Biogeochemistry **26:** 67–83, 1994.

Ammonium sorption to channel and riparian sediments: A transient storage pool for dissolved inorganic nitrogen

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Received 14 March 1994; accepted 27 June 1994

Key words: ammonium, riparian, sediments, sorption, storage, streams

Abstract. Sediment (0.5 mm–2.0 mm grain size) was incubated in nylon bags (200 μm mesh) below the water table in the channel and in two transects of shallow wells perpendicular to the banks (to 18 m) of a third-order stream during August, 1987. One transect of wells drained steep old-growth forest, and the other a steep 23 year-old clear-cut partially regenerated in alder. At approximately 6-week intervals between October, 1987, and June, 1988, bags were retrieved. Total exchangeable ammonium was determined on sediment, and dissolved oxygen, nitrate and ammonium were determined in stream and well water. Exchangeable ammonium ranged from 10 μeq/100 g of sediment in the stream where nitrification potential and subsurface exchange with stream water were high, to 115 μeq/100 g sediment 18 m inland where channel water-groundwater mixing and nitrification potential were both low. Sorbed ammonium was highest during summer/autumn base flow and lowest during winter storm flow. Both channel and well water contained measurable dissolved oxygen at all times. Ammonium concentration was typically < 10 μg-N/L in channel water, increased with distance inland, but did not exceed 365 μg-N/L at any site. Nitrate concentration was typically higher in well water than channel water. Nitrate levels increased dramatically in wells at the base of the clear-cut following the onset of autumn rains. The results indicate a potential for temporary storage of ammonium on riparian sediments which may influence biotic nitrogen cycling, and alter the timing and form of dissolved inorganic nitrogen transport from the watershed.

Introduction

The ability of sediment to serve as a transient storage pool for ammonium varies by location because it is determined by numerous factors, including the cation exchange capacity (CEC) of sediment, sediment surface area in contact with stream water, and ammonium concentration of interstitial water. Variability in these factors from site-to-site has led to divergent conclusions on the role of sediment as a significant ammonium pool. For example, Richey et al. (1985) reported ammonium disappearance in excess of measured uptake or nitrification during a brief amendment study at Bear Brook, New Hampshire, USA. This observation, in conjunction with concurrent sediment desorption assays, led them to conclude that channel sediment can contain a significant pool of ammonium which can be subsequently oxidized to nitrate and transported from the system. The opposite was concluded by Newbold et al.

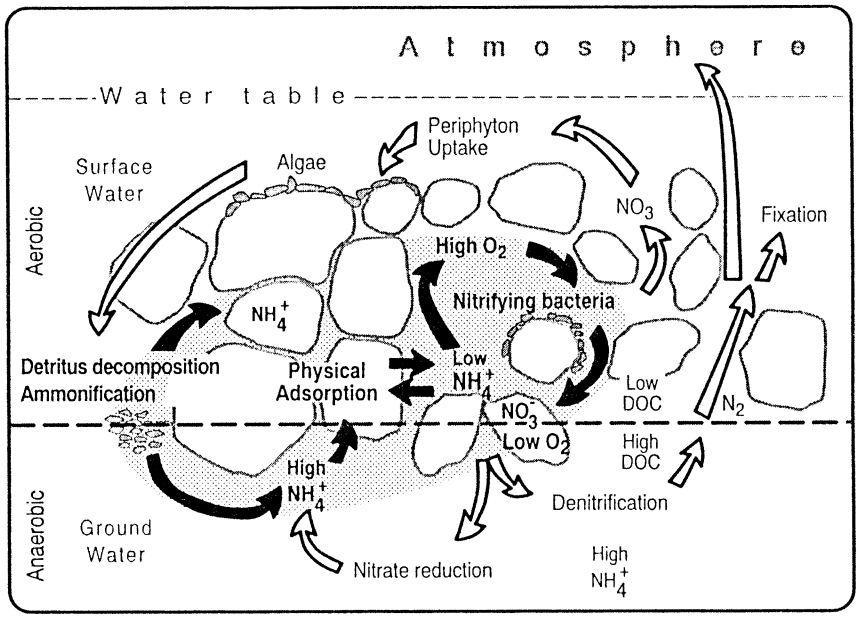

Fig. 1. Conceptual model indicating linkage between physical sorption of ammonia to sediments, its sources (groundwater input, ammonification), and DIN transformations (nitrification, denitrification, nitrate reduction) at the groundwater-surface water interface of a third-order channel. Adapted from Triska et al. (1993a).

(1983). They reported insignificant sediment sorption during a 90-day ammonium enrichment to Walker Branch, Tennessee, USA. Ammonium disappearance could be accounted for by nitrification and biotic uptake associated with detritus. Along the Pacific coast of the United States, the coastal mountain range consists of uplifted marine sediment. As a result, channel sediments can be rich in minerals with higher CEC than those associated with igneous parent material. Triska et al. (1993a) presented a hypothetical model of nitrogen cycling at the groundwater-stream water interface of a third-order, coast range stream (Fig. 1). A central premise of this model was transient retention of ammonium on hyporheic sediments by physical adsorption. The hypothetical sources of ammonium were decomposition of organic matter (ammonification) and that dissolved in emerging groundwater. We hypothesized that the retention of ammonium by sorption temporally regulated the availability of ammonium for biotic uptake, nitrification and dissolved inorganic nitrogen (DIN) transport from the stream.

