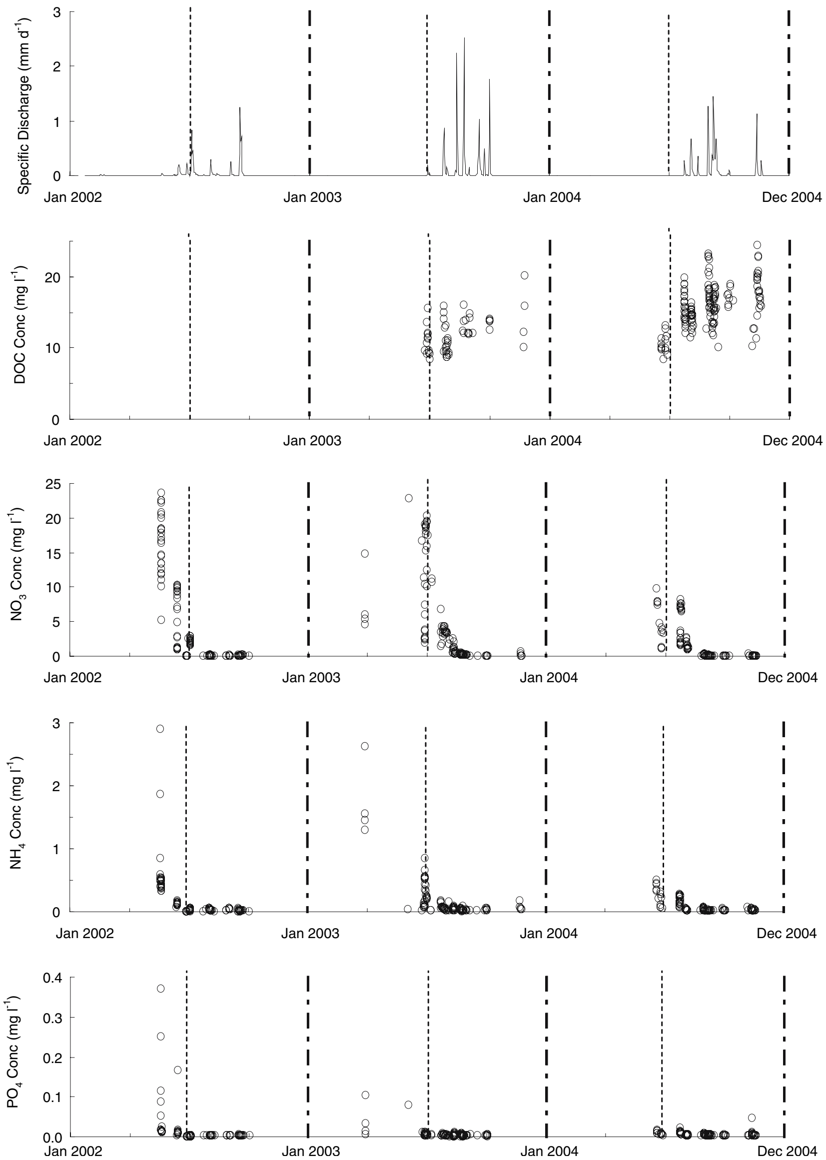


Fig. 2 Kileys Run pasture catchment annual hydrographs and carbon and dissolved nutrient concentration time series

Fig. 3 Red Hill forest catchment annual hydrographs and carbon and dissolved nutrient concentration time series



events is similar to that observed at Kileys Run. During rainfall events, discharge rises rapidly (within an hour) after rainfall commences and begins to decline shortly after rainfall ends with a return to baseflow typically in ~24 h. While both catchments would be regarded as ''flashy'', the forested Red Hill catchment is considerably ''flashier'' than Kileys Run (R–B Indices 0.86 and 0.45 respectively) (Baker et al. 2004). As a result of the drought conditions that prevailed during this study the stream in the pasture catchment also ceased flowing for up to 3 weeks during the summer and autumn months.

Stream water chemistry

Streams of both catchments exhibit similar variations in conductivity and water temperature. The annual range of stream water conductivity is 20–250 μS cm^{-1} and annual temperature range is 0–31°C. The stream in the forested catchment has lower pH (average = 5.9; range 4.3–7.8) compared to the pasture stream (average 7.5; range 6.4–8.2).

