Biogeochemistry (2005) 72: 169–190
DOI 10.1007/s10533-004-0358-9

Patterns in groundwater nitrogen concentration in the floodplain of a subtropical stream (Wollombi Brook, New South Wales)

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Received 25 September 2003; accepted in revised form 24 March 2004

Key words: Floodplain, Groundwater, Nitrogen, Subtropical stream

Abstract. The sources of groundwater and the patterns in groundwater dissolved N and DOC concentration in the floodplain of a subtropical stream (Wollombi Brook, New South Wales) were studied over a 2-year period using three piezometer transects. While the stream was generally a discharge area for regional groundwater, this source represented only a small contribution to either the water or N budget of the alluvial aquifer. Groundwater–surface water interactions appeared mostly driven by cycles of bank recharge and discharge between the stream and the alluvial aquifer. DON and NH_4^+ were the principal forms of dissolved N in groundwater, consistent with the primarily suboxic to anoxic conditions in the alluvial aquifer. A plume of groundwater NO_3^- was found at one transect where oxic conditions persisted within the riparian zone. The origin of the NO_3^- plume was hypothesized to be soil NO_3^- from the riparian zone flushed to the water table during recharge events. When present, NO_3^- did not reach surface water because conditions in the alluvial aquifer in the vicinity of the stream were always reduced. The concentration of groundwater DOC was variable across the floodplain and may be related to the extent of the vegetation cover. Overall, transformation and recycling of N during lateral exchange processes, as opposed to discharge of new N inputs from regional groundwater, appears to primarily control N cycling during groundwater–surface water interactions in this subtropical floodplain.

Introduction

The risks associated with the formation of large algal blooms are a continuing concern in Australian rivers (Donnelly et al. 1997). In Australia, the two main drivers of increased incidences of algal blooms in rivers are thought to be the modifications to their flow regime (Sherman et al. 1998) and the increased input of nutrients from catchments (primarily N and P; Harris 2001). For nutrients, the original emphasis to prevent eutrophication was on controlling P exports (Weaver et al. 1998). However, it is increasingly recognised that many freshwater, estuarine, and coastal ecosystems can also be N limited (Roberston 1999; Baker et al. 2000). It is not clear at the present whether the measures taken to control P exports in Australian catchments will also be successful to prevent excess N exports (McKergow et al. 2003). This is of concern because the rate of use of nitrogen fertilisers is increasing rapidly (NLWRAP 2001). One major difference between N and P export from catchments to receiving water bodies is that groundwater can be an important vector for N export (Linderfelt and Turner 2001; Lamontagne 2002), whereas it usually is not for P. While high NO_3^- concentration in groundwater can occur naturally in Australia, significant anthropogenic contamination of aquifers in agricultural, industrial, and urban areas has also occurred (Lawrence 1983).

In temperate climates, many floodplains and riparian zones have been found to be efficient at removing NO_3^- from incoming polluted groundwater (Hill 1996; Sabater et al. 2003). Significant efforts have been spent to understand the mechanisms of NO_3^- attenuation and the geomorphic properties of the floodplains that are efficient at attenuating NO_3^- (Burt et al. 1999; Hill et al. 2000; Pinay et al. 2000; Burt et al. 2002a). Comparatively little research on N cycling in floodplains has occurred in climates other than humid temperate ones (Hill 1996; Martí et al. 2000). In addition, the emphasis has generally been on NO_3^- removal rather than on the balance between N imports and exports. In other words, while floodplains may be efficient at attenuating groundwater NO_3^-, they may also export other N forms such as NH_4^+ and dissolved organic N (DON) to surface waters (Burt et al. 2002a; Pinay et al. 2002). In Australia, carbon (Roberston et al. 1999) and salt exchange (Jolly et al. 1994; Jolly 1996) between floodplains and rivers have been studied in some detail. However, little is known about N exchange and processing at the scale of floodplains.

The patterns in N concentration and transformations were studied over a 2-year period at Wollombi Brook (NSW), a subtropical sandbed stream. The goals of the study were to (1) understand groundwater–surface water interactions at the scale of the floodplain; (2) determine the main forms of N in groundwater; and (3) infer some of the biogeochemical transformations occurring during the movement of groundwater in the floodplain from the patterns in redox conditions, DOC concentrations, and dissolved N concentrations in the alluvial aquifer. Hydrological processes will be presented in a companion paper and only summarised briefly here. This manuscript will focus on the patterns in N concentration in groundwater and on the inferred biogeochemical processes.

Methods

Site description

Wollombi Brook is part of the Hunter River catchment of east Central NSW (Figure 1). It has a subtropical climate (with predominantly summer rainfall)

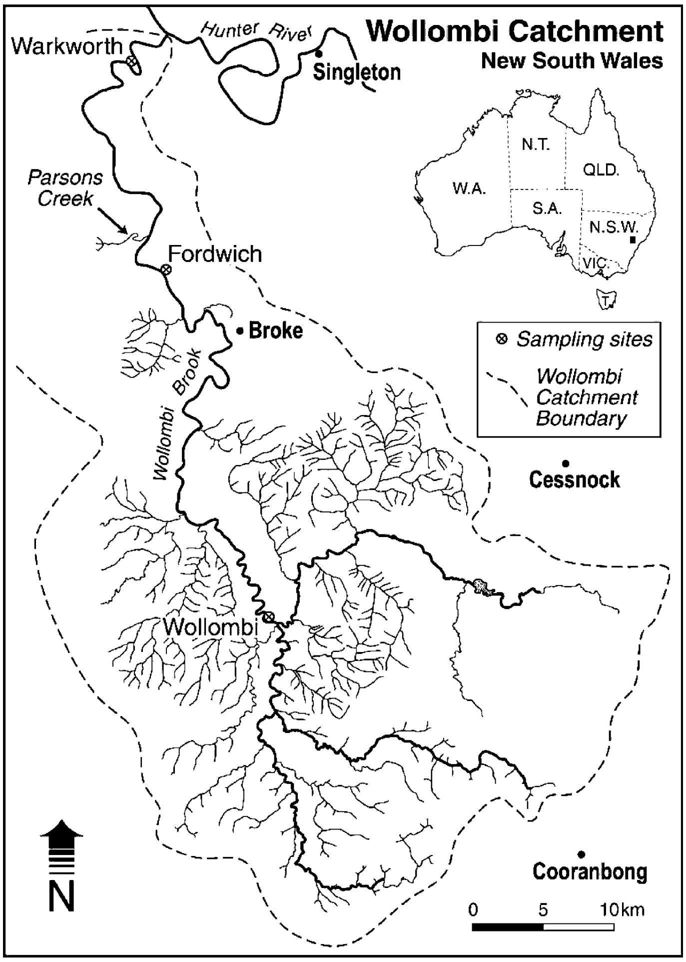


Figure 1. Location of the Wollombi Brook catchment and the three transects of bores and piezometers.

ranging from 1110 mm at Coorabong near the upper reaches of the catchment to 650 mm at Broke. Much of the upper part of the catchment is pristine or plantation forest, with steep rocky slopes. In the lower reaches, the river broadens into an alluvial plain. Activities in the valleys include coal mining, cattle grazing, and irrigated agriculture (grapes, olives, and pastures). Triassic sandstone is the most common rock type in the upper part of the catchment (Erskine 1996). A variety of other rock types (including Quaternary alluvium, basalt, conglomerate, and coal) also occur within the lower reaches. Because the regional groundwater is generally brackish (800–8000 μs cm^{-1}), the river and its alluvial aquifer are important supplies of freshwater for irrigation, stock watering, and private use (groundwater frequently has high salinities in semi-arid and subtropical regions of Australia because of very low recharge rates under native vegetation; Allison et al. 1990).