This study addressed the temporal variability in retention of dissolved inorganic nitrogen by channel and riparian sediments of an upland stream under ambient nutrient and discharge conditions. The study period, August

1987–June 1988, spanned distinct annual hydrologic shifts including summer-autumn base flow, winter storm flows and spring base flow. Temporal patterns in the pool of sorbed ammonium on channel and bankside sediments up to 18 m from the channel were compared. Patterns of sorbed ammonium were also compared between bankside sediments of old-growth forest and a 23-year old clear-cut partially regenerated in red alder, a nitrogen-fixing species.

Study site

The study was conducted at Little Lost Man Creek, a third-order gravel-cobble stream in northwestern Humboldt County, California (Fig 2A). The watershed area is 9.4 km^2 and ranges in altitude from 24–695 m (387 m mean altitude). The watershed is long, narrow and faces northwest. The drainage basin is underlain by the Franciscan Formation of late Jurassic and early Cretaceous age consisting primarily of unmetamorphosed sedimentary rocks (Iwatsubo et al. 1975). Microscopic analysis of sediment grains comprising size classes from 0.19–4.0 mm indicates a predominance (>80%) of mudstones plus siltstones (Jackman & Ng 1986).

The overall channel gradient of Little Lost Man Creek is 0.066 (Iwatsubo & Averett 1981) and 0.018 in the study reach. In addition to the coarse and poorly-sorted cobbles and gravels, large particulate organic matter including logs is common in the channel. The sediment is highly permeable with significant interflow of streamwater to the channel subsurface and lateral riparian subsurface (Bencala et al. 1984, Triska et al. 1989, 1993b).

The area is characterized by cool wet winters and warm dry summers. Average annual precipitation is 178 cm at a rain gage approximately 3 km northwest of the study site. Monthly precipitation historically peaks in January at 32 cm, is typically <12.5 cm/month from October through April, and is low in June–August (2.5 cm/month).

Approximately 92% of the watershed is vegetated in old-growth coastal redwood forest (*Sequoia sempervirens*) in association with Douglas-fir (*Pseudotsuga menziesii*) and western hemlock (*Tsuga heterophylla*). In 1965 approximately 8% of the watershed was clear-cut. The logged area near the base of the watershed has regenerated with a significant component of red alder (*Alnus rubra*), a nitrogen-fixing species.

Materials and methods

Sediments were collected from an exposed deposit of alluvium in the incised channel. Bulk sediment was returned to the laboratory, dried and sieved to a size class 0.5–2.0 mm. Sediments were mixed by hand then passed through a sample splitter to insure uniform size distribution of particles between

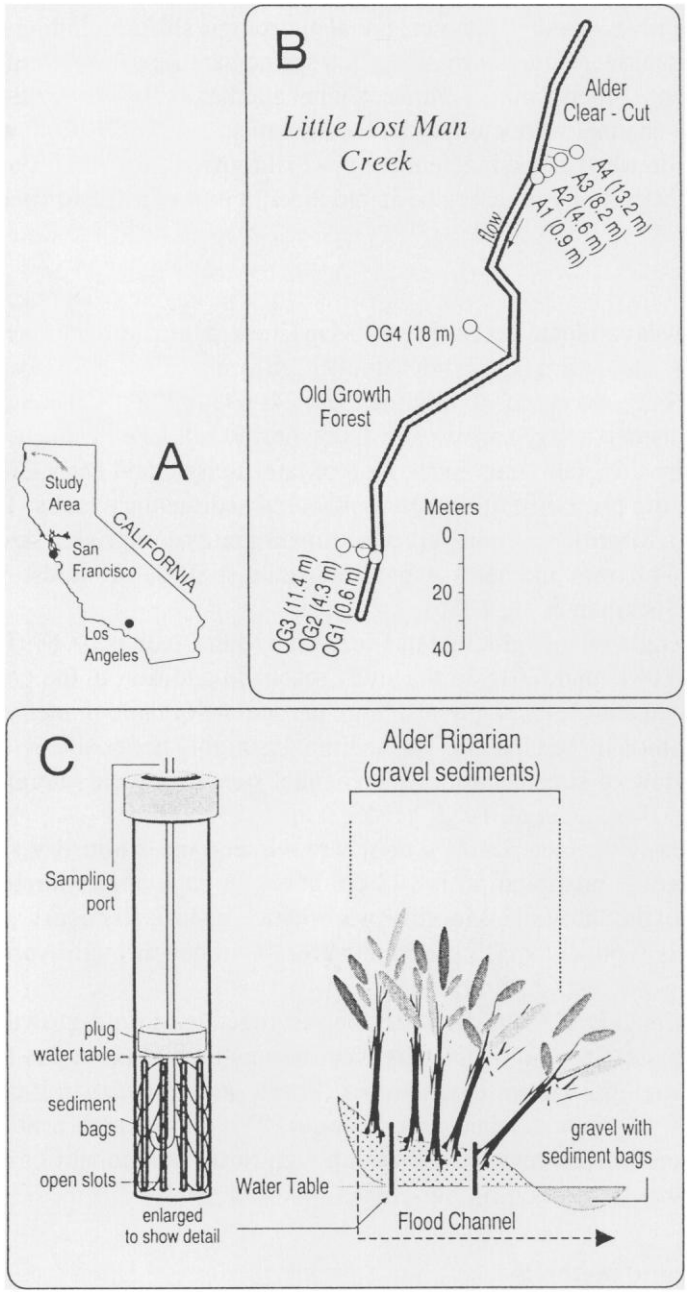

Fig. 2. Schematic diagrams indicating: (a) location of the study site in California, USA, (b) plan view site map indicating the position of sampling wells relative to the channel of Little Lost Man Creek, and (c) cross-sectional diagram indicating the position of wells relative to the water table, and enlargement of a well indicating its construction, and the placement of sediment bags.