The annual average and flow weighted average carbon, nutrient and TSS concentrations measured at each site during this study are shown in Table 2.

Table 2 Summary of nutrient concentrations measured at Kileys Run pasture and Red Hill forest catchments for 2002–2004

		Kileys Run Pasture	Red Hill Forest
DOC (mg C l^{-1})	N	282	197
	Average	9.6	13.8
	s.d.	1.85	2.81
	FWavg	14.5	15.4
NO_3^- (mg N l^{-1})	N	629	396
	Average	0.13	3.40
	s.d.	0.40	4.23
	FWavg	0.28	0.54
NH_4^+ (mg N l^{-1})	N	506	304
	Average	0.071	0.17
	s.d.	0.15	0.22
	FWavg	0.11	0.047
PO_4^{3-} (ug P l^{-1})	N	622	386
	Average	17.1	8.7
	s.d.	22.4	8.1
	FWavg	25.1	6.5
TN (mg N l^{-1})	N	287	204
	Average	1.58	4.78
	s.d.	1.44	4.65
	FWavg	2.42	3.04
TP (mg P l^{-1})	N	287	204
	Average	0.17	0.065
	s.d.	0.18	0.035
	FWavg	0.25	0.072
TSS (mg l^{-1})	N	255	229
	Average	148	29
	s.d.	220	21
	FWavg	261	24

Total suspended solids concentrations (TSS) are also reported. FWAvg is the flow weighted average concentration and *N* = number of determinations. Note all concentrations are given as mg l^{-1} except PO_4^{3-} which is μg l^{-1}

The time series of discharge and dissolved carbon and nutrient concentrations for each catchment are presented in Figs. 2 and 3. It is important to note that with the exception of a few manual samples from Kileys Run, water samples for nutrient analyses were not collected prior to May 2002. The short term variations seen in Figs. 2 and 3 are due to rapid concentration changes during storm runoff events.

Although considerable variation in nutrient concentrations were observed at each site (Figs. 2 and 3, Table 2), on average stream waters in the pasture catchment, Kileys Run, were more enriched in PO_4^{3-} while the Red Hill forested catchment stream waters had higher TOC, DOC and DIN concentrations. Stream water DOC concentrations were almost twice as high in the forested catchment (range 8–24 mg l^{-1}) compared to the pasture catchment, typical range 4–12 mg C l^{-1} (Figs. 2 and 3). NO_3^- concentrations up to 23 mg N l^{-1} were observed during summer and autumn runoff events at Red Hill in 2002 and 2003. These NO_3^- concentrations were almost 5 times the values determined during the same events at Kileys Run (Figs. 2 and 3). In contrast to DOC and NO_3^-, the range of NH_4^+ and PO_4^{3-} concentrations tended to be similar between the catchments (Figs. 2 and 3).

Low suspended solids concentrations were observed in the streams of both catchments. The annual average suspended solids concentration in the forested catchment was 29 mg l^{-1} (annual flow weighted average 24 mg l^{-1}) and 148 mg l^{-1} in the pasture catchment stream (flow weighted average 261 mg l^{-1}) (Table 2). Average nitrogen contents of the suspended solids were 0.06% (s.d. = 0.01) N in the forested stream and 0.3% (s.d. = 0.1) N in the pasture stream. Thus, the annual flow weighted average PN content are 0.01 mg l^{-1} and 0.8 mg l^{-1} for the forest and pasture streams, respectively. Given these annual estimates of the PN concentrations, the flow weighted average DON concentration (DON = TN-PN-DIN) made up approximately 50% of the annual dissolved nitrogen flux from both catchments.

In both catchments, on average 90% of TOC was in dissolved form (Fig. 4). DOC concentrations in the stream water from the forest catchment were higher than the concentrations in the pasture stream (Figs. 2, 3).