The hydrograph of the Wollombi Brook catchment is highly variable, with prolonged low flow periods when the river becomes a series of disconnected pools and infrequent, short-lived, but potentially catastrophic floods (Erskine 1996). As for many rivers in southeastern Australia, river morphology has changed substantially since European settlement, as described in detail by Scott and Erskine (1994) and Erskine (1996). Simply put, there has been substantial erosion of river banks and massive deposition of sediments (i.e. 'sand slugs') in the river channel, thereby in-filling the river valley. In the lower reaches (i.e. between the townships of Wollombi and Warkworth; Figure 1), a cross-section of the floodplain would generally include an elevated terrace, a forested slope (or riparian zone), a sparsely vegetated sandy alluvial plain (most commonly with *Casuarina cunninghamiana*, *Juncus acutus* and a few herbs) and a sand-bed channel with occasional bedrock outcrops (see example for the Warkworth transect in Figure 2).

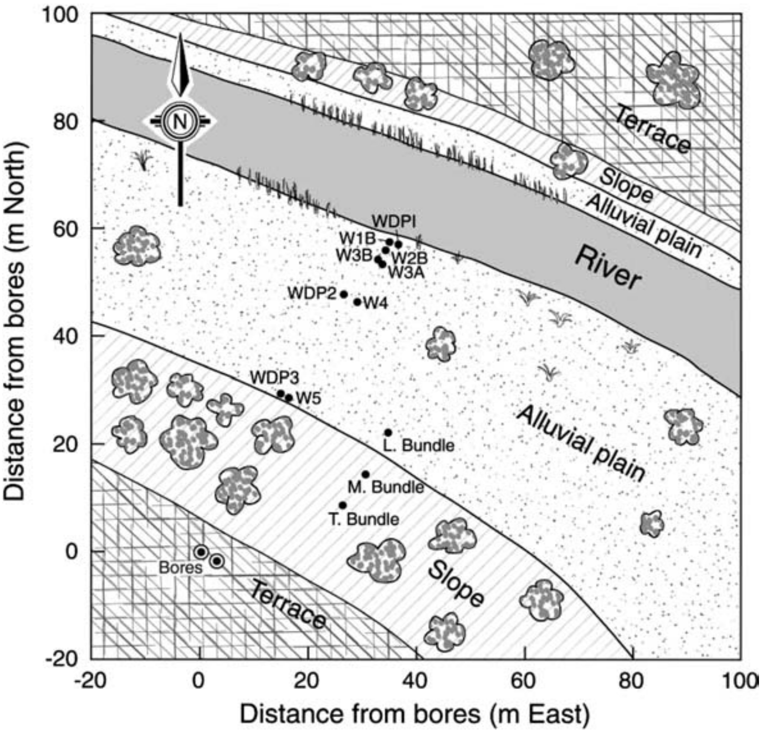


Figure 2. Planar view of the floodplain at the Warkworth site.