samples. Sediments were weighed into 100 g samples, sewn into 100 × 100 mm nylon bags (200 μm mesh) and strung along nylon cords. Strings of sediment bags were either tethered to a rock and buried just beneath the surface of the channel or placed within two transects of water table wells (Fig 2b, c) during August 1987. One transect of wells, the alder transect, was located at the base of the hillslope clear cut in 1965. Wells along this transect were located at distances of 1 m (A1), 5 m (A2), 8 m (A3), and 13 m (A4) perpendicular to the channel. The second transect of wells, the old-growth transect, drained primary, coastal redwood forest. Wells along this transect were located at distances of 1 m (OG1), 4 m (OG2), 11 m (OG3), and 18 m (OG4) perpendicular to the channel.

One sediment bag from each site was collected at approximately six-week intervals. Bags were drained of excess water, immediately frozen, and returned to the laboratory for ammonium extraction. Approximately 40 g of thawed sediment was extracted three times in 2.0 M KCl. Each extraction exceeded 24-hours after which the liquid was decanted and filtered. The extracts were combined and analyzed on a Wescan Ammonium Analyzer in which the ammonium ions are converted to ammonia at high pH and the ammonia passes through a selective membrane into an absorber solution where the ammonia is detected by a sensitive differential conductivity detector. This instrument can readily detect low concentrations of ammonium in aqueous solutions of high ionic strength. Precision of the extraction procedure is within 10%, and analytical precision for ammonia is within 5% for concentrations encountered in this study. Extracted sediments were dried and weighed to determine total exchangeable ammonium in microequivalents/100 g dry sediment.

The partition coefficient for ammonium on the sediment, or the ratio of sorbed ammonium to that in interstitial water (μg NH_4-N/g sediment: μg NH_4-N/g interstitial water) was then calculated. Since sediment was incubated in bags, interstitial water drained from the bags during removal and could not be recovered. To compute the partition coefficient we therefore sampled stream and well water prior to removing the sediment bag, and analyzed it for ammonium.

Prior to removing the sediment bags, we also recorded water temperature, dissolved oxygen concentration and sampled water for nitrate plus nitrite. Dissolved oxygen was measured by passing a gentle flow of well water peristaltically through an upright tube containing an stirring oxygen probe connected to a Yellow Springs Scientific Model 57 oxygen meter. After approximately 3 volumes of water overflowed the tube, temperature and dissolved oxygen were recorded. An inline filter containing a 0.45 μm Gelman membrane filter was then attached and water was passed into new unwashed

polyethelene bottles. Membranes were leached and bottles rinsed three times with sample water before taking each sample. Water samples were frozen at 20 °C until analysis. Nitrate plus nitrite, henceforth referred to as nitrate, was determined by an automated cadmium reduction method (Technicon Industrial Method #158-71W, December 1972). Ammonium was determined using an automated phenol-hypochlorite method (Technicon Industrial Method #154-71W, February 1973). Analytical precision for nitrate nitrogen was ± 1 μg/L below 100 μg/L and approximately ± 1% above. Precision for ammonium nitrogen was approximately 2 μg/L for levels encountered in this study. Discharge data was supplied from a USGS Gaging Station located approximately 100 m upstream of the study reach.

Results

The seasonal range in afternoon stream water temperature for all sampling dates was <7.0 °C (14.5–7.8 °C) August 1987–August 1988 along both transects (Table 1) and hyporheic water temperatures beneath the riparian zone were similar to stream water. The temperatures along the alder transect from the stream to the most inland well varied only by 2.5 °C in August, 1987, and by 2.6 °C in August, 1988. Temperature decreased toward the inland wells during summer–autumn. A temperature difference of 1.5 °C and 1.0 °C was observed between the channel and wells in January and March, 1988, respectively, increasing in the inland direction. Temperature variation along the alder transect at other times were <1.0 °C. The temperature pattern along the old-growth transect was nearly identical to the alder transect. Mean annual temperature was 11.1 °C for the stream and 10.7 °C for the most inland well of both transects.

Dissolved oxygen concentration in stream water ranged between 9.0–11.3 mg/L throughout the study (Table 1). Dissolved oxygen was always detectable in stream and hyporheic waters and a concentration <1.0 mg/L was detected only once. Spatial variation in dissolved oxygen concentration exceeded seasonal variation along both transects. Oxygen concentration in interstitial water dropped dramatically with increasing distance inland due to biotic activity within the hyporheic zone. In both transects mean annual oxygen concentration was lowest at the most inland well but still detectable. Thus both the stream and hyporheic zone were oxic during the entire study.

Total exchangeable ammonium on channel sediments showed temporal, spatial and land use patterns. The temporal pattern was related to mean discharge between samples (Fig 3a). During the experiment mean discharge between sample dates ranged from a low of 4.5 L/s, during October 4–28, to a high of 812 L/s, December 7–January 20. Sorbed ammonium increased on channel sediments from the time of incubation through October 28 (Fig

Table 1. Water temperature (°C) and dissolved oxygen concentration (mg/L) in channel and bankside interstitial waters at Little Lost Man Creek, August 4, 1987–August 3, 1988.

