

Denitrification as a component of the nitrogen budget for a large plains river

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Abstract. Nitrogen dynamics of a plains reach of the South Platte River were studied over a 12-month cycle for the purpose of quantifying denitrification rates. The working hypothesis of the study was that denitrification would be of extraordinary importance in the system because of large amounts of water exchange between the channel and an extensive subsurface alluvium consisting of gravel. Denitrification losses of nitrate were quantified through the use of a mass-balance model based on detailed hydrologic information and field quantification of the rates of nitrate accrual through surface and subsurface input of water as well as nitrification. Denitrification rates ranged between 2 and 100 mg N/m²/hr. Distance required to achieve 90% reduction of nitrate was as short as 6 km during mid-summer and as long as 300 km during mid-winter. On an annual basis, close to half of nitrate input to a 100-km reach was removed by denitrification (3.6×10^6 kg/yr). Rates of nitrate loss to denitrification (annual mean, 28 mg N/m²/h) and overall percent removal of nitrate by denitrification were approximately 10 times as high as rates documented for rivers in the eastern U.S. The study shows that high rates of hyporheic exchange can support extraordinary rates of denitrification.

Introduction

Denitrification is potentially an important component of the nitrogen budget in aquatic ecosystems (Brezonik 1977, Seitzinger 1988), but its measurement presents numerous technical difficulties. The acetylene block method is sensitive to relatively low rates of denitrification, and is the source of most existing information on denitrification rates (Seitzinger 1993). Direct measurement of N₂ evolution from nitrate is possible, but has been used less frequently because analysis of N₂ accumulation in an N₂-rich medium is difficult (Seitzinger 1990). Nitrate disappearance over cores or tracer methods involving ¹⁵N also can be used, but present various interpretational difficulties (Seitzinger 1988).

The acetylene block, incubations for measurement of N₂ release or NO₃⁻ disappearance, and stable isotope methods require the use of enclosures (chambers or incubated samples). The interpretation of data from enclosures is most feasible where the distribution of redox conditions has a high degree

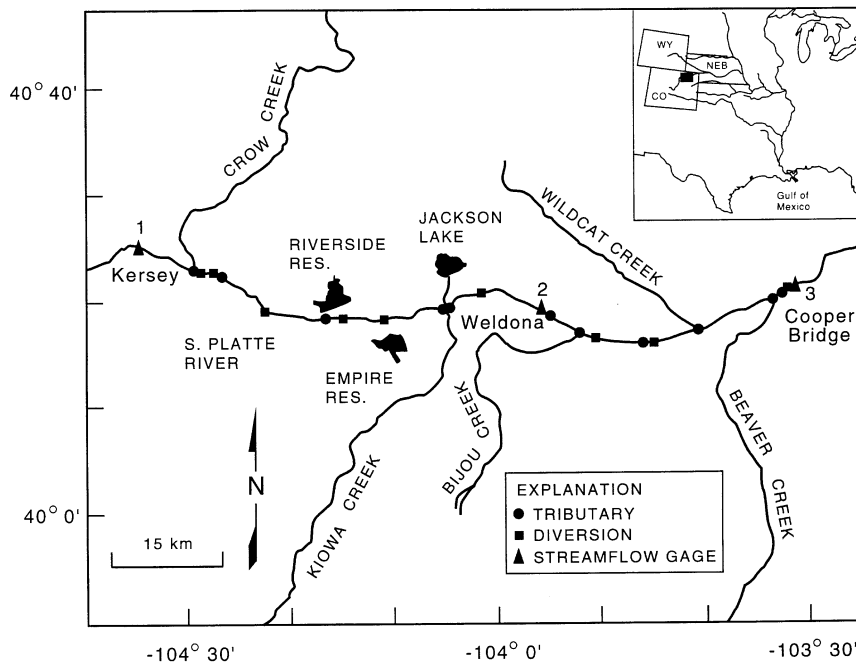


Figure 1. Location of the study segment showing river gages and sampling sites for synoptic field studies.

of spatial organization. Under these circumstances, as one might find in some lakes and estuaries, the extrapolation of results from small enclosures to much larger areas of sediment or water may be feasible. In running waters, incubation methods are more difficult to apply because of the great heterogeneity of the substrate and the possibility that denitrification may occur well below the sediment-water interface, where metabolic processes cannot easily be mapped (Jones & Holmes 1996). Thus a system-level quantification of denitrification in running waters is seldom accomplished by use of enclosures.