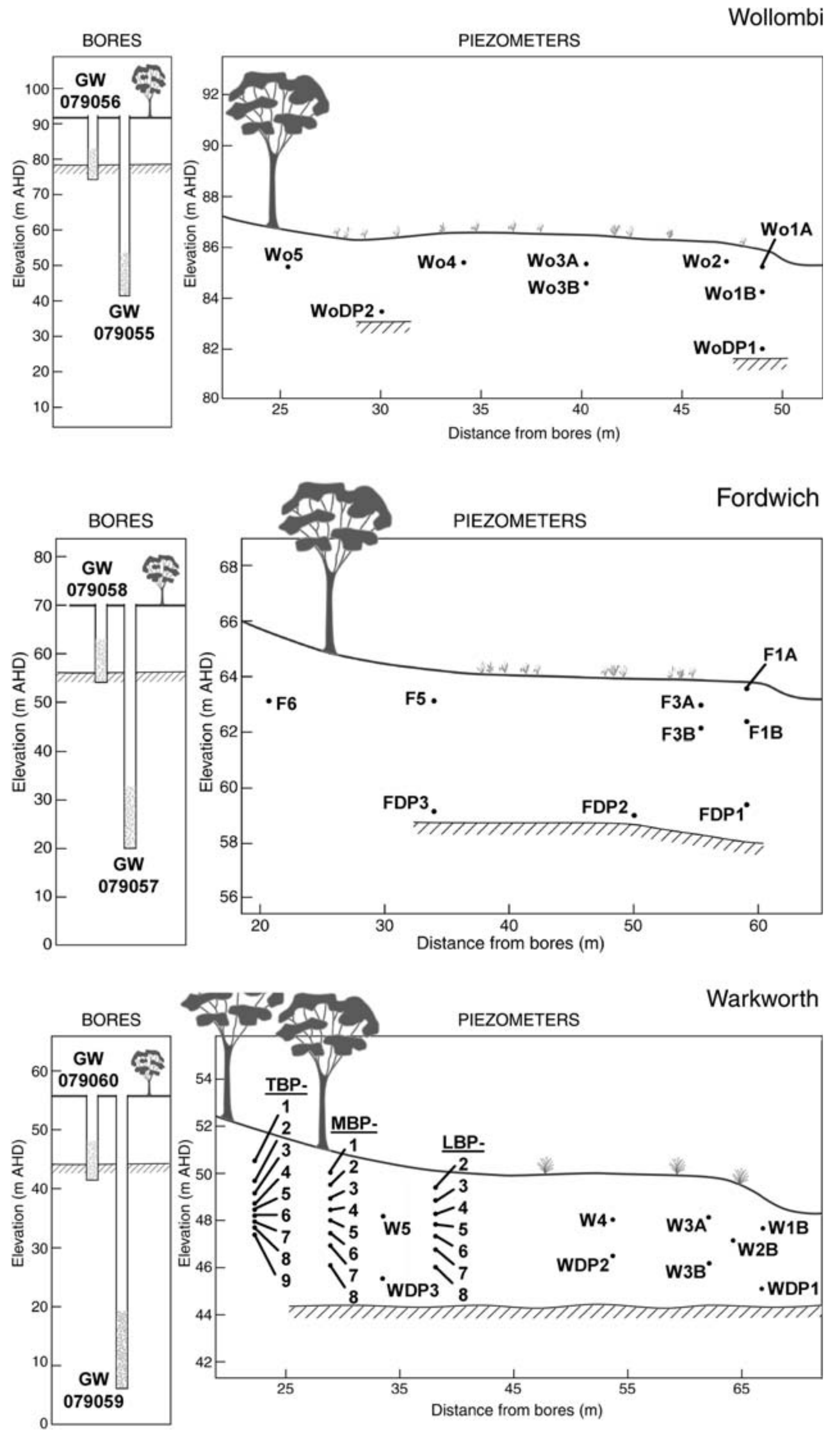
Regional and floodplain hydrogeology

The hydrogeology of the Wollombi Brook catchment will be presented in detail elsewhere and will only be summarised here. The Wollombi Brook is associated with a regional fractured bedrock aquifer and, in the valleys, an unconfined sand aquifer. While the brook was probably a significant discharge area for the bedrock aquifer in the past, dewatering of coal seams during mining operations has reduced or reversed hydraulic gradients in some sections of the bedrock aquifer. Currently, groundwater discharge from the fractured bedrock aquifer only contributes a small proportion of the baseflow but occasionally generates areas with high groundwater salinities (up to 6.4 mS cm^{-1}) within the floodplain. At the scale of the floodplain, the water table in the unconfined aquifer is essentially a reflection of river level, with weak gradients towards or away from the river at baseflow. During storms, the water table in the floodplain adjusts within hours to changes in river levels. Bank recharge during storms results in the formation of a groundwater mound where the alluvial plain meets the riparian zone (Figure 2). As the groundwater mound dissipates during flow recession, groundwater flows back towards the brook. During prolonged dry periods, bank discharge from the unconfined aquifer contributes most of the stream flow in the lower section of the brook.

For convenience, the section of the unconfined aquifer within the floodplain will hereafter be referred to as 'alluvial aquifer'. This distinction between the alluvial aquifer and the rest of the unconfined aquifer is also justified by the different origin of groundwater in each system (primarily surface water infiltration in the alluvial and diffuse rainfall recharge in the unconfined aquifer; A.L. Herczeg, CSIRO Land & Water, unpublished data).

Floodplain transects

Three transects were selected in the lower section of the catchment to study the exchange of water and nutrients between the regional aquifers, the alluvial aquifer, and the river (Figure 1). The transect near the town of Wollombi is immediately downstream from the confluence of two major tributaries and is at the transition between the upper and lower section of the brook. The Fordwich and Warkworth transects are characterised by lower gradients, wider alluvial plains, and a larger accumulation of sediments (Figure 3). In March to May 2000, each site was instrumented with two bores installed at the margin of the terrace and with a network of nested piezometers in the alluvial plain. Bores were installed using a rotary drill. At each site, one shallow bore (15–17 m below the surface) was located at the interface between the unconfined sand aquifer and the fractured bedrock aquifer. The second bore (50 m below the surface) tapped the regional bedrock aquifer only. Each bore consisted of a PVC casing screened over the lower 3 m and a 5–12 m gravel capped by a bentonite seal. At each transect, piezometers were installed at 5–6 locations


Wollombi
BORES
PIEZOMETERS
GW 079056
GW 079055
Elevation (m AHD)
Wo5
Wo4
Wo3A
Wo3B
Wo2
Wo1A
Wo1B
WoDP2
WoDP1
Distance from bores (m)
Fordwich
BORES
PIEZOMETERS
GW 079058
GW 079057
Elevation (m AHD)
F6
F5
F3A
F3B
F1A
F1B
FDP3
FDP2
FDP1
Distance from bores (m)
Warkworth
BORES
PIEZOMETERS
GW 079060
GW 079059
Elevation (m AHD)
TBP-
MBP-
LBP-
W5
WDP3
W4
WDP2
W3A
W3B
W1B
W2B
WDP1
Distance from bores (m)

across the alluvial plain, usually in nests of two or three. The piezometers were made of 5.0 cm ID PVC slotted along the lower 50 cm and covered with an outer lining to restrict the input of sand and silt during water sampling. Several piezometers were lost during the course of the study, mostly because of damage during floods.

In October 2000, the piezometer network was supplemented at each site with 2 or 3 drive points at depths ranging from 3 to 6 m (i.e. usually near the bottom of the alluvial aquifer). The drive points were made of 1.2 cm ID PVC with a 5 cm fritted stainless steel filter (mesh size = 200 μm). To minimise damage during floods, the drive points were cut approximately 30 cm above ground level and tightly capped. In addition to drive points, mini-piezometer bundles were installed to collect detailed vertical groundwater profiles at the Wollombi and Fordwich sites in October 2000 but were lost in a subsequent flood. Three other bundles were installed at Warkworth in March 2001. Mini-piezometer bundles were designed to collect groundwater samples at 25–50 cm intervals for up to 3 m below the water table. The bundles consisted of various lengths 6 mm OD nylon tubing attached on a 12 mm OD PVC pipe for support. It was subsequently discovered that groundwater samples collected with the nylon tubing were contaminated with organic C and organic N (Lamontagne et al. 2003). DOC and DON data in mini-piezometers and in the drive points (which were also sampled using the nylon tubing) will not be further discussed here. More details on the construction, installation, and sampling of drive points and mini-piezometers are presented elsewhere (Lamontagne et al. 2003).

The thickness of the alluvial aquifer along the transects was measured using steel rods. It was assumed that the depth to hard contact represented either bedrock or a paleochannel. The depths of contact obtained with the steel rods in the alluvial aquifer were consistent with the depth to bedrock recorded during the drilling of nearby bores on the terraces. The location of piezometers, drive points, and mini-piezometers was surveyed using a laser theodolite. The direction of groundwater flow in the floodplain was inferred from the slope of the water table. In the streambed, hydraulic gradients were measured using a potentiomanometer (Winter et al. 1988).

Groundwater sampling

On the first day of each sampling trip, water level was measured and the bores and piezometers were pumped to dryness or were flushed for several well

Figure 3. Cross-sections of the (a) Wollombi, (b) Fordwich and (c) Warkworth transects. Labels with 'DP' are drive points, those with 'BP' are mini-piezometer. The shallow groundwater bores are located at the interface between the unconfined sand aquifer and the fractured bedrock aquifer. The deeper bores are located solely within the fractured bedrock aquifer. The shaded area within the bores represent the extent of the gravel packs. AHD - Australian Height Datum.

volumes. On the following day, groundwater was collected with minimal exposure to the atmosphere by inserting the end of the pump line into the bottom of a large, pre-rinsed, Erlenmeyer flask allowing overflow. Field EC, pH, dissolved oxygen, and temperature were measured using a WTW Multiline P4 Universal meter. Subsamples were collected from the bottom of the flask using a large syringe connected to a three-way valve. Samples were immediately filtered on-line with a 0.45 μm Supor© membrane filter (Pall). A small filtered subsample was collected for Cl^- analysis in a scintillation vial. Another subsample was added to a small pre-prepared vial containing the reagents for Fe^{2+} analysis. The remaining filtered water was collected in a 125-ml bottle and acidified to pH < 2 using analytical grade HCl. Alkalinity was usually measured on site using a field titration kit (Hach). Prior to each sampling trip, all sampling bottles and filtering equipment were washed in P-free detergent and in a mild acid bath before thorough rising with distilled deionised water. For piezometers that were slow to recover, it was not always possible to remove three piezometer volumes prior to sample collection and sampling commenced soon after pumping on the 2nd day. Samples were stored at 4 °C and sent to the laboratory for analysis within 2–4 days. Drive points were pumped dry on the day prior to sampling using a sipper (6 mm OD nylon tubing) and a hand pump. Samples were collected on the following day by pumping directly into a pre-rinsed 125-ml bottle that was allowed to overflow. Samples were then handled as described above. Individual mini-piezometers were flushed for two or three volumes on the day prior to sampling using a hand pump. Between 50–100 ml was collected on the next day and handled as described above.