Site	WATER TEMPERATURE							
	1987				1988			
Date	8/4	9/24	10/28	12/7	1/21	3/8	5/26	8/3
Stream:	14.5	12.2	11.5	10.0	7.8	8.0	10.5	14.2
Well								
A1	14.2	12.5	11.9	10.0	8.0	8.0	11.0	14.2
A2	13.5	12.2	11.8	9.8	7.5	7.9	10.5	13.0
A3	12.9	12.0	11.7	10.2	9.0	8.9	10.1	12.1
A4	12.0	11.9	11.4	10.4	9.3	9.1	10.0	11.6
OG.1	14.7	12.8	—	9.5	7.2	7.2	11.0	12.0
OG.2	13.6	12.1	—	10.0	7.8	7.8	10.8	12.9
OG.3	—	—	—	10.2	8.9	9.0	10.0	11.4
OG.4	13.0	—	—	10.8	8.8	9.1	10.5	11.8
	DISSOLVED OXYGEN							
	1987				1988			
Date	8/4	9/24	10/28	12/7	1/21	3/8	5/26	8/3
Stream:	9.6	10.0	9.0	10.6	11.0	13.3	10.8	9.6
Well								
A1	8.2	8.4	8.2	10.6	9.6	11.1	10.7	9.8
A2	4.4	4.9	4.6	5.2	5.5	6.1	5.8	5.6
A3	4.0	3.6	3.8	6.9	7.3	5.6	5.2	4.6
A4	3.0	2.0	3.5	4.6	8.1	3.4	4.2	3.0
OG.1	9.1	8.7	—	10.5	10.4	11.3	10.8	10.7
OG.2	7.2	6.8	—	5.6	9.0	9.5	9.0	8.8
OG.3	—	—	—	5.5	5.8	3.1	0.8	2.2
OG.4	2.8	—	—	—	4.5	3.3	2.2	1.3

3b, c). Sorbed ammonium decreased with the first flush of high discharge in November, remained low throughout the winter and then increased through spring as discharge returned to base flow conditions.

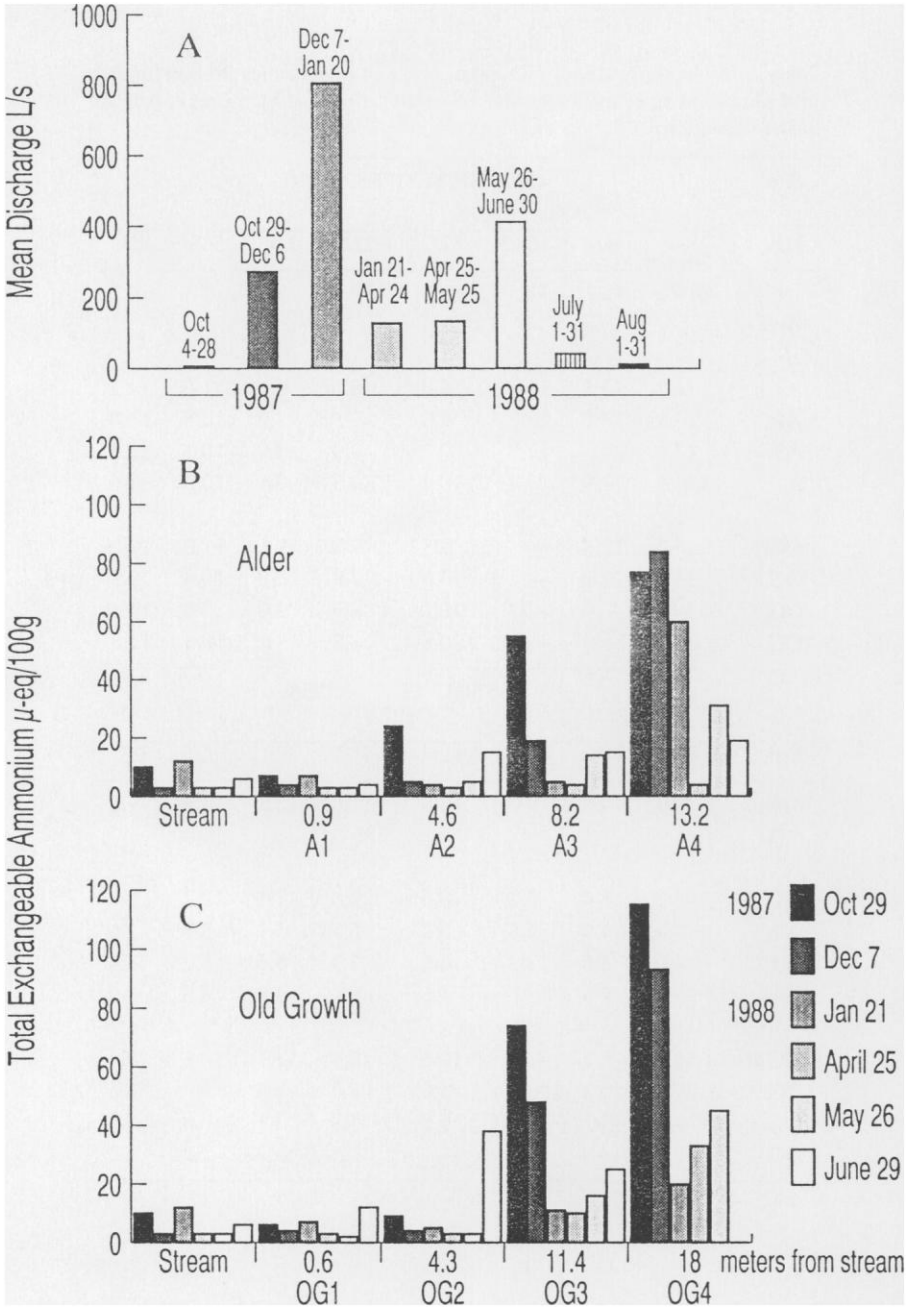

Fig. 3. Mean of daily discharge between sampling dates (A). Total exchangeable ammonium (μeq/100 g) on sediments (0.5–2.0 mm) incubated in nylon bags in the channel and well transects draining an alder-dominated (B); and old-growth hillslope (C) at Little Lost Man Creek.