Annual and interannual stream water concentration trends

Similar annual and inter-annual trends in DOC and dissolved nutrient concentrations were observed in both catchments (Figs. 2 and 3). Dissolved nutrient concentrations, and in particular NO_3^- concentrations in runoff events during the first 6 months of

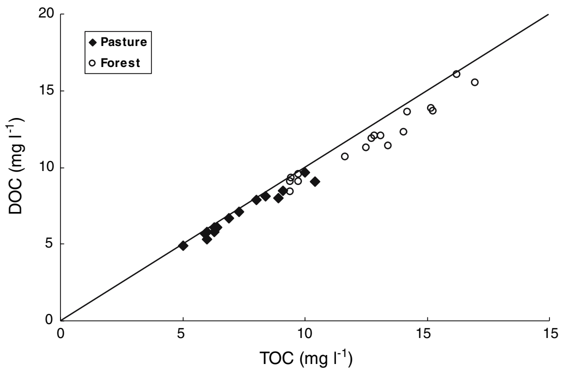


Fig. 4 Relationship between TOC and DOC in stream waters from both catchments. Solid line is 1:1 relationship. Data from the pasture catchment are represented by (◆) and data from the forested catchment are represented by (○)

each year, were notably higher in 2002 and 2003 compared to 2004 (Figs. 2, 3).

Maximum DIN and DIP concentrations clearly occur during the initial runoff events each year and well in advance of maximum annual discharge (Figs. 2, 3). In contrast, DOC concentrations do not show appreciable annual or interannual variability. In the pasture catchment, high nutrient concentration discharges tended to occur in late summer and autumn (Fig. 2). In the forested catchment, flows with high nutrient concentrations were delayed relative to the pasture catchment and tended to occur in autumn and early winter as the stream commenced flowing (Fig. 3). Dissolved nutrient concentrations subsequently declined in the streams of both catchments and remained low throughout the remainder of winter, spring and early summer (Figs. 2 and 3).

As noted above, on an annual basis approximately 50% of the TN is exported as DON. However, the relative contribution of dissolved organic nutrients and dissolved inorganic nutrients in the runoff changes throughout the year (Fig. 5). This is particularly noticeable in the forested catchment where NO_3^- contributed on average ~80% of the TN during the first few runoff events and baseflow early in the year. The proportion of NO_3^- then decreased to 5%, on average, during later winter and spring flows (Fig. 5). In the pasture catchment, on average only 11% of TN was NO_3^-, although the same temporal pattern of a higher proportion of DIN (ca.30%) early in the year was observed. As noted above particulate N concentrations were relatively low throughout the year in the streams of both these catchments. Consequently, as NO_3^- concentrations declined, DON became the dominant component of the dissolved nitrogen flux particularly during winter and spring. Although the proportion of DIP varied during individual runoff events (Fig. 5), on an annual basis the average proportion of DIP in TP was relatively constant throughout the year. On average 13% of TP in stream waters of the forested catchment and 23% of the TP in stream waters of the pasture catchment is present as DIP.

As NO_3^- concentrations were so high during the first few runoff events each year (Figs. 2, 3), the average DOC:NO_3^- ratios in stream waters of the forested catchment were low and dissolved N:P ratios were correspondingly high. For example, average DOC:NO_3^- = 3:1 and NO_3^-:PO_4^{3-} = 138:1 for the first 3 runoff events from the forest catchment in

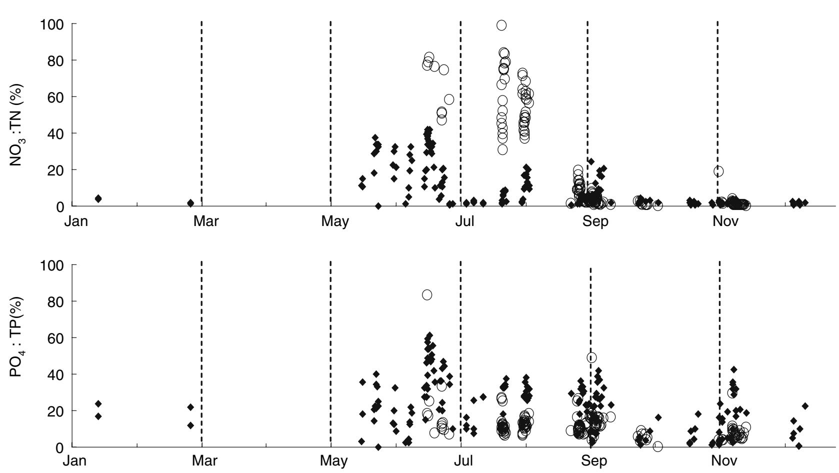


Fig. 5 Proportion of NO_3^-: Total N and PO_4^{3-}: Total P in stream waters determined during 2004 in both catchments. Data are presented as % of total. Data from the pasture catchment are represented by (◆) and data from the forested catchment are represented by (○)

June–July 2004. In contrast, the dissolved C:N:P ratios in the pasture catchment stream waters deviated only slightly from Redfield ratio (N:P = 16:1) with dissolved N:P ratios averaging 28:1 during initial runoff events.