A mass-balance approach to the analysis of denitrification often is practical for stratified lakes (e.g., Likens & Loucks 1978). A similar approach is also possible for streams or rivers where the fluxes of water and nitrogen can be measured, and may be the only means of quantifying whole-system denitrification in large rivers. Even so, only a few mass-balance estimates of denitrification are available for running waters (e.g. Hill 1979, 1983). This paper reports the results of a mass-balance study in which denitrification rates are estimated for two reaches of the South Platte River in the plains region below Denver.

Study site

The South Platte River drains an area of 69,400 km², most of which lies in northeastern Colorado (Figure 1). The headwaters of the South Platte are fed by snowmelt, and natural flow is augmented by transmountain diversions from the western slope of the central Rockies. Water use occurs primarily in urban areas of the foothills and plains and in the semiarid irrigated agricultural zone located downstream of Denver (mean annual precipitation, 38 cm: Dennehy et al. 1995). The South Platte River below Denver has an extensive porous alluvium. The alluvium is 3.2–12.9 km wide and 6.1–36.6 m deep; its hydraulic transmissivity ranges from 58 to 462 m³/day/m (Hurr et al. 1972a, b, c).

The waters of the South Platte are subject to numerous human influences. In a year of median flow, virtually the entire discharge of the South Platte is withdrawn for municipal and agricultural use within 200 km of Denver. The efficiency of water use is augmented by storage of water in reservoirs, which occurs primarily during the nonirrigation season and is followed by release of water for irrigation or municipal use in other months. Water returns to the South Platte primarily through wastewater discharges, which account for approximately 50% of the flow in the 50 km below Denver, and alluvial seepage maintained by agricultural water use, which is an increasingly important element of the water budget below Denver (Sjodin et al. 1997).

Along its entire course beyond the foothills, the South Platte's transport of fixed nitrogen is augmented by municipal discharges and agricultural fertilizers. Point-source discharges release concentrations of nitrate that may exceed 10 mg/ℓ NO₃⁻-N. They also release ammonia (often at concentrations above 10 mg/ℓ NH₄⁺-N), which is converted to nitrate by nitrification in the oxygenated surface waters of the South Platte channel (Dennehy et al. 1995). Agriculture also augments nitrogen concentrations. Weld and Morgan counties, which make up most of the watershed for the study segment, rank first and third in agricultural production for Colorado (ERS 1995). Much plains cropland is subject to heavy fertilization; the percentage of wheat cropland in Colorado that is fertilized with nitrogen has increased sixfold since 1964 (ERS 1995). Under both municipal and agricultural influences, concentrations of nitrate in the South Platte River have risen steadily over the last 25 years (about 50 μg/ℓ/yr: Figure 2).

The present study of nitrogen mass balance was conducted over a 105-km segment of the South Platte River extending from Kersey to Cooper Bridge (Figure 1). This segment is located approximately 50 km below Denver in a region where the South Platte has completed its transition from foothills to plains and has taken on a characteristic braided channel morphology. The median width of the channel along the study reach is close to 70 m, and the