Total exchangeable ammonium on sediments exposed to stream water were very low over the entire study with a range of 3–12 μeq/100 g. Total exchangeable ammonium in bankside sediments immediately adjacent to the channel (A1 and OG1) was nearly identical to the channel. Total exchangeable ammonium was highest in autumn, decreased in winter and rose again in spring. The temporal pattern at other inland wells was similar to the channel. However, the magnitude of ammonium sorption increased dramatically with distance inland. Total exchangeable ammonium at the most inland wells (A4 and OG4) was often an order of magnitude higher than equivalent channel sediments. The annual range for A4 sediment was 4–84 μeq/100 g and for OG4 sediment was 20–115 μeq/100 g. The lowest winter levels at OG4 exceeded the highest autumn concentration on channel sediments.

Dissolved ammonium concentration was always low in channel water, and with the exception of December 7, 1987, did not exceed 10 μg-N/L (Fig. 4). Ammonium concentration was also typically low in bankside wells <5 m from the channel. Thus at sites where exchangeable ammonium was low, ammonium concentration in interstitial water also was low. Interstitial ammonium concentration increased with distance inland, especially at A4 and OG4. At OG4 ammonium concentration during late autumn and late spring was more than an order of magnitude higher than channel concentrations. OG4 also had the same midwinter depletion in concentration that was observed in exchangeable ammonium. At the alder wells A3 and A4 ammonium was not flushed out in midwinter as at OG3 and OG4.

The ratio of extractable ammonium in sediment to that available in interstitial water (μg-N/g sediment: μg-N/g H_20) was >10:1 and usually >100:1 (Fig. 5). Depending on date and location, the ammonium pool on sediment was up to 2800 times that in interstitial water. On each date the exchangeable ammonium pool was higher in well sediments >5 m from the bank compared with channel sediment or hyporheic sediment <5 m from the bank. With the exception of the October 1987 sample, the ratio of sorbed to dissolved ammonium was higher along the old-growth transect.

Nitrate concentration in stream water ranged between 16–153 μg-N/L over the period of the study (Fig. 6). Nitrate nitrogen was highest December-January (>100 μg/L) after the onset of autumn rains, and lowest in October (16 μg/L) during the period of lowest discharge. Bankside wells within 1 m of the channel were slightly higher in nitrate concentration than stream water. Wells further inland were always higher in nitrate. Nitrate concentration rose dramatically with the onset of autumn rains, especially along the alder transect. By December 7, 1987, nitrate concentration rose from <100 μgN/L to 2000–3000 μg-N/L in wells A2-A4. Nitrate concentration decreased slowly from late autumn for the duration of the study. By August 1988, nitrate