Nitrogen mineralisation

Potential sources of NH_4^+ and NO_3^- for groundwater across the floodplain were evaluated using buried bag nitrogen mineralisation assays (Eno 1960) at Wollombi in October 2000. Polyethylene bags filled with ~75 g of soil were incubated in triplicate at several depths at four stations spanning the floodplain (i.e. from the terrace to the stream bank). Subsamples were collected to determine initial exchangeable NH_4^+ and NO_3^- concentrations, as described below. For stations on alluvial sand, bags were incubated just below the surface, above the water table, and below the water table. Stations on alluvial sand had no developed soil but occasionally had a sparse litter cover. On the terrace, the LF horizon and the underlying alluvial sand were incubated. Buried bags were incubated for 10 days. Following retrieval of the bags, samples were stored at 4 °C and exchangeable NH_4^+ and NO_3^- extracted from 5 g subsamples using 2 M KCl. Water content and soil dry weights were measured by drying ~25 g wet weight soil subsamples at 50 °C for 24 h. Net N mineralisation (in mg N [g dry soil]$^{-1}$ d^{-1}) and net nitrification rates were estimated from the changes in exchangeable mineral N and NO_3^- concentration between final and initial bags, respectively.

Analytical methods

All samples were analysed at the CSIRO Land and Water Urrbrae analytical facilities. Ammonium and NO_3^- concentrations were measured by colorimetry (automated phenate method and cadmium reduction methods, respectively; American Public Health Association 1999). Note that the method used does not discriminate between NO_3^- and NO_2^-. Dissolved organic carbon (DOC) was measured by high temperature oxidation followed by infrared detection using a SKALAR FormacsHT TOC/TN analyser. Total dissolved N (TDN) was measured by high temperature oxidation to NO_2 followed by detection by thermoluminescence. Dissolved organic N was estimated as TDN – (NH_4^+ + NO_3^-). Chloride was measured by ion chromatography and Fe^{2+} by a modified phenanthroline method. Total dissolved Fe (TDFe) and major cations were measured by ICP emission spectrometry.

Results

General patterns in dissolved solute concentration

Groundwater samples were collected during field trips in March, May, and October 2000, and March–April and November 2001. For brevity, emphasis will be given here to the March–April 2001 and November 2001 field trips where more detailed vertical profiles were collected in the alluvial aquifer. These corresponded to the receding phase of a storm hydrograph and a prolonged period of baseflow, respectively. A range of geochemical environments was present across the floodplain but some general trends emerged between regional groundwater (as represented by the bores), alluvial groundwater (as represented by piezometers and drive points but excluding the Warkworth mini-piezometers), and river water (Table 1). Groundwater from the regional and the alluvial aquifers tended to be suboxic to anoxic (as shown by relatively low dissolved O_2 and high Fe^{2+} concentrations), but oxygenated pockets were occasionally present. A wide range in salinity (as represented by EC) was found in all three types of water. On average, regional groundwater was brackish (2.3 mS cm^{-1}) but tended to be more fresh in the shallow bores (0.74–1.9 mS cm^{-1}) than in the deep bores (0.97–7.6 mS cm^{-1}). Alluvial groundwater and river water tended to be fresh (i.e. < 1.5 mS cm^{-1}), with the exception of the occasional intrusion of saline groundwater in the bottom of the alluvial aquifer (i.e. EC > 5 mS cm^{-1}). All waters were circumneutral (pH = 6.1–8.0) and usually alkaline. On average, NH_4^+ and NO_3^- concentrations were higher in regional groundwater (860 and 160 μg N l^{-1}, respectively) and alluvial groundwater (460 and 140 μg N l^{-1}) than in river water (67 and 45 μg N l^{-1}). However, NO_3^- concentration in the alluvial aquifer was extremely variable, ranging between < 5 and 4600 μg N l^{-1} (and up to 5600 μg N l^{-1} including the Warkworth mini-piezometers). DON was a significant

Table 1. Mean and range in dissolved solutes and water quality parameters for regional groundwater, alluvial groundwater (excluding the Warkworth mini-piezometers), and river water for all sampling trips. The true range may be larger for some water types (i.e. stream water) because not all flow conditions were sampled during the study. Data in mg l^{-1} unless otherwise shown. Data from the Warkworth mini-piezometers were not included in this comparison because their large number would bias averages towards the conditions found at that transect

	Bores (Regional groundwater)	Alluvial groundwater	River
Temp. (°C)	20.3 (18–23.8)	19.6 (9.4–25.3)	13.6 (8.5–22)
Field pH	6.9 (6.1–7.6)	6.8 (6.0–7.7)	7.4 (6.4–8.0)
Dissolved O_2	0.2 (< 0.1–0.4)	0.4 (< 0.1–2.4)	8.3 (7.4–9.2)
EC (mS cm^{-1})	2.3 (0.74–7.6)	0.71 (0.16–6.4)	0.60 (0.39–1.4)
Alk. (meq l^{-1})	8.8 (0.64–19)	2.0 (0.35–8.8)	1.8 (0.97–3.2)
NH_4^+ (μg N l^{-1})	860 (< 20–2200)	460 (< 20–2170)	67 (< 20–280)
NO_3^- (μg N l^{-1})	160 (< 5–1700)	140 (< 5–4600)	45 (< 5–190)
DON (μg N l^{-1})	260 (< 50–520)	310 (110–530)	380 (190–570)
Fe^{2+}	8.5 (< 0.01–40)	11 (< 0.01–44)	0.20 (< 0.01–0.30)
TDFe	6.9 (0.02–54)	11 (< 0.1–126)	0.27 (0.040–0.89)
DOC	2.3 (< 0.5–6.7)	4.5 (2.5–14)	6.3 (4.9–8.4)

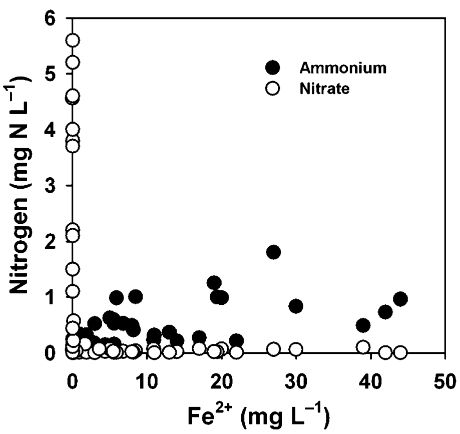


Figure 4. Fe^{2+} concentration versus mineral – N concentration in alluvial groundwater during the March–April and November 2001 field trips.

proportion of the dissolved N pool in regional groundwater (260 μg N l^{-1}) and alluvial groundwater (310 μg N l^{-1}) and the main form in river water (380 μg N l^{-1}). The form of mineral N present in the alluvial and regional aquifers was related to indicators of the redox status of the aquifer (Figure 4). For example, high concentrations of NO_3^- were only found when Fe^{2+} concentrations were less than 1 mg l^{-1} (indicating oxic conditions). The pattern for NH_4^+ was not as clear but there was a tendency for higher concentrations when Fe^{2+} was greater than 1 mg l^{-1} (indicating suboxic to anoxic conditions).