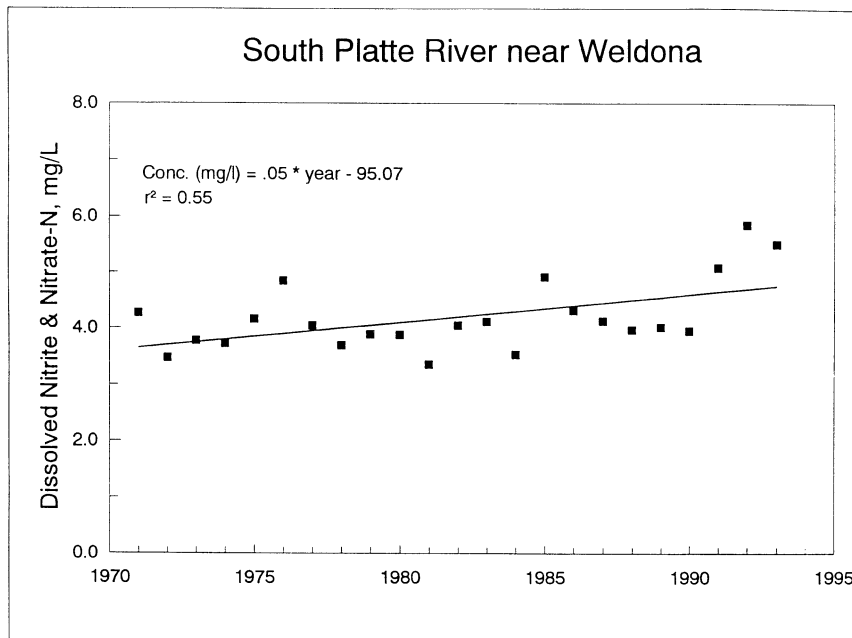


Figure 2. Long-term trend in nitrate concentrations of the South Platte River near Weldona (USGS monitoring data station 06758500). Each data point is an average yearly value.

median water depth along the thalweg ranges between approximately 30 cm at low discharge and 150 cm at high discharge. For purposes of the mass-balance study, the study segment was divided into two reaches: Kersey to Weldona (67 km), and Weldona to Cooper Bridge (38 km).

The hydrology of the study segment has been thoroughly documented (Sjodin et al. 1997). The hydrograph of the river along this segment reflects seasonal increases in flow caused by snowmelt. Superimposed on the seasonal pattern are spikes associated with individual storms of short duration. During all seasons, substantial amounts of water are removed upstream and within the study segment for municipal and agricultural purposes. Thus ditch diversions play a major role in the water budget.

Components of the water budget are as summarized in Table 1. As shown by the table, tributaries contribute only minor amounts to the two study reaches. Reservoir releases do not occur in the lower reach, and are of only minor significance to the overall budget in the upper reach. Seepage is a major contributor of flow, especially during July, August, and September; on an annual basis, flow to each segment is augmented 15 to 17% by seepage. Losses are also shown in Table 1. Irrigation withdrawals figure importantly in the budget, except during the winter months when reservoir storage becomes

Table 1. Water budgets of the upper reach (Kersey to Weldona) and lower reach (Weldona to Cooper Bridge) as monthly and annual daily means across a 10-year interval (1983–93)

Month	Mean Daily Flow, $\text{m}^3 \times 10^3$	Sources, Percent			Losses, Percent		
		Platte Input	Tributaries, Releases	Seepage	Platte Output	Irrigation Storage	Recharge
Upper Reach							
Jan	2778	83.6	0.4	5.9	76.0	23.7	0.4
Feb	2987	81.8	0.4	17.7	69.4	29.8	0.8
Mar	3175	85.1	0.5	14.4	48.3	50.3	1.4
Apr	3698	82.1	2.2	15.7	60.1	35.1	4.8
May	5190	87.4	2.0	10.7	67.1	24.4	8.5
Jun	5732	87.0	2.0	11.0	55.0	33.3	11.7
Jul	2822	61.3	8.5	30.1	40.7	56.0	3.3
Aug	3138	64.7	10.4	24.9	48.8	46.1	5.1
Sep	3152	67.1	7.3	25.6	57.0	42.2	0.8
Oct	3110	79.8	0.9	19.3	57.0	41.5	1.5
Nov	3170	84.6	0.5	14.9	50.6	49.1	0.3
Dec	2785	82.4	0.4	17.2	64.8	35.0	0.2
Annual	3477	79.9	2.9	17.2	58.0	37.9	4.1
Lower Reach							
Jan	2608	80.9	1.7	17.4	83.9	15.9	0.2
Feb	2503	82.8	1.9	15.3	83.8	11.8	4.4
Mar	1882	81.4	2.9	15.6	83.3	12.5	4.2
Apr	2587	85.9	5.4	8.7	72.7	23.5	3.9
May	4040	86.2	3.9	9.8	78.8	17.7	3.5
Jun	4072	77.4	4.0	18.6	77.6	20.6	1.8
Jul	1543	74.4	8.4	17.2	56.5	39.1	4.4
Aug	1947	78.6	7.7	13.7	65.8	30.4	3.7
Sep	2316	77.5	8.0	14.5	71.7	27.1	1.2
Oct	2379	74.5	5.6	19.9	49.6	49.8	0.6
Nov	2070	77.4	3.3	19.3	48.9	49.6	1.5
Dec	2190	82.4	2.0	15.6	70.7	27.6	1.7
Annual	2509	80.4	4.4	15.2	71.7	25.8	2.5

predominant over irrigation. Recharge of the alluvial zone, which only occurs at very high discharge, plays a minor role on an annual basis.