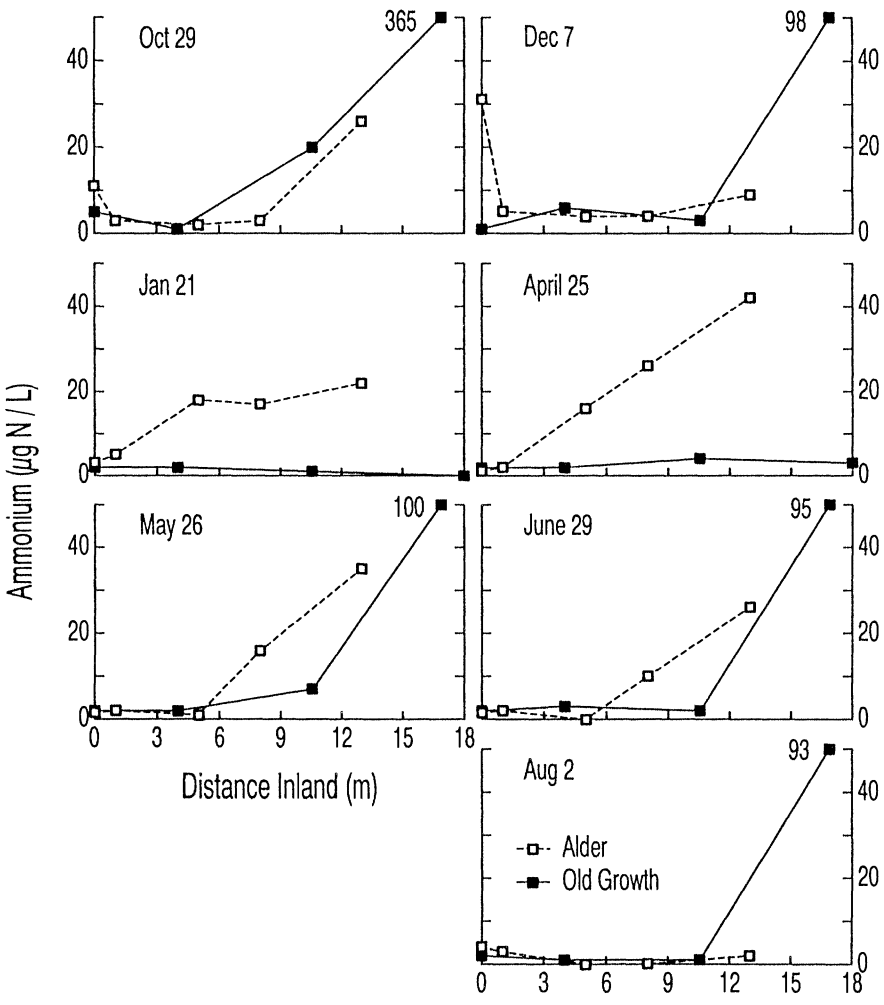

Fig. 4. Seasonal variation in ammonium nitrogen concentration (μg-N/L) in the channel (0) and in interstitial well waters 1-18 m perpendicular to the channel. Off-scale sample points are indicated by the actual concentration.

concentration in bankside wells was <200 μg-N/L. Along the old-growth transect, nitrate concentration was usually higher than in stream water but low compared to equivalent sites on the alder transect. The highest nitrate concentration observed along the old-growth transect was at OG4 where it exceeded 300 μg-N/L from May–August.

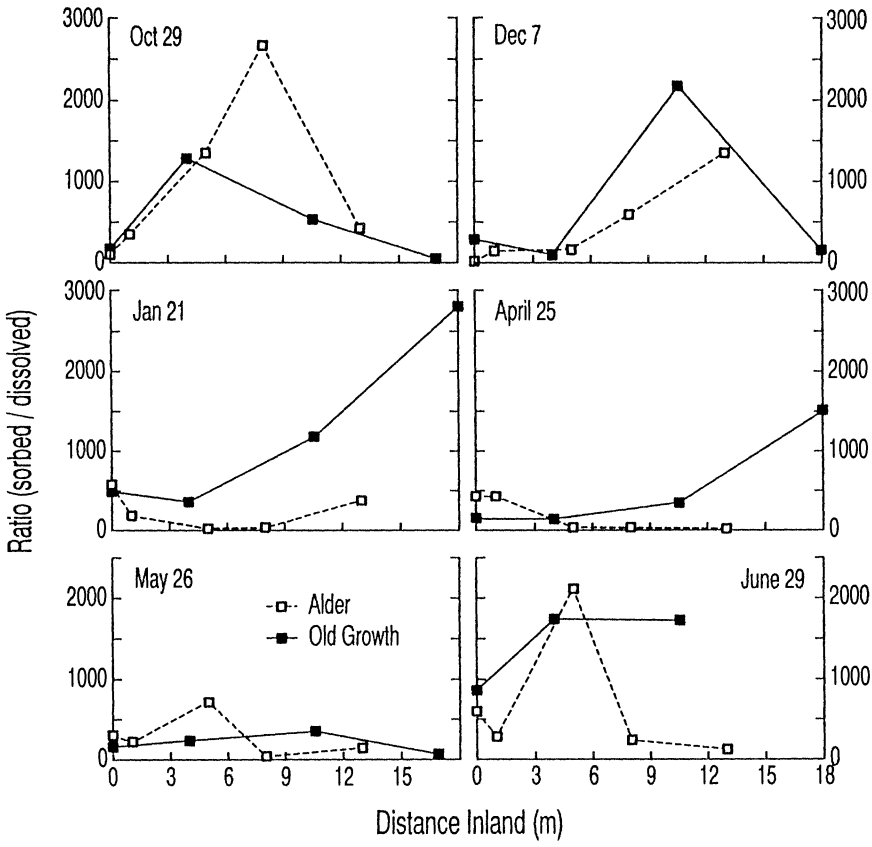

Fig. 5. Ratio of total exchangeable ammonia to that available in interstitial water (μg N/g sediment: μg N/g H_20) from the channel and wells up to 18 m perpendicular to the channel.

Discussion

Hyporheic sediments at Little Lost Man Creek constitute a large and temporally-variable pool for sorbed ammonium. The inherent capacity to provide this transient function is controlled by sediment lithology. Jackman & Ng (1986) reported that channel sediments from Little Lost Man Creek (size classes 0.5–2.0 mm) consisted of approximately 49% quartz, 27% plagioclase, 8% chlorite/smectite and 19% illite/mica. While the dominant minerals quartz and plagioclase would not be significantly involved in the ammonium retention that we observed, the latter minerals are clays having a significant capacity for sorption. Drever (1982) reports the cation exchange capacity (CEC) in meq/100 g of sediment is <10 for chlorite, 80–150 for smectite and 10–40 for illite. CEC for Little Lost Man Creek sediments is approximately