Cross-sectional profiles

There were some differences in the spatial distribution of mineral – N between the three study sites. Based on elevated Fe^{2+} concentrations, the Wollombi and Fordwich transects had a reducing environment throughout the floodplain (Figure 5). In contrast, a pocket of oxic (that is Fe^{2+} free) groundwater was always present at the toe of the slope at Warkworth (Figure 5). These differences in reducing conditions were reflected in the distribution of the mineral – N species. While NO_3^- was only present in trace amounts at Wollombi and Fordwich, concentrations up to 5600 μg N l^{-1} were found within the oxic pocket at Warkworth (Figure 6). Because the analytical method used does not discriminate between NO_3^- and NO_2^-, some of the trace concentrations of 'NO_3^-' under suboxic conditions may have been mostly NO_2^- or a combination of the two. At Warkworth, the pocket of NO_3^--rich groundwater appeared to move downslope between March–April 2001 and November 2001, consistent with the direction of groundwater flow at those times. Ammonium had the opposite pattern to NO_3^- at Warkworth, with concentrations generally increasing from the toe of the slope to the river (Figure 7).

Only limited spatial patterns in DOC and DON concentration were available because of the contamination of mini-piezometer samples and drive points by the nylon tubing. Using data from the larger piezometers only, there was a weak trend for DOC and DON concentration to be highest near the slope and lowest closest to the river (Figure 8). With the exception of one site (piezometer F6) within a well-developed riparian cover, DOC concentrations were always < 10 mg C l^{-1} in the alluvial aquifer. DOC concentration in streamwater tended to be similar to the ones found in the alluvial aquifer. However, the DOC:DON ratio in streamwater ($\sim$9) was lower than in the alluvial aquifer (10–43).

Water table profiles

Despite a reducing aquifer environment at Wollombi and Fordwich, it was hypothesised that an oxygenated fringe occurred at the interface between the water table and the unsaturated zone. This hypothesis was tested with the mini-piezometer bundles installed at both Wollombi and Fordwich in October 2000. Evidence of a sharp redox interface was found in three of the four water table profiles (Figure 9). With the exception of one profile at Wollombi, a sharp gradient in TDFe concentration occurred at a depth ranging from 20 to 80 cm below the water table. Low TDFe concentrations (presumably representing oxic conditions) were found near the water table but tended to rapidly increase with depth (presumably from higher concentrations of dissolved Fe^{2+} under suboxic or anoxic conditions). Ammonium concentration also tended to increase with depth below the water table,

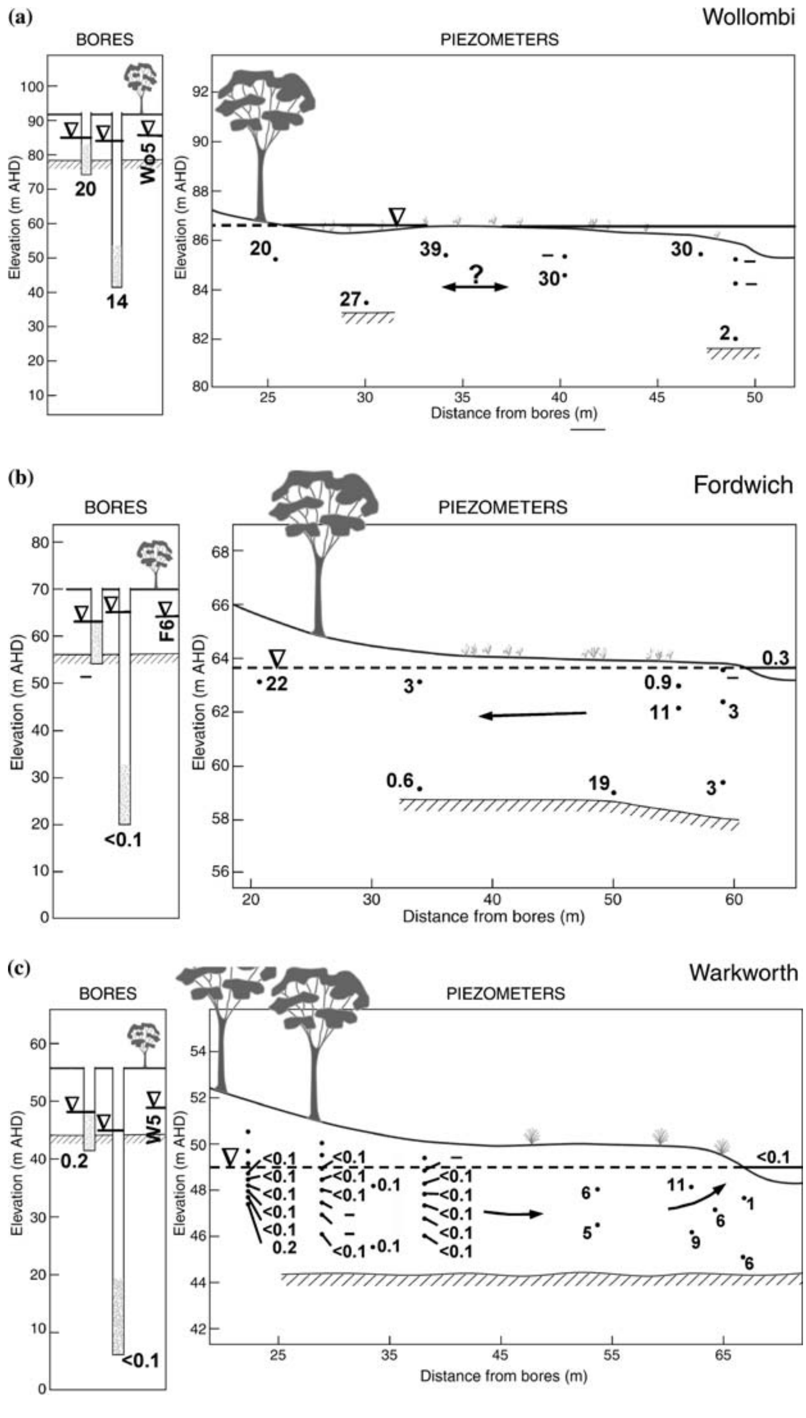

(a)
Wollombi
BORES
PIEZOMETERS
Elevation (m AHD)
Wo5
20
14
39
27
30
2
?
Distance from bores (m)
(b)
Fordwich
BORES
PIEZOMETERS
F6
<0.1
22
0.3
0.9
11
3
0.6
19
(c)
Warkworth
BORES
PIEZOMETERS
W5
0.2
<0.1
0.1
6
5
11
1
9

Figure 5. Fe^{2+} concentration (in mg l^{-1}) in alluvial groundwater at the (a) Wollombi, (b) Fordwich and (c) Wollombi transects, March–April 2001 field trip. '–' indicates no data available. The position of the water table (or the piezometric surface for the deeper bores) is represented by the inverted triangles. Arrows represent the direction of groundwater flow at the time of sampling (arrows labeled with '?' denote that the direction was uncertain because of flat gradients).

but without the same sharp gradient observed for TDFe. Nitrate concentration remained at or below the detection limit in all the profiles (data not shown).