At river discharges below $41 \text{ m}^3/\text{s}$, there is a net flux of water from the alluvial zone into the river (seepage). The rate is quantitatively significant ($0.10 \text{ m}^3/\text{km/s}$) and shows a seasonal pattern that reflects the use of irrigation

water. When river discharge exceeds $41 \text{ m}^3/\text{s}$, seepage is suppressed progressively and becomes nil at about $58 \text{ m}^3/\text{s}$. As discharge increases above $58 \text{ m}^3/\text{s}$, net flux of water is from the channel into the alluvium (recharge). The relationship of river discharge to net alluvial flux is highly predictable and is very similar for the two reaches in the study segment.

In addition to net exchange of water between the channel and the alluvium, there is also constant alluvial exchange involving the passage of water into the hyporheic zone and then back into the channel. Hydrologic studies on nearby river reaches indicate that the water in the channel at low to moderate discharges passes through the alluvium multiple times over a reach of river as long as the study segment (McMahon et al. 1995).

Alluvial exchange is important to denitrification because it is the only means by which water can be exposed to low redox potential. Water in the channel of the South Platte River is constantly oxygenated at $3 \text{ mg}/\ell$ or more (typically above $5 \text{ mg}/\ell$), and thus will not support denitrification. The sediments are anoxic, however, and waters passing into the hyporheic zone quickly lose their oxygen content because the water contains large amounts of labile organic matter from municipal and agricultural sources and, in the absence of reaeration, is depleted of oxygen by microbial respiration (McMahon et al. 1995). Thus alluvial exchange is critical to the occurrence of denitrification in the South Platte.

Methods

The denitrification analysis is based on seven synoptic studies extending over a broad range of hydrologic and seasonal conditions between January 1994 and November 1995. For each synoptic study, a complete water budget was constructed for each of the two reaches in the study segment. The basis for the water budget was as follows: (1) daily records for the three USGS gages in the study segment, (2) daily ditch diversion and reservoir outflow data from the Colorado State Engineer's office, (3) tributary flows from the Colorado State Engineer's office, (4) estimates of net alluvial exchange based on previous detailed hydrologic studies of alluvial exchange in this segment (Sjodin et al. 1997).

Each synoptic study included water samples at 9–16 locations along the South Platte main stem and at tributary mouths. The samples were taken at mid-channel; sampling sites were located sufficiently far downstream of any tributary sources or other point sources that the water column was fully mixed horizontally (as shown by conductance). Samples were filtered within 12 hours of collection through glass-fiber filters (Whatman GF/C; nominal pore size $1.2 \mu\text{m}$), and were analyzed within 36 hours.

Concentrations of ammonia in the water were determined colorimetrically by modified Solorzano method involving the production of indophenol blue (Grashoff 1976). Concentrations of nitrate were measured with an ion chromatograph. A minimum of 10% of the field samples were replicated, and the replicate samples were carried through the entire filtration and analytical procedures in order to provide an estimate of error variance (mean deviation of duplicates, 1.0%). In addition, some laboratory analyses were performed in duplicate (mean deviation of duplicates, 3.8%).

Each of the synoptic studies involved measurements of water temperature at each of the sampling stations. Temperature is important for the estimation of temperature-dependent conversion rates for nitrogen species.

The concentrations of nitrate and ammonium in groundwater were estimated from previous studies of the South Platte River alluvium, as reported in the results section.

Denitrification was estimated by means of a mass-balance model that divides the study segment into 93 sections. The length of individual sections was determined according to the distribution of major water sources (tributaries or reservoir return flows) or major water losses (ditch diversions) along the river. Major influences on discharge (additions, withdrawals) were used as boundaries for sections in the model. Where no such influences were present, sections were assigned a length of 3.2 km. Division of the study segment into small sections acknowledges that rates of biological processes (nitrification, denitrification) are likely to change along the river, and allows calibration of these changes by use of the multistation synoptic data.