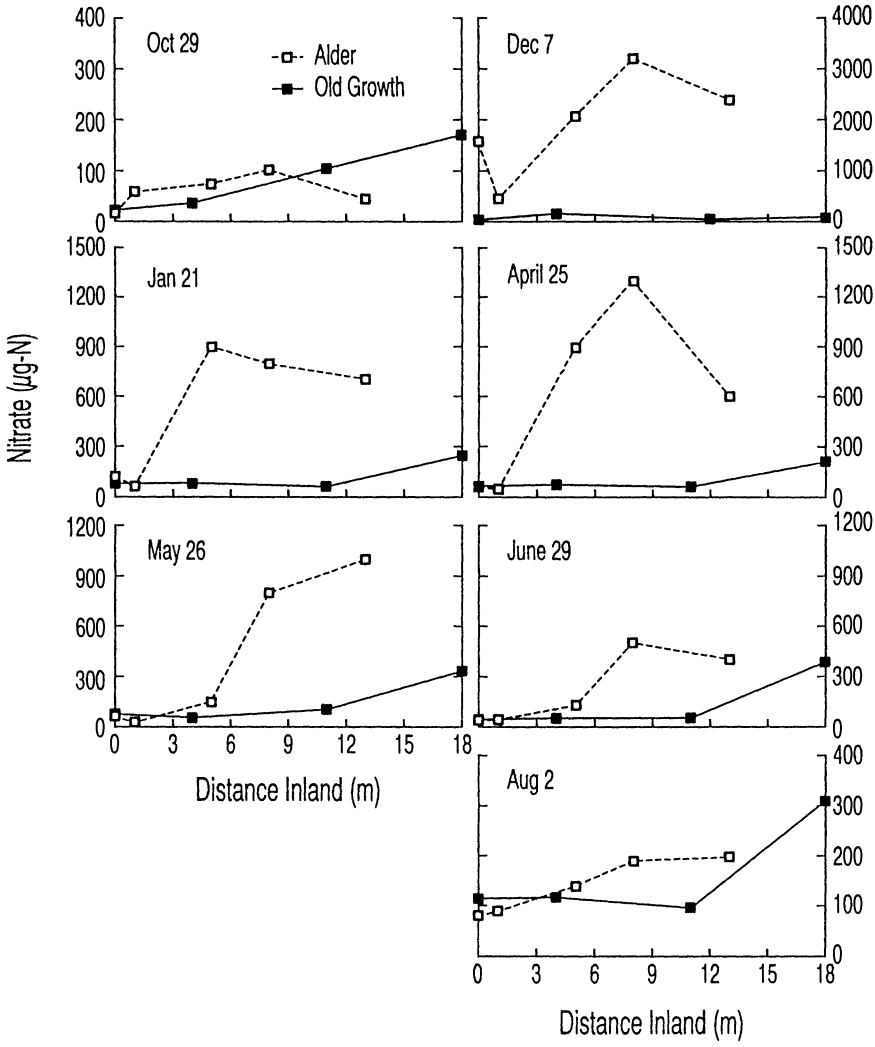

Fig. 6. Nitrate concentration (μg-N/L) in channel water (0) and in interstitial well waters up to 18 m perpendicular to the channel. Note scale changes between dates.

10.25 meq/100 g sediment for the size classes used in our study (Jackman & Ng 1986). This is a reasonable estimate considering that: (a) clay minerals constitute less than 20% of total sediment; (b) CEC is highly dependent on amorphous oxihydroxides and organic surface coatings; and (3) CEC is strongly dependent on pH.

Total exchangeable ammonium constituted a miniscule component of the sediment's total CEC relative to the estimates of Jackman & Ng (1986).

Most exchange sites are probably occupied by the divalent cations calcium and magnesium and the monovalent cation sodium, since they are present at base flow in mg/L concentrations versus μg/L concentrations for ammonium (Zellweger et al. 1986). Extractable ammonium in our study ranged between 2–115 μeq/100 g sediment. This range constitutes from <0.1% to approximately 1.0% of available sites.

Richey et al. (1985) reported that exchangeable ammonium on Bear Brook sediment varied between 1–9 μg NH4-N/g sediment. This compares with 0.4–1.7 μg NH4-N/g sediment for channel sediments of Little Lost Man Creek. The highest amount of exchangeable ammonium recovered during the Bear Brook study was 16.1 μg-N/g sediment. Higher recoveries at Bear Brook may be related to the amount and lithology of fine sediments in their samples. At both sites significant ammonium was readily extracted from the sediments indicating an availability for subsequent biotic transformation.

Although the amount of ammonium sorbed/unit sediment is small, the volume of sediment in direct contact with interstitial water is large at Little Lost Man Creek. Numerous earlier studies at the same site, using chloride as a tracer, have indicated extensive interflow up to 18 m from the channel (Triska et al. 1990). Bencala et al. (1984) fitted chemical parameters to a one-dimensional transport model and estimated that the subsurface cross-sectional area was equivalent to channel cross-sectional area at many sites during summer base flow. Zellweger et al.(1989) compared dye and tracer dilution techniques to mechanical estimates of surface discharge, and estimated that the hyporheic component of discharge was approximately 4 L/s. At this level hyporheic flows constituted approximately 10% of mean discharge during May–June, 1987, and the hyporheic component would exceed 35% of surface water discharge during lowest summer flows (July–October, 1987, and July, 1988). The highest accumulation of extractable ammonium on incubated sediments occurred during late summer and early autumn when base flow was lowest.

High permeability of sediments even with low CEC can enhance retention of ions in groundwater discharge. For example, Drever (1982) states that an aquifer with an exchange capacity of 5 meq/100 g sediment and a porosity of 20% has an exchange capacity equivalent to 500 meq/L of groundwater. Since ammonium concentration is very low in interstitial waters of Little Lost Man Creek, ion exchange with hyporheic sediments could exert strong control on ammonium concentration in both interstitial and channel water.

When exchangeable ions such as ammonium are present at very low levels, sorption is directly related to concentration, and sediment can effectively buffer the impact of pulsed inputs. This was previously demonstrated at Little Lost Man Creek using tracer-ammonium injection studies. Triska et al.