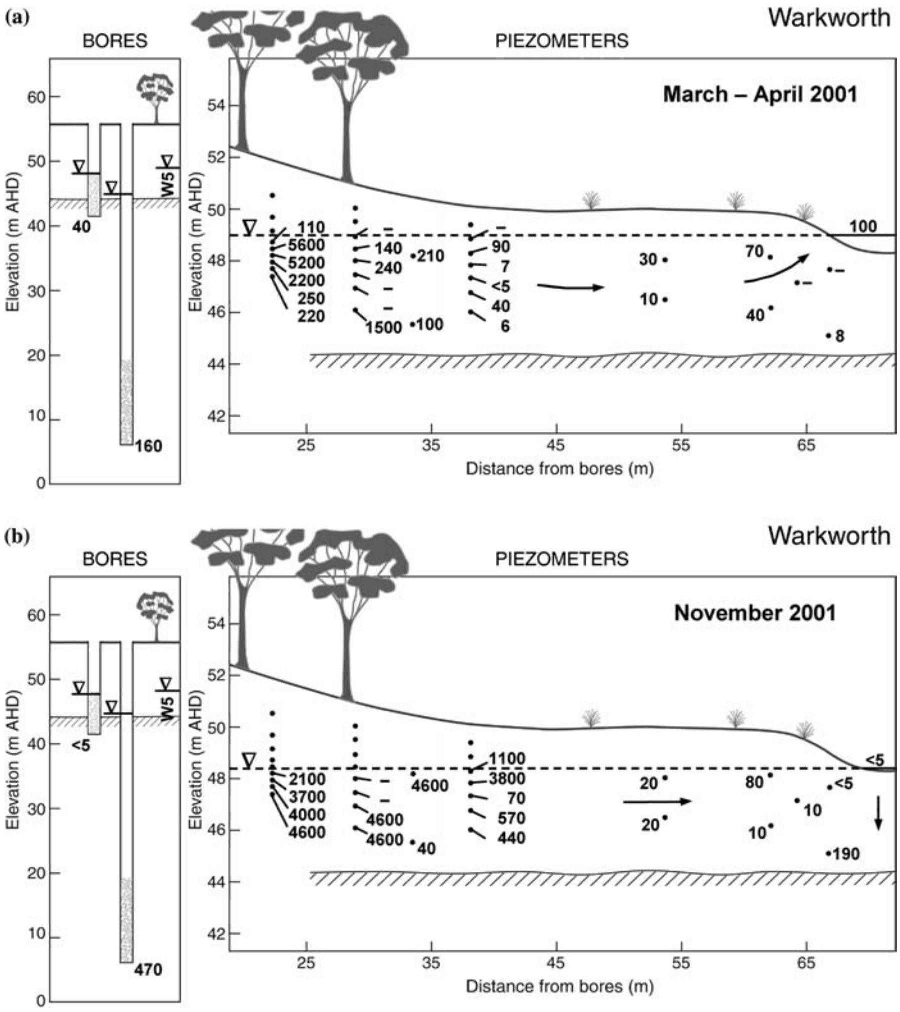


Figure 6. Nitrate concentration (in μg N l^{-1}) at Warkworth on (a) March–April 2001 and (b) November 2001.

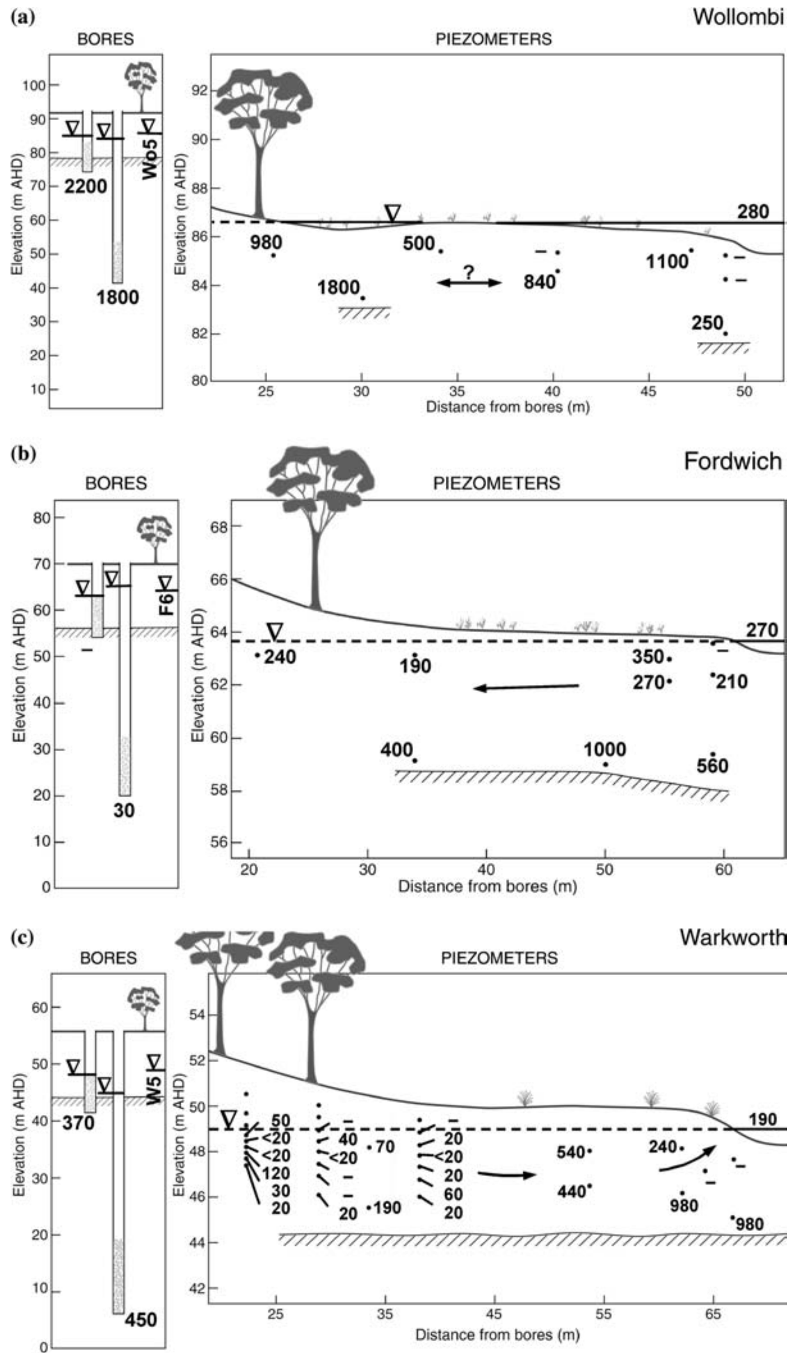


Figure 7. Ammonium concentration (in μg N l^{-1}) at (a) Wollombi, (b) Fordwich and (c) Warkworth on March–April 2001.