Processes affecting nitrate transport were analyzed for each compartment according to the following equation:

$$O_i = I_i + S_i - R_i + N_i - D_i$$

where the terms of the equation represent flux of nitrate (mass/time) accountable to surface outflow from the segment (O_i), surface input to the segment (I_i), seepage (S_i), recharge (R_i), nitrification (conversion of ammonium to nitrate, N_i), and denitrification (conversion of nitrate to $N_2 + N_2O$, D_i). In principle, this equation could also contain a term for autotrophic uptake of nitrate. In this instance, however, the abundance of autotrophs is very small (less than 5% areal coverage for periphytic algae) because of the shifting nature of the substrate, and could not have any significant effect on the very high mass flux of inorganic nitrogen (ca. 50 kg of inorganic N per day flowing over 1 m² of substrate). Thus autotrophic uptake is not included in the equation.

Release of ammonia through decomposition of organic matter (ammonification) adds some ammonia constantly to the stream. To the extent that

ammonification is ignored, nitrification rates may be underestimated, which in turn might produce an underestimate of denitrification rate. Previous studies of river metabolism just upstream of the study reach, however, have shown that the ammonification rate for the South Platte consistently falls below 10% of the nitrification rates (unpublished data). Thus while ammonification must occur in the South Platte, it need not be taken into account in the mass balance analysis because its rate is low relative to the rate of nitrification.

Of the parameters in the equation, only denitrification (D_i) is not estimated from field data. Thus the equation provides a basis for estimating D_i as a residual.

Results

Exchanges between the channel and the alluvium

The mass balance model requires information on the amount and inorganic nitrogen content of alluvial exchange. The mass flux of water between the alluvium and the main channel is based on equations developed by Sjodin et al. (1997) for the study segment.

Gaggiani (1984) studied the concentrations of nitrate in the South Platte alluvium during 1980 on the basis of samples from 55 wells. A few of the wells showed very high concentrations that probably reflect local influences. For this reason, we use the median concentration from Gaggiani's studies ($8.8 \text{ mg/l NO}_3^- \text{-N}$). Even though a few wells showed very high concentrations, the standard error is relatively low (0.9 mg/l), suggesting that 8.8 mg/l is a reasonable approximation of characteristic nitrate concentrations for shallow groundwater. Given that fertilizer use has been increasing, some change in nitrate concentrations might have occurred between 1980 and the time of the study. The relationship shown in Figure 2 serves as a guide to the probable increases ($50 \text{ } \mu\text{g/l/yr}$). Over the 15-year interval, the anticipated increase would be $750 \text{ } \mu\text{g/l}$. Because this amount falls within the standard error of the estimate, no correction is warranted, nor would a correction of this size substantially alter the results of the modeling.

The concentration of ammonium in groundwater was estimated separately on the basis of data compiled by Dennehy et al. (1995). From 113 samples collected between 1980 and 1992, Dennehy et al. estimated that the median ammonium content of groundwater in the shallow alluvium is approximately 0.03 mg/l . This concentration is insignificant to the mass-balance calculations, i.e., for practical purposes the ammonium content of the alluvial water is nil.

Estimation of nitrification rates

Nitrification was estimated from decline in ammonia concentrations not accounted for by physical exchanges (seepage, alluvial recharge, tributaries, diversions). After allowance was made for physical exchanges affecting ammonia, nitrification rates were determined by iteration so that the squared deviation between observed and predicted ammonia concentrations was minimized.

Estimates of nitrification rate constants were made for the upper reach only (Kersey to Weldon) because the amount of ammonia below Weldon was usually too small to support estimates for the lower reach. Rates for the upper reach are used in modeling for the lower reach. Any error in the assumption that rates are the same in the two reaches will be unimportant to final results because of the small amount of ammonia in the lower reach (Table 2). For reasons mentioned in the methods section (low standing stock of autotrophs), autotrophic uptake of ammonia and ammonification are treated as nil.

The nitrification rates obtained by empirical fit to the observed ammonia concentrations were converted by the Arrhenius convention (Jørgensen 1983; $Q_{10} = 2.0$) to a common base temperature of 20 °C so that they can be compared across the two reaches and across months. The results are given in Table 2. The temperature-adjusted nitrification rates fall within a fairly narrow range (3–5 d⁻¹ at 20 °C) except in February (2 d⁻¹), when populations may be numerically suppressed by prolonged cold weather.