Soil carbon and nitrogen content

Surface soils from the forested catchment had higher carbon content, 7.42 ± 0.53%C, than the pasture soils (4.80 ± 0.78%C). There was no difference in the nitrogen content of soils from the catchments (forest soils: 0.40 ± 0.12%N, pasture soils 0.40 ± 0.067%N). The C:N ratio of soils from the forest and pasture catchments were 18 and 12, respectively.

Annual nutrient budgets

Annual stream water dissolved C, N, P budgets were calculated from data collected in 2003 and 2004, and annual area-averaged values are presented in Table 3 together with the estimated annual inputs of nutrients via rainfall. The standard deviations in Table 3 represent inter-annual variation, not the overall (large) uncertainties associated with these calculations. Results from 2002 were not used to calculate annual budgets because of inadequate sampling, particularly during summer and autumn. Annual DOC export (Table 3) was calculated using 2004 data only.

Only nitrate export from the forested catchment showed substantial inter-annual variation between the 2 years, with the higher NO_3^- load occurring in the higher discharge year (2003, Table 1). In terms of differences in dissolved nutrient exports between catchments, the annual exports of DOC, NH_4^+, and PO_4^{3-} are greater from the pasture catchment than from the forest catchment (Table 3), whereas higher NO_3^- export occurred from the forest catchment. In the context of our estimated nutrient inputs via rainfall, the pasture catchment exported 41% of DOC inputs and 3% and 1% of NO_3^- and NH_4^+ inputs, respectively. Comparatively less DOC but more NO_3^- were exported from the forest catchment (Table 3). NH_4^+ export was particularly low from both catchments. Overall, both catchments were net sinks for DOC and the dissolved nutrients.

Greater export of TOC, TN and TP was observed from the pasture catchment (Table 4). Additionally,

Table 3 Annual nutrient budgets (Kg km^{-2} year^{-1}) calculated for 2003 and 2004

	Pasture				Forest			
	DOC	NO3	NH4	PO4	DOC	NO3	NH4	PO4
Stream export	577	3.4 (±0.46)	1.6 (±0.12)	0.95 (±0.30)	94	15 (±14)	0.61 (±0.34)	0.06 (±0.005)
Precipitation input	1407[b] (±238)	100[a] (±17)	133[a] (±22)	8[c] (±1)	1407[b] (±238)	100[a] (±17)	133[a] (±22)	8[c] (±1)
Net Balance	830	96	131	7	1313	85	132	8
% exported	41	3	1	12	7	15	0.5	0.7

DOC export was calculated using only 2004 data. Export estimates of dissolved N and P species are the average flux for both years (±1 s.d.). Estimated precipitation inputs are also included (see text for details). Net balance is the difference between rainfall input and stream export. % exported is the percentage of the rainfall input of each constituent exported via the streams

[a] Rainwater concentrations from Ayers and Manton (1991)

[b] Rainwater DOC concentrations from Willey et al. (2000)

[c] Rainwater concentrations from Turner et al. (1996)

Table 4 Estimated annual total C, N, P exports and export ratios calculated for the pasture and forest streams and for livestock exported from the pasture catchment

	Annual export (kg km^{-2} $year^{-1}$)			C:N:P
	TOC	TN	TP	(molar)
Pasture stream	582	61	6.4	236:21:1
Forest stream	133	19	0.6	607:74:1
Livestock export	1857	287	62	77:10:1

Units for calculated export are kg km^{-2} $year^{-1}$. Export ratio is given on a molar basis

the C:N:P export ratio was considerably lower in the pasture catchment and closer to Redfield ratio (C:N:P = 106:16:1; Redfield 1958) (Table 4). Comparing the total outputs (i.e. particulate plus dissolved) (Table 4) with the annual dissolved rainfall inputs (Table 3) shows that neither catchment is a net exporter of C and N through the stream system. Most of the DOC input via rainfall is exported as DOC while the majority of the N input via rainfall exits as DIN or DON depending on the time of the year. Only stream export of TP from the pasture catchment is in approximate balance between rainfall inputs and stream outputs taking account of the uncertainties in these calculations.