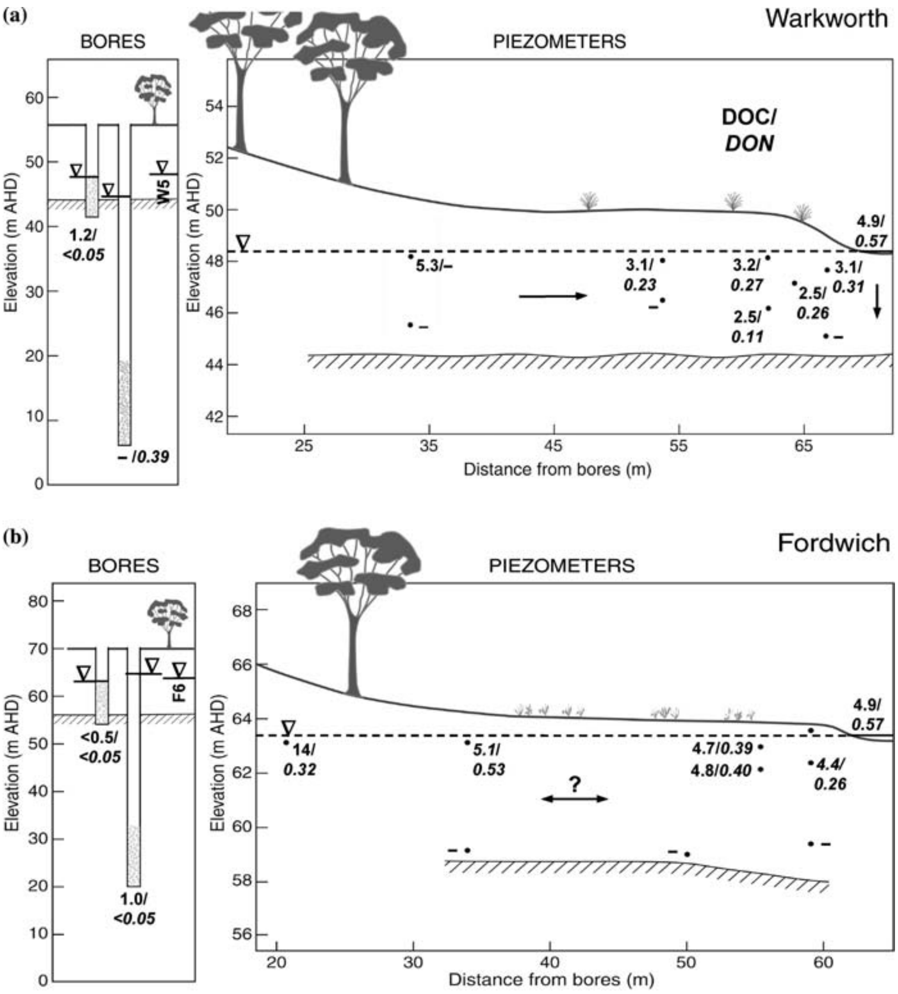


Figure 8. DOC and DON concentration (in mg C or N per l) at Fordwich and Warkworth during the November 2001 field trip. Data presented as DOC conc./*DON conc*. at each sampling point.

Nitrogen mineralisation

There was a distinct pattern in net N mineralisation and net nitrification rates across the floodplain at the Wollombi transect. In general, net mineralisation and nitrification rates were higher in the litter layer and shallow alluvial sand than in alluvial sand above or below the water table (Table 2). Rates were also lowest near the stream bank and highest at the toe of the slope and on the terrace. These patterns in N mineralisation suggest that a significant pool of soil NH_4^+ and NO_3^- could accumulate in shallow soil and alluvial sand between flooding and rainfall events, especially on the terrace and the toe of the slope.

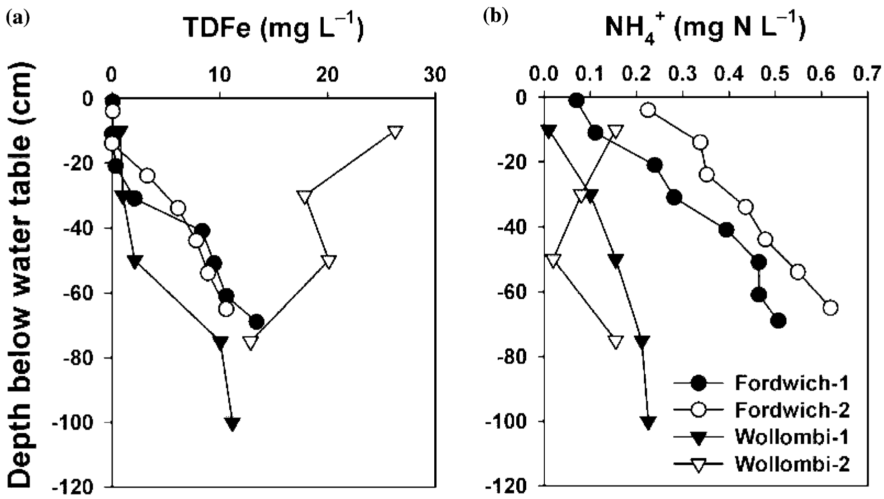


Figure 9. Vertical profiles in (a) TDFe and (b) NH_4^+ concentrations at the interface between the unsaturated zone and the water table in the Wollombi Brook alluvial aquifer.

Table 2. Net nitrogen mineralisation and net nitrification rate across a floodplain (Wollombi transect) in October 2000

Landscape position	Net N mineralisation rate (μg N g^{-1} d^{-1})	Net nitrification rate (μg N g^{-1} d^{-1})
Terrace		
LF horizon	10 ± 1	17 ± 15
Sand below LF	3.1 ± 0.6	2.0 ± 2.0
Toe of slope		
Surface	68 ± 39	21 ± 17
Above water table	0.2 ± 0.1	0.1 ± 0.06
Below water table	0.7 ± 0.7	0.1 ± 0.1
Alluvial Plain		
Surface	5.3 ± 5.8	1.7 ± 2.7
Above water table	0.09 ± 0.2	0.04 ± 0.1
Below water table	0.5 ± 0.5	0.01 ± 0.04
Stream bank		
Above water table	−2.8 ± 0.4	1.0 ± 1.0
Below water table	−1.0 ± 3.2	0.01 ± 0.1

Mean and standard deviation for three replicates. LF, litter layer.

Discussion

There are three important observations about the N cycle in subtropical streams from the Wollombi Brook study. These are (1) that groundwater–surface water interactions can be principally driven by local lateral exchange processes such as cycles of bank recharge and discharge, (2) that DON and NH_4^+ were the principal forms of N delivered from the alluvial aquifer to the brook during low flow periods, and (3) that a large proportion of the alluvial groundwater N pool may be derived from the floodplain or produced within the aquifer. These will be reviewed in some detail in the following section.