Nitrification is a source of nitrate. Therefore, the nitrification rates shown in Table 2 can be used to estimate the nitrate derived from nitrification in any of the spatial compartments of the mass balance model for specific time of year and location. Figure 3 shows a characteristic plot of the observed and expected changes in ammonia concentration caused by nitrification.

Estimates of denitrification

The mass-balance model was used to predict the expected concentrations of nitrate in the river in the absence of any internal nitrate sink (denitrification). The observed concentrations of nitrate were then plotted on the same axes. The deviation between the observed nitrate concentrations and the concentrations of nitrate expected in the absence of denitrification was the basis for estimating the denitrification rates. As shown by the example in Figure 4, the effect of denitrification is very large.

Estimates of denitrification rates were made separately on each date and for each of the two reaches. No rates are available in the downstream section for November because of sampling problems. The method of estimation was the same as for the nitrification rates, i.e., it involved a least-squares fit between

Table 2. Summary of rates and concentrations

	Jan	Feb	Jun (early)	Jun (late)	Jul	Aug	Nov
<i>Upper Reach</i>							
Ammonia concentration, top of reach (mg/ℓ)	0.79	1.26	0.12	0.43	0.03	0.16	0.55
Ammonia: observed vs. predicted (mg/ℓ)*	0.04	0.03	0.02	0.07	0.01	0.03	0.04
Nitrification rate constant (d ⁻¹)	1.00	0.66	5.20	3.04	3.22	4.18	1.56
Nitrification rate, constant (d ⁻¹), at 20 °C	3.17	1.90	4.20	2.90	3.02	4.04	5.00
Nitrification rate, volume (mg N/ℓ/d)	0.39	0.56	0.07	0.13	0.01	0.08	0.29
Nitrification rate, area (mg N/m ² /h)	12.0	17.6	2.2	2.2	0.2	1.9	8.7
Nitrate: Concentration (mg/ℓ)	6.57	5.94	4.00	2.63	6.45	5.29	9.45
Nitrate: Observed vs. predicted*	0.29	0.12	0.22	0.67	0.87	0.42	0.68
Denitrification rate (d ⁻¹)	0.30	0.40	1.06	5.15	1.36	1.12	0.82
Denitrification rate constant (d ⁻¹) at 20 °C	0.57	0.74	0.94	5.28	1.31	1.10	1.59
Denitrification rate (mg/ℓ/d)	0.89	0.95	1.02	0.13	2.03	0.97	3.38
Denitrification rate (mg N/m ² /h)	25.5	27.6	30.0	1.83	37.3	22.2	102.1
Distance to 90% reduction (km)	292	221	84	10.5	52	71	102
Time to 90% reduction (hr)	184	138	52	12	41	49	67

Table 2. Continued

	Jan	Feb	Jun (early)	Jun (late)	Jul	Aug	Nov
<i>Lower Reach</i>							
Ammonium concentration, top of reach (mg/l)	0.11	0.30	0.00	0.09	0.01	0.01	0.02
Nitrification rate, volume (mg N/l/d)	0.09	0.22	0.00	0.04	0.00	0.00	0.01
Nitrification rate, area (mg N/m ² /h)	2.2	5.4	0.02	0.54	0.08	0.04	0.22
Nitrate: Concentration (mg/l)	5.01	4.30	2.24	2.91	2.07	3.42	3.23
Nitrate: Observed vs. predicted*	0.29	0.75	0.16	0.45	0.35	0.35	—
Denitrification rate constant (d ⁻¹)	0.26	0.27	0.86	5.42	2.10	1.05	—
Denitrification rate constant (d ⁻¹) at 20 °C	0.57	0.74	0.62	4.12	1.61	0.89	—
Denitrification rate (mg/l/d)	0.99	1.14	0.28	0.53	0.52	0.72	—
Denitrification rate (mg N/m ² /h)	30.0	35.8	7.1	7.7	11.1	14.7	—
Distance to 90% reduction (km)	223	137	84	6	30	60	—
Time to 90% reduction (hr)	147	85	64	10	26	52	—

* Square root of mean squared deviation.