The C, N, and P contents of the wool and livestock which were estimated to be removed annually from the pasture catchment are also shown in Table 4. These estimates represent the maximum possible export via these components since during this study stock feed was supplemented due to insufficient pasture growth during the drought. Clearly there is net export of C and nutrients from the pasture catchment through livestock and wool yields. Similarly, over longer timescales, the forested catchment remains a sink for the dissolved nutrients as inputs are accumulated as tree biomass until the plantation is harvested and these accumulated nutrients are exported from the catchment.

Discussion

Annual carbon and nutrient export

The export of dissolved nutrients from the two catchments in this study, as either TN, TP or DIN (NO_3^- + NH_4^+) and DIP is at the lower end of the range reported for temperate catchments in other parts of the world (Howarth et al. 1996; Smith et al. 2005). Nutrient export from catchments in Australia, including those that are relatively heavily impacted, are generally low relative to values reported for catchments in North America and Europe (Howarth et al. 1996; Smith et al. 2005; Harris 2001; Young et al. 1996). This has been attributed, in part, to low atmospheric nutrient inputs (Holland et al. 1997), and lower anthropogenic influences such as population density and less intensive agricultural land use, particularly with respect to fertilizer application (Harris 2001; Howarth et al. 1996; Caraco and Cole 1999; Smith et al. 2005). However, N and P export from the catchments in this study are also low relative to many other temperate Australian catchments (Harris 2001; Young et al. 1996) reflecting both the influence of the factors outlined above but also the low discharges reported during this study.

Total N and P export were 61 kg N km^{-2} $year^{-1}$ and 6.4 kg P km^{-2} $year^{-1}$ from the pasture catchment and 19 kg N km^{-2} $year^{-1}$ and 0.6 kg P km^{-2} $year^{-1}$from the forest catchment (Table 4). Young et al. (1996) reported typical values for TN and TP export from unimproved pastures as 220 kg N km^{-2} $year^{-1}$ and 7 kg P km^{-2} $year^{-1}$ and from forests as 110 kg N km^{-2} $year^{-1}$ and 6 kg P km^{-2} $year^{-1}$. These values are 3–6 times higher than the TN exported from the catchments in this work and 10 times higher than the TP exported from the forested catchment in this study. The Kileys Run pasture catchment exported about the same amount of TP as the unimproved pasture catchment reported in Young et al. (1996).

Dissolved inorganic N and P exports from the pasture were 5 kg N km^{-2} $year^{-1}$ and 0.1 kg P km^{-2} $year^{-1}$, while the forested area delivered 15 kg N km^{-2} $year^{-1}$ and 0.06 kg P km^{-2} $year^{-1}$(Table 3). DIN exports, including the high NO_3^- flux from the forest catchment in this study, were within the range reported for undisturbed temperate watersheds in the Americas and well below those reported for tropical watersheds (Lewis et al. 1999). Stream water DOC export estimated for the catchments in this study are also lower than determined in temperate forested catchments in New England (Campbell et al. 2000).

Although carbon and nutrient export from our study catchments was relatively low, streamwater carbon and nutrient concentrations were similar to those typically reported for less intensive agricultural and forested catchments (Johnson et al. 1997; Hornbeck et al. 1997; Bren and Hopmans 2003; Richey et al. 1990; Meyer et al. 1988; Flinn et al. 1979; Hornberger et al. 1994; Smith and Nathan 2002; Harris 2001). As noted above, DOC has not been extensively investigated in Australian headwater streams. However, stream water DOC concentrations determined in this study were within the range of values reported for other Australian streams (Nelson et al. 1993; Robertson et al. 1999), and streams and rivers in North and South America and Europe (Maybeck 1982; Jardine et al. 1990).

Given that the stream water carbon and nutrient concentrations were similar to values determined in other temperate catchments with higher annual nutrient export, lower water yield from the catchments in this study undoubtedly plays a role in the relatively low annual export of carbon and nutrients via streams draining these catchments. Stream flow (Table 1) was approximately 10% of rainfall in the pasture catchment and only 2% in the forested catchment. This latter value is an order of magnitude less than observed for forested watersheds in Northeastern United States (Campbell et al. 2004). The importance of the hydrological regime in controlling stream nutrient export is further exemplified by the higher annual TOC and TN exports observed from the pasture catchment relative to the forested catchment (Tables 3, 4), in spite of higher stream water concentrations of these constituents being measured in the forest catchment.