Bank recharge and discharge

According to the flood-pulse theory, the exchange of water, organic matter, and nutrients between rivers and floodplains occurs when surface water connectivity is re-established, principally during floods (Junk et al. 1989). However, rivers and floodplains can remain connected following floods even when surface water connections are severed through processes such as bank discharge (Woessner 2000; Burt et al. 2002b). This maintenance of a groundwater connection between floodplains and rivers can have important implications for the extent and timing of salt and nutrient loads to surface water. For example, in the Chowilla floodplain on the lower River Murray (in semi-arid Australia), an increased load of salt through bank discharge persisted for 18 months following a medium-size flood (Jolly et al. 1994). A similar process may occur for several nutrient species which frequently have an elevated concentration in groundwater (including PO_4^{3-}, NH_4^+, Si, and Fe^{2+}) but is poorly characterised for semi-arid and subtropical floodplains. The input of nutrients from groundwater may contribute to the pulse in biological activity observed in semi-arid rivers following floods but is yet to be accurately quantified.

Sources of N to the alluvial aquifer

The predominance of lateral exchange processes at Wollombi Brook suggests that a large fraction of the dissolved N pool found in the alluvial aquifer is derived from the floodplain. Among the external sources of N to the alluvial aquifer, regional groundwater discharge from the fractured bedrock aquifer only occurred in some areas of the floodplain and appeared to only represent a small proportion of stream flow (Herczeg, CSIRO Land & Water, unpublished data). Similarly, because of the presence of groundwater mounds underneath the riparian zone, the unconfined sand aquifer did not always discharge to the floodplain. Recharge by floodwater may be a significant source of N to the alluvial aquifer (Martí et al. 2000). In addition, vertical recharge during floods has the potential to leach DON from soil organic matter (Baldwin 1999; Kalbitz et al. 2000) and to displace mineral – N stored in the unsaturated zone (Lamontagne et al. 2002). Finally, both DON and ammonium may be produced during the decomposition of organic matter by anaerobic metabolism within anoxic sections of the alluvial aquifer (Pinay et al. 2002; Schade et al. 2002).

There are several possible origins for the plume of NO_3^- found at Warkworth. The plume did not originate from groundwater discharge from the unconfined sand aquifer or the fractured bedrock aquifer because regional groundwater flow was away from the floodplain throughout the flood cycle at this transect. The plume may have originated from the recharge of NO_3^--rich surface water during a flood. Following this scenario, NO_3^- would have been found throughout the floodplain soon after the flood but would have only persisted under the Warkworth riparian zone, where oxic conditions persisted. An alternative origin for the Warkworth NO_3^- plume is that it was derived from the soil NO_3^- pool within the riparian zone. The October 2000 N mineralisation assay indicated that net nitrification rates were highest in the riparian zone (as opposed to the alluvial plain) suggesting that a pool of soil NO_3^- could accumulate in this section of the floodplain between recharge events. Unlike NH_4^+, NO_3^- is quite mobile in the unsaturated zone (Vitousek and Melillo 1979; Aber et al. 1989) and can easily be displaced to the water table during recharge events (i.e., large rainfall, inundation, or bank recharge). Similarly, at the Hattah floodplain on the River Murray (in semi-arid Australia), Lamontagne et al. (2002) demonstrated that the vertical displacement of unsaturated zone NO_3^- could have easily accounted for a transient increase in groundwater NO_3^- concentration following a flood. The production of NO_3^- in subtropical floodplain soils during droughts and its subsequent loss by denitrification following recharge to suboxic or anoxic sections of alluvial aquifers may be an important mechanism of N removal from this ecosystem. This tendency to lose N during internal recycling would be consistent with the N rather than P limitation of plant growth observed in Australian semi-arid floodplains (Odgen and Thoms 2002; Ogden et al. 2002)

The significance of regional groundwater discharge to the N load in subtropical floodplains may be underestimated at Wollombi Brook because current land use (that is coal mining) has reduced or reversed hydraulic gradients towards the brook. Even if regional groundwater was only a small source of water or N to the alluvial aquifer, it could still considerably impact the geochemical environment in the aquifer because it is saline to brackish. Density stratification induced by saline groundwater intrusions can foster the development of anoxic conditions in deeper river pools or in the lower section of alluvial aquifers (Anderson and Morison 1989). In turn, anoxia in saline pools may foster processes such as denitrification, increased rates of sulfate reduction, and release of PO_4^{3-} from Fe oxides complexes (Baldwin and Mitchell 2000).

Aquifer redox status

Many studies have identified that floodplain and sand aquifers with shallow water tables tend to have reducing environments (Starr and Gillham 1993; Hill 1996; Pinay et al. 2000). Several mechanisms have been proposed to explain this relationship between water table depth and aquifer redox status. Floodplains with shallow water tables are more likely to have groundwater flowpaths through organic-rich surface soils and sediments that promote bacterial activity (Pusch et al. 1998; Hill et al. 2000). In addition, the depth to the water table can also determine the rate of recharge of DOC from the unsaturated zone (Starr and Gillham 1993; Pabich et al. 2001). Where water tables are deeper, most of the DOC produced in organic soil horizons is retained by adsorption or consumed by microorganisms in the unsaturated zone before reaching the water table (Qualls and Haines 1992; Kalbitz et al. 2000). As a result, not enough labile DOC reaches groundwater to produce the suboxic to anoxic conditions required for NO_3^- reduction (Starr and Gillham 1993). Alternatively, factors independent of water table depth could control aquifer redox status, including the weathering of reduced S and Fe mineral deposits (Appelo and Postma 1993; Böhlke et al. 2002).

At Wollombi Brook, there was no clear relationship between water table depth and aquifer redox status. For example, at the Warkworth transect, oxic conditions were found when the water table was deeper than 2 m. However, the aquifer was completely reduced at the Fordwich transect for a similar range in water table depths. A potential relationship between water table depth and aquifer redox status may have been obscured at Wollombi Brook by the large differences in plant and organic soil cover across the floodplain. For example, despite deeper water tables, the highest DOC concentrations were measured within the riparian zones as opposed to the sparsely vegetated alluvial plains. Thus, the redox status of subtropical floodplains is probably not simply a function of aquifer thickness but some combination of factors such as the potential for DOC recharge during floods, the availability of buried organic deposits, and the presence of reduced minerals in the aquifer.

Conclusion

The role of subtropical floodplains and riparian zones in controlling N exports from catchments may be different to similar environments in humid temperate climates. While a role in filtering N inputs from groundwater may occur under some circumstances, the storage of water during flood pulses may be more significant. It is still not clear whether subtropical floodplains will be net sources or net sinks for N in surface water during whole flood cycles because while they retain some N forms (NO_3^-), they could export others (NH_4^+ and DON). DON was the main form of dissolved N in surface water at low flows at Wollombi Brook, which is thought to be a feature of environments with strong mechanisms for biological N retention (Hedin et al. 1995; Harris 2001). While most of the DON pool is usually considered unavailable to plants and microorganisms in freshwater, it may still contribute to the N cycle in downstream environments (Stepanauskas et al. 1999). Future studies on the N cycle in subtropical floodplains should seek to characterise the fluxes of water and N in groundwater during whole flood cycles and to better understand the processes of N transformations during transport in alluvial groundwater.

Acknowledgements

This study was supported by funding from Land and Water Australia project CLW7, by the New South Wales Department of Infrastucture, Planning and Natural Resources and by CSIRO Land and Water. Andrew Boulton, Christy Fellows, Mike Grace and Bill Ullman provided useful advice at various stages of the project.

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