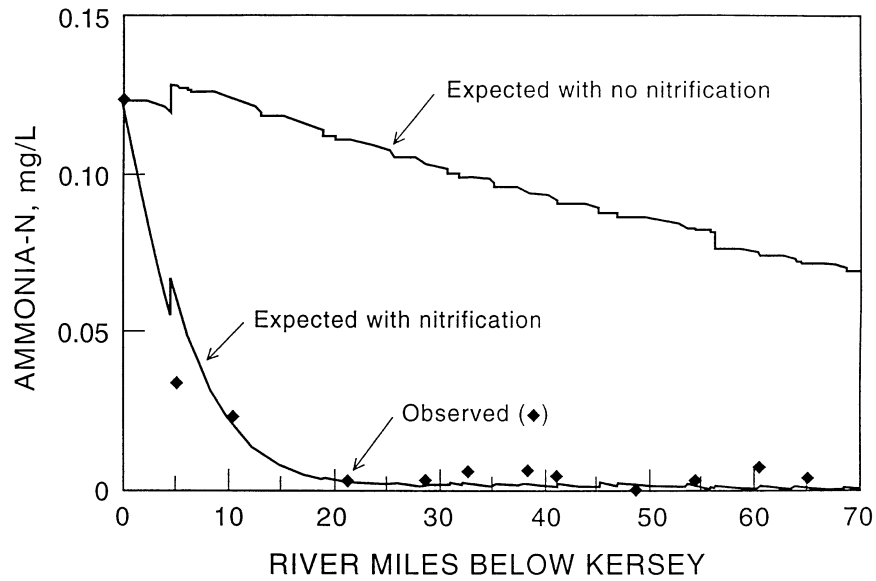


Figure 3. Effects of nitrification of ammonia in the study reach.

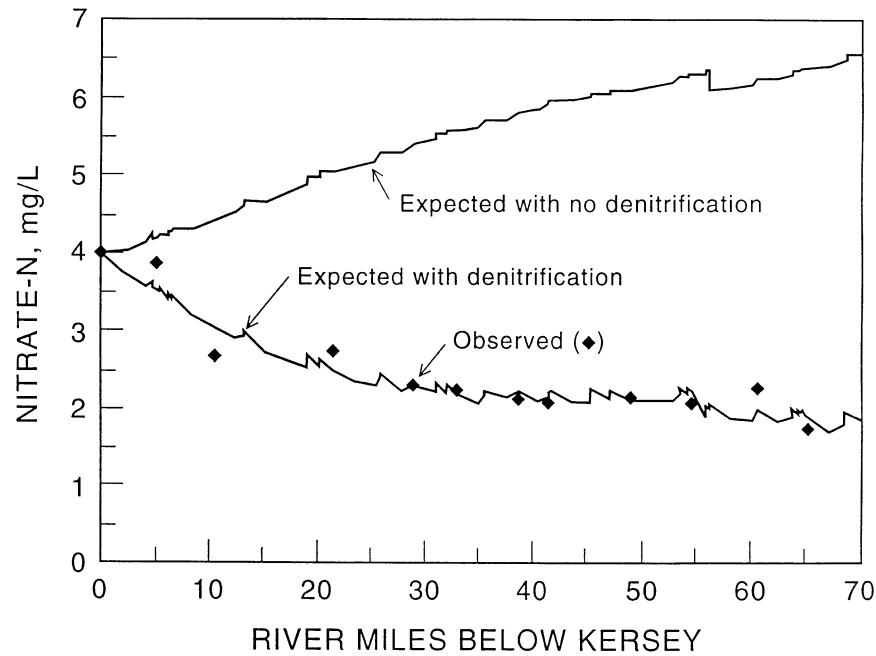


Figure 4. Effects of denitrification in the study reach.

the observed points and a first-order equation incorporating temperature and a denitrification rate constant. The denitrification rates are summarized in Table 2.

Denitrification rates were computed not only on the basis of volume ($\text{mg}/\ell/\text{h}$), but also on the basis of sediment area, on grounds that denitrification must involve exchange between the sediment and the overlying water column. Both sets of values are given in Table 2. They indicate somewhat higher denitrification rates in the upper reach than in the lower reach, and a considerable amount of variation through time.