Landuse impact on carbon and nutrient fluxes

Directly relating differences in stream water chemistry to changes in landuse in these catchments is somewhat tenuous since stream water nutrient concentrations were not measured prior to establishment of the forest and thus we cannot establish that the stream water chemistry of these two catchments was similar before the change. Furthermore, we have not measured the rates of biogeochemical processes controlling carbon and nutrient cycling in the landscape. However, it has been definitively shown that landuse change has altered the hydrological regime of these sites. Hickel (2001) and Brown et al. (2005) showed that reductions in both baseflow and peak flows that have occurred in the forested catchment relative to the pasture catchment could be attributed to changing water balance of the forested catchment through increasing evapotranspiration during the development of the plantation. Given that hydrology impacts the biogeochemical processes that also regulate carbon and nutrient export (e.g. Belnap et al. 2005; BassiriRad et al. 1999) it is reasonable to attribute differences in the stream chemistry to changes in landuse of these catchments.

Discharge from the pasture catchment was approximately 4 times the discharge from the forested catchment, yet on average, 6 times more DOC and 16 times more DIP was exported from the pasture catchment (Table 3). By contrast, 4 times more DIN was exported from the forested catchment, mostly in the form of NO_3^- (Table 3). This differing pattern of DIN export relative to DOC and DIP from these catchments suggests that either there is an additional net source of N to the forest catchment or conversely that an N sink is diminished. We cannot identify any external sources that exclusively input N, and more particularly NO_3^-, to the forested catchment. Indeed external N input to the pasture catchment is likely to be higher than to the forest catchment through N fixation by clover. Using the range of N-fixation rates determined by Jarvis et al. (2002) for New Zealand grasslands we calculate that N input to the pasture catchment via this process would be between 230–5300 kg N year^{-1}.

Relatively more NO_3^- can be available for export via streams if production via nitrification is enhanced (Creed et al. 1996) or conversely if NO_3^- removal via plant uptake (terrestrial and in-stream) (Schiff et al. 2002) or denitrification is reduced (Cirmo and McDonnell 1997; Schiff et al. 2002). In the forested catchment investigated in this study, NO_3^- supply to the stream may be increased due to enhanced nitrification as a result of increased supply of decomposing organic matter through litterfall and a more favourable microclimate, particularly during summer, for microbial decomposition reactions in surface soils under the forest canopy. Direct measurements of nitrification rates or isotopic measurements of dissolved NO_3^- (Burns and Kendall 2002) are required to determine if nitrification rates vary between these catchments. Similarly denitrification rates need to be directly measured in these catchments. We hypothesize however, that the denitrification capacity of the forest catchment has been substantially reduced as a consequence of changes to the water balance of the catchment. In the following discussion we present a conceptual model that describes the hydrological and biogeochemical processes that result in the annual sequence of stream water carbon and nutrient concentrations in these catchments. We outline how changes to the hydrology of the forest catchment have reduced the denitrification capacity of the catchment by reducing both the area within the catchment and the amount of time where conditions suitable for denitrification occur.

Seasonal hydrological and biogeochemical interactions

The general trend where maximum stream water nutrient concentrations occur prior to maximum annual discharge (Figs. 2, 3) is characteristic of flushing as the primary export mechanism. Similar annual patterns of elevated stream water NO_3^- concentrations during spring snow melt (Creed and Band 1998; McNamara et al. 2005) and during commencement of streamflow after drought (Schiff et al. 2002; Creed and Band 1998) have been observed in other temperate catchments. Hornberger et al. (1994) and Boyer et al. (1997) also observed elevated DOC concentrations during the snowmelt period in a forested catchment in Colorado. We expect a similar mechanism to operate in the catchments investigated in this study, wherein nutrients produced by degradation of organic matter in surface soils accumulate in the catchments during dry summer and autumn periods. During these periods, rainfall events do not typically generate any runoff at the outlet of the forest catchment and only a small amount of runoff at the outlet of the pasture catchment (Figs. 2a, 3a). Although little or no stream export occurs, nutrients may be translocated within the respective catchments during each rainfall event, for example from surface soils to the water table as observed in the Harp Lake watershed in Ontario (Schiff et al. 2002). When events of sufficient magnitude to generate stream runoff at the respective catchment outlets occur during or at the end of this dry period, the runoff contains high concentrations of DIN and DIP relative to similar sized events that occur later in the year (Figs. 2, 3). Concentrations decline rapidly during subsequent runoff events presumably due to dilution of soil waters with incoming rainfall and attenuation of nutrient supply due to lower rates of organic matter decomposition reactions with lower winter temperatures. During spring, as temperatures rise, microbial degradation of soil organic matter would increase the supply of mobilisable nutrients. However, stream water DIN and DIP concentrations remained low suggesting that either the rate of nutrient supply was insufficient to replenish the soil water nutrient pool relative to removal via flushing or that increased uptake via terrestrial and instream vegetation rapidly depleted available nutrients as shown in other systems (Mullholland 1992; McHale et al. 2000).