(1990) injected sulfate as a tracer with ammonium into an aerobic subsurface flow path parallel to the channel. Subsurface water sampled approximately 3 m downflow indicated a tracer travel time of less than 3 hours. Coinjected ammonium however was retarded for nearly 3 days before reaching a plateau concentration of approximately 900 μg-N/L. At cutoff, the decline in ammonium concentration lagged sulfate for nearly 12 hours as desorption occurred, and remained above background concentration for several days. Nitrate concentration increased within hours of ammonium injection and remained elevated above background several days following cutoff, probably from nitrification of some of the added ammonium. In this field experiment, the ammonium concentration pulse was effectively buffered, increasing biotic transformation via nitrification and altering the timing of DIN transport.

We do not know to what extent ammonium transport in runoff is similarly pulsed under natural conditions. We do know that nitrate pulses are correlated with seasonal increase in discharge, with a lag of several weeks. It is possible that ammonium pulses also occur but are buffered by hyporheic sediments as in the experimental manipulation described above. We also cannot speculate to what extent the nitrate gain in interstitial water during autumn represents a loss of exchangeable ammonium from hyporheic sediments as in Fig 1. The temporal pattern of nitrate concentration may also represent variation in the infiltration rate of autumnal rains into hillslope soils, causing temporal alteration of the source and chemical composition of runoff. A combination of both mechanisms also would explain the observed temporal patterns of exchangeable ammonium and nitrate.

The ratio of sorbed ammonium concentration (μg-N/kg sediment) to interstitial water concentration (μg-N/L) had a range of 10–2800 but was typically greater than 100 (Fig. 2). Bencala (1984) concluded that the volume of interstitial water which regularly exchanged with the stream was greater than the volume of stream water. If the interstitial void volume in the sediments per meter of stream length is at least as great as the volume of water in the channel per meter of stream length, and if the void fraction in the sediments is about 0.3 of the total sediment volume, then there will be about 3.3 m^3 of total sediment volume and about 2.3 m^3 of solid sediment volume per m^3 of water in the channel. Assuming a specific gravity 2.5 for the solid sediment, there will be about 6 kg of sediments per kg (or liter) of water in the channel. If 300 times as much ammonium is adsorbed to a kg of sediment as is present in a liter of streamwater, then there will be at least 600 times as much ammonium adsorbed to the sediments as is present in the stream water. Therefore, even sediments in direct contact with the channel constitute a large pool for ammonium relative to adjacent interstitial water. Because the ratio increases to above 100 in inland wells the fraction of available ammonium adsorbed

to sediment is actually higher than 600. Richey et al. (1985) estimated that ammonium sorbed to channel sediment at Bear Brook, N.H. was 100 to 1000 times greater than mean values in the water column which is within the range we observed in this study.

Previous studies at Little Lost Man Creek have indicated potential for both nitrification (Triska et al. 1990) and denitrification (Duff & Triska 1990) in the hyporheic zone during summer base flow. Rates of biological DIN transformation are dependent on both concentration and temperature. This study indicates continuous presence of a temporally varying ammonium pool sorbed to sediment available for nitrification. The data also indicate the absence of large annual temperature fluctuations. Although the data are scant, summer temperatures up to 20 °C have been observed (Triska et al. 1989). Northern California has both cooler and wetter winters than either the central or southern coast which would moderate temperature of channel and hyporheic waters. Dense canopy development during April–November has a similar moderating impact on water temperature. Although more intensive characterization of seasonality in temperature and microbial process will be required to verify the rate of biotic uptake and transformation at seasons other than summer, the rates of DIN transformation may be high at all times.

Sorption of ammonium on sediment can be important for mass balance and transport studies of dissolved nitrogen in streams. Budget calculations by Richey et al. (1985) indicated that retention of dissolved nitrogen during warmer summer months by processes including sorption could account for 12–25% of nitrate export during the winter months. Thus sorption of ammonium to hyporheic sediments increases the long-term availability of ammonium for in-channel transformations, and regulates the timing of DIN export from a reach.

High nitrate levels along the alder transect indicate a land management impact on groundwater nutrient chemistry almost 25 years after clear-cutting, presumably due to regeneration by N-fixing alder. These results are comparable to observations of Goldman (1961), who reported an order of magnitude difference in nitrate concentration in springs draining alder stands along the east shore of Castle Lake, CA, compared to west-shore springs which lacked alder. The ability of red alder to contribute to forest soil fertility is well known (e.g. Cole et al. 1978, Atkinson & Hamilton 1978), particularly in the first 10–15 years of stand age.

To conclude, sorption of ammonium to hyporheic sediments varied temporally, spatially and in response to past land use management and may have an impact on the timing and cycling of DIN transported from Little Lost Man Creek. This buffering effect on transport will vary at other catchments depending on parent lithology, grain size and porosity of hyporheic sediments.

Sorption will be most significant in pristine catchments that have low ammonium levels, that drain sediments with high CEC and that have a high porosity. Under these conditions ammonium sorption should be examined as a critical component of nitrogen cycling within the catchment. It is the interaction of geochemical processes such as sorption, in concert with hydrologic transport and biotic assimilation and transformation, that regulates the concentration and composition of dissolved nitrogen in surface waters.

Acknowledgements

The authors would like to recognize the assistance of students Yeung Je Kim, Letita Pan, Claire Tanglao, and Eve Tracey, University of California, Davis, CA. Research funds were provided by the National Research Program, Water Resources Division, US Geological Survey. Use of product names is for identification only, and does not constitute endorsement by the US Geological Survey.

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