Discussion

The temperature-corrected rate constant for denitrification changed greatly in both the upper and lower reaches between early and late June. This change was associated with the trend toward lower discharges, longer travel times, and shallower depths of water in the river between spring and summer. The implication of the change in rate constant is that microbial populations capable of conducting denitrification increase greatly in abundance, or that the volume of underground substrate with appropriate redox conditions (anoxia) to support denitrification increases greatly in the transition from spring to summer, or both. These possibilities cannot be distinguished on the basis of the present study.

Comparisons of seasonal changes in the rate constant for denitrification are not possible because such rates have apparently not been quantified on a year-round basis for rivers. The South Platte data indicate that denitrification could not be characterized accurately by use of a single rate constant. The representation of denitrification by a mass-balance model, at least for the South Platte, needs to take into account seasonal changes in the temperature-corrected rate of denitrification.

Comparisons with literature values are most feasible on the basis of denitrification per unit area. The closest comparison is with a mass-balance study by Hill (1983) on the Nottawasaga River (6th order; with nitrate pollution). The annual rate of removal for the South Platte (annual mean, $28 \text{ mg N}/\text{m}^2/\text{hr}$) is several times higher than for the Nottawasaga, perhaps because the Platte has a much more extensive hyporheic exchange. Holmes et al. (1996) demonstrated that denitrification in the hyporheic zone has a strong influence on the nitrogen budget of Sycamore Creek, Arizona, but direct comparison of rates could be misleading because Sycamore Creek is not polluted with nitrate. Duff et al. (1996) have recently summarized denitrification rates for streams as determined by incubations. All but a few of the values are much lower than those of the South Platte. Some high rates of denitrification have been

Table 3. Budget for nitrate-N in the 105-km study reach of the South Platte River (upper and lower segments combined)

Budget Component	Thousands of kg/d						Annual	Annual
	January	February	June	July	August	November	10 ⁶ kg	%
River Input	12.6	10.9	4.8	2.4	7.5	21.0	3.9	+53.9
Seepage Gain	4.3	5.2	5.8	11.4	11.0	0.3	2.1	+36.3
Tributary Gain	0.0	0.0	5.7	0.3	0.4	6.9	1.0	+13.7
Nitrification Gain	1.0	1.4	0.5	0.1	0.3	0.7	0.3	+3.6
Diversion Loss	4.0	2.8	5.0	4.2	6.0	15.0	2.4	-33.5
Denitrification Loss	5.5	6.9	10.8	8.8	10.7	13.9	3.6	-49.7
River Output	8.3	7.7	0.9	1.1	2.4	0.0	1.2	-16.8

documented for riparian zones (e.g., Seitzinger 1994), but these would not necessarily involve the same (hyporheic) process.

Removal of nitrate in the South Platte River is approximately an order of magnitude higher than the values summarized by Seitzinger (1988) for two eastern rivers carrying high nitrate concentrations, but is consistent with indications of high rates as obtained by McMahon and Böhlke (1996) and Pfenning and McMahon (1996) by acetylene reduction incubations and N-15 ratios. The data reported by Seitzinger (for the Delaware and Potomac rivers) are derived from incubations over sediment cores. A method of this type can represent denitrification only over a vertical segment of the substrate represented by the cores, and not by the entire hyporheic zone. In tidal zones of low-gradient rivers such as the Delaware and Potomac, the hyporheic zone may play a negligible role. If so, cores may represent overall rates accurately. The high denitrification values of the South Platte River underscore, however, the potential importance of denitrification remote from the surface. A generally similar picture could be expected for any river, such as the large tributaries of the Platte (e.g., Boulder Creek, Cache la Poudre River, etc.), with a large hyporheic exchange and strong augmentation of the nitrate budget by agriculture or municipal waste.

In some months, the upper and lower reaches of the South Platte had considerably different denitrification rates as expressed either volumetrically or on a unit-area basis (Table 2). In terms of time or distance required to achieve 90% removal of nitrate by denitrification, however, the two reaches are quite similar and thus can be lumped for the overall analysis of mass balance, as shown in Table 3.

As indicated by Table 3, denitrification is such an important feature of the nitrogen dynamics in the South Platte River that it can dispose of half

of the nitrate input over a 100-km river reach. Input continues, of course, in the form of agricultural return flows and point source wastewater outfalls, but the addition of nitrate is continuously offset by efficient denitrification. High efficiency of denitrification may be characteristic of rivers with large amounts of hyporheic exchange.

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