The lack of seasonal changes in stream water DOC concentrations in these catchments was surprising given the distinct seasonality in dissolved inorganic nutrient concentrations (Figs. 2, 3). As noted above, Hornberger et al. (1994) and Boyer et al. (1997) have shown clear peaks in stream water DOC during spring snow melt in an upland forested catchment. Campbell et al. (2000) showed there was a weak but significant correlation between stream water DOC concentrations and discharge in several forested catchments in New England (USA), but DON concentrations were not significantly related to discharge. In future work measuring specific components of DOC rather than bulk DOC determined in this study may facilitate a better understanding of catchment scale carbon and nutrient cycling.

Reduction of catchment denitrification capacity

The role of near-stream saturated areas such as wetlands, riparian buffers and floodplains in controlling N cycling in catchments has been well established (Cirmo and McDonnell 1997; Hill et al. 2000; Rassam et al. 2006; Creed and Band 1998). The capacity of these areas to attenuate NO_3^- concentrations via denitrification will depend on both hydrological factors such as residence time of water in saturated zone (Rassam et al. 2006), depth to water table (Creed and Band 1998) and chemical conditions such as organic carbon content (Hill et al. 2000), dissolved O_2 concentrations (Hill et al. 2000) and pH (Simek and Cooper 2002). In addition, antecedent moisture conditions play an important role in determining denitrification rates. Ohte et al. (1997) showed experimentally that it can take several months under saturated conditions for denitrification activity in previously dry soils to become significant. Similarly, field experiments have suggested that bacterial populations may need priming with high NO_3^- concentrations to stimulate denitrification (Cirmo and McDonnell 1997).

During growth of the plantation, the saturated water table in the forested catchment in this study has been lowered through water use by the trees and consequent increased evapotranspiration (Hickel 2001; Brown et al. 2003). Deeper water tables have been shown in other catchments to preserve high NO_3^- concentrations through either increasing drainage, thereby reducing the residence time of water in surface soils (Creed and Band 1998) or through recharge below the root zone making dissolved nutrients unavailable for uptake (Schiff et al. 2002). Further consequences of the increased evapotranspiration and subsequent decreased runoff from the forested catchment are that the maximum areal extent of the near-stream saturated area of the forested catchment is likely to be much smaller than in the pasture catchment, based on predictions from other pasture and forested catchments (O'Loughlin 1981; Western and Grayson 2000), and that the organic rich surface soils in the near-stream/riparian area are not saturated most of the year. These two factors could significantly reduce the denitrification capacity of the forested catchment relative to the pasture catchment by limiting both amount of time and also the area of the catchment where suitable conditions exist for denitrification to proceed. This situation is particularly acute as the forest stream commences flow. During these events, previously dry surface soils are only briefly inundated (on the order of hours) by water containing high NO_3^- concentrations. The short inundation time is likely to be insufficient for development of low oxygen conditions required for denitrification (Simek and Cooper 2002). Once the stream has commenced flowing, conditions are more likely to become suitable for denitrification to occur in the near-stream/riparian zone (Baldwin and Mitchell 2000; Rassam et al. 2006; Bormans et al. 2004). However other factors such as the low pH of stream waters in the forested catchment may retard denitrification in this catchment relative to the pasture catchment (Simek and Cooper 2002). The nature of hydrological interactions between the groundwater, streamwater and flow from hillslopes, particularly in the near-stream/riparian zones, in conjunction with direct measurements of denitrification requires further investigation in these catchments.

Export ratios and implications for stream ecological processes

The ratio of organic:inorganic nutrient export and the bioavailable C:N:P ratio, especially its congruence with Redfield ratio (C_{106}:N_{16}:P), are important parameters in determining aquatic ecosystem function. Decreased export of organic carbon and nutrients along with a declining organic:inorganic nutrient export ratio will tend to favour autotrophy over heterotrophy in headwater streams.

While organic carbon export from the catchments in this study is clearly dominated by dissolved phase throughout the year (Tables 3 and 4, Fig. 4), the relative contribution of dissolved organic and inorganic N and P clearly changes depending on the time of year. This switch is particularly evident in regard to nitrogen cycling in the forested catchment. DON has been shown to be the dominant form of nitrogen exported from temperate and tropical forest catchments in the Americas (Hedin et al. 1995; Campbell et al. 2000; Lewis et al. 1999) and also boreal forests (Kortelainen et al.1997). Harris (2001) suggested that nitrogen export from native forested headwater catchments in Australia were dominated by DON and particulate N. Bren and Hopmans (2003) also showed that for both *Eucalyptus* sp. and newly established pine plantations, NO_3^- accounted for only 18% and 32% respectively of the total dissolved N output. While on average 50% of the annual TN export from the catchments in this study was in the form of DON, NO_3^- clearly dominates TN export during the initial runoff events particularly from the forested catchment (Fig. 5). The high concentration of

NO_3^- leads to especially low C:N ratios ($\sim$2:1) during these runoff events and the N:P ratio ($\sim$100:1) is also markedly different from the Redfield ratio (C:N:P = 106:16:1). Thus the stream in the forested catchment is strongly P limited during the initial runoff events. In contrast, the C:N:P ratios measured during initial runoff events from the pasture catchment ($\sim$220:24:1) are much closer to the Redfield ratio. These differences in the C:N:P stoichiometry of the dissolved nutrients delivered to the streams will benefit some algal species relative to others and highlights an additional potential impact of increasing plantation forestry on the downstream ecology.

Summary and conclusions

The export of TN and TP, and dissolved organic carbon and inorganic nutrients was measured across multiple individual rainfall events in two adjacent catchments in upland southeastern Australia. Both catchments were originally cleared of native forest vegetation over a hundred years ago for use as grazed pastures. One catchment was subsequently planted with *Pinus radiata* in 1989. The water yield from the forested catchment declined relative to the pasture catchment as the plantation has matured. Although the study site is in the temperate zone, evapotranspiration exceeds precipitation for much of the year and the annual exports of dissolved nutrients from both catchments are reduced relative to comparable systems in Europe and North America. Stream water dissolved nutrient concentrations are comparable to these other systems and the decreased export is further accentuated by the reduced discharge from these catchments when compared to other temperate catchments.

There were significant differences between the two catchments in terms of the concentrations of nutrient species, and the export of nutrients in the streams. Flow weighted average concentrations of DOC, NH_4^+, PO_4^{3-}, and TP were higher from the pasture catchment, while NO_3^- concentrations were higher in stream waters from the forested catchment. There were no major differences between the two catchments for annual TN export. Both catchments were highly effective at retaining all nutrients received from atmospheric sources. There were clear differences between the catchments in terms of the proportions of dissolved species exported on an annual basis: the pasture catchment exported a higher percentage of DOC and a smaller fraction of NO_3^- received via rainfall inputs.

On shorter time scales there are marked differences between the two catchments which arise in part from relatively rapid changes in the output chemistry of the forested catchment following the first rains in autumn. As the forested catchment stream starts to flow, stream water NO_3^- concentrations were about 5 times higher than observed in the pasture catchment. DON is only a small fraction of the total dissolved nitrogen flux as the forest stream begins to flow. During these runoff events, stream water C:N is of order 2 and the N:P is about 100. The C:N:P ratio for the dissolved outputs from the pasture catchment for the same events is approximately 220:22:1. In subsequent events the NO_3^- concentrations in stream waters of the forest catchment decline and N export becomes dominated by DON. We attribute this behaviour to the reduction of the denitrification capacity in the forest catchment as a secondary consequence of changing the water balance during growth of the plantation. Once the stream has commenced flowing, denitrification is probably facilitated, as well as removal of dissolved inorganic nutrients by plant and forest growth so the discharge of NO_3^- declines. The wide fluctuations in stream water NO_3^- concentrations have implications for the stoichiometry of downstream biological processes and vitiate attempts to draw conclusions regarding landuse impacts on stream ecology based on annual average stream water composition.

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