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Geochemistry of Inorganic Nitrogen in Waters Released from Coal-Bed Natural Gas Production Wells in the Powder River Basin, Wyoming

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Water originating from coal-bed natural gas (CBNG) production wells typically contains ammonium and is often disposed via discharge to ephemeral channels. A study conducted in the Powder River Basin, Wyoming, documented downstream changes in CBNG water composition, emphasizing nitrogen-cycling processes and the fate of ammonium. Dissolved ammonium concentrations from 19 CBNG discharge points ranged from 95 to 527 μM. Within specific channels, ammonium concentrations decreased with transport distance, with subsequent increases in nitrite and nitrate concentrations. Removal efficiency, or uptake, of total dissolved inorganic nitrogen (DIN) varied between channel types. DIN uptake was greater in the gentle-sloped, vegetated channel as compared to the incised, steep, and sparsely vegetated channel and was highly correlated with diel patterns of incident light and dissolved oxygen concentration. In a larger main channel with multiple discharge inputs ($n = 13$), DIN concentrations were >300 μM, with pH > 8.5, after 5 km of transport. Ammonium represented 25–30% of the large-channel DIN, and ammonium concentrations remained relatively constant with time, with only a weak diel pattern evident. In July 2003, the average daily large-channel DIN load was 23 kg N day^{-1} entering the Powder River, an amount which substantially increased the total Powder River DIN load after the channel confluence. These results suggest that CBNG discharge may be an important source of DIN to western watersheds, at least at certain times of the year, and that net oxidation and/or removal is dependent upon the extent of contact with sediment and biomass, type of drainage channel, and time of day.

Introduction

Throughout much of the United States, particularly in the western states, production of coal-bed natural gas (CBNG) is a rapidly increasing source of natural gas. In 2002, the annual U.S. CBNG production was nearly 1.6 trillion ft^3 or slightly more than 7% of the U.S. natural gas consumption for the same year (*1, 2*). Conservative estimates of recoverable, remaining CBNG resources are about 163 trillion ft^3, with slightly more than 50% located in the Powder River Basin (PRB, eastern Wyoming and Montana) and Alaska (*2*). Large quantities of methane-rich gas are often trapped in subsurface coals due to hydrostatic pressure and sorption of methane into the coal matrix. Much of this natural gas can be readily extracted from coal by installing wells in the coal seam and pumping water from the coal-bed aquifer. The process of pumping water to the surface releases the natural gas from the coal, thus providing a cost-effective means for gas recovery.

A byproduct of CBNG production is the large volume of water that is pumped from the coal. In 2006, CBNG water production in Wyoming was 1.1×10^8 m^3 (*3*), or equivalent to nearly 80% of the 2006 Powder River discharge at Moorhead, MT (*4*). Disposal of CBNG production water is a topic of major concern, the method of choice usually being dictated by the geochemistry of the water and the formation from which the water originated. PRB coal-seam water salinity (primarily from the Fort Union formation) is relatively low (0.2–4.0 g L^{-1} total dissolved solids) (*5*), resulting in a large portion of the PRB CBNG production water being discharged into streams, drainage channels, impoundments, and stock ponds. The total dissolved solids, major ion composition, pH, and sodium adsorption ratio (SAR) are parameters that have received the greatest amount of attention because of potential effects on downstream waters and ecosystems, livestock in rangelands, or crops, if the water is used for irrigation (*6–8*). The SAR, which is the ratio of the concentration of sodium relative to calcium and magnesium concentrations, is an issue because the sodium concentration in the production water is relatively high. The issue is further complicated by the presence of highly soluble salt loads in the semiarid soils. These salts can be mobilized by discharge of CBNG water, particularly when impoundments are installed in upland areas, resulting in moving fronts of high-salinity water in the subsurface beneath the impoundment (*9*).

Methane is not the only reduced, decomposition product present in coals. Recalcitrant organic compounds, sulfides, and ammonium also can be present. The relative amount of each in CBNG production water varies between coal formations. In many locales, such as the PRB, sulfide concentrations in coal-seam water are generally low. The presence of sulfide “sours” natural gas and is routinely assessed, but unlike sulfide, much less is known about reduced inorganic nitrogen in CBNG production waters. Ammonium is present in CBNG well water in the PRB, with concentration ranges in one study of 60–290 μM (*7*). The transport and fate of that ammonium, particularly once it is released into ephemeral channels, where the composition of the CBNG production waters can change downstream with time and distance, are largely unknown. What happens to the ammonium? How much of it is delivered as dissolved inorganic nitrogen (DIN) to perennial rivers, many of which are pristine, nutrient-limited systems?

The purpose of this study was to assess the occurrence of ammonium in CBNG production water in the PRB and the fate and transport of the ammonium once it was discharged into natural, ephemeral drainage channels leading to the Powder River. Production water geochemistry from several discharge locations was characterized as well as synoptic and diel studies in channels receiving water from individual or multiple discharge points. This study documents the net effect of uptake on ammonium and DIN transport in these channels and demonstrates the importance of including day–night fluctuations in nitrogen speciation when considering the effect of CBNG activities. Uptake is defined here as the combined net effect of all processes leading to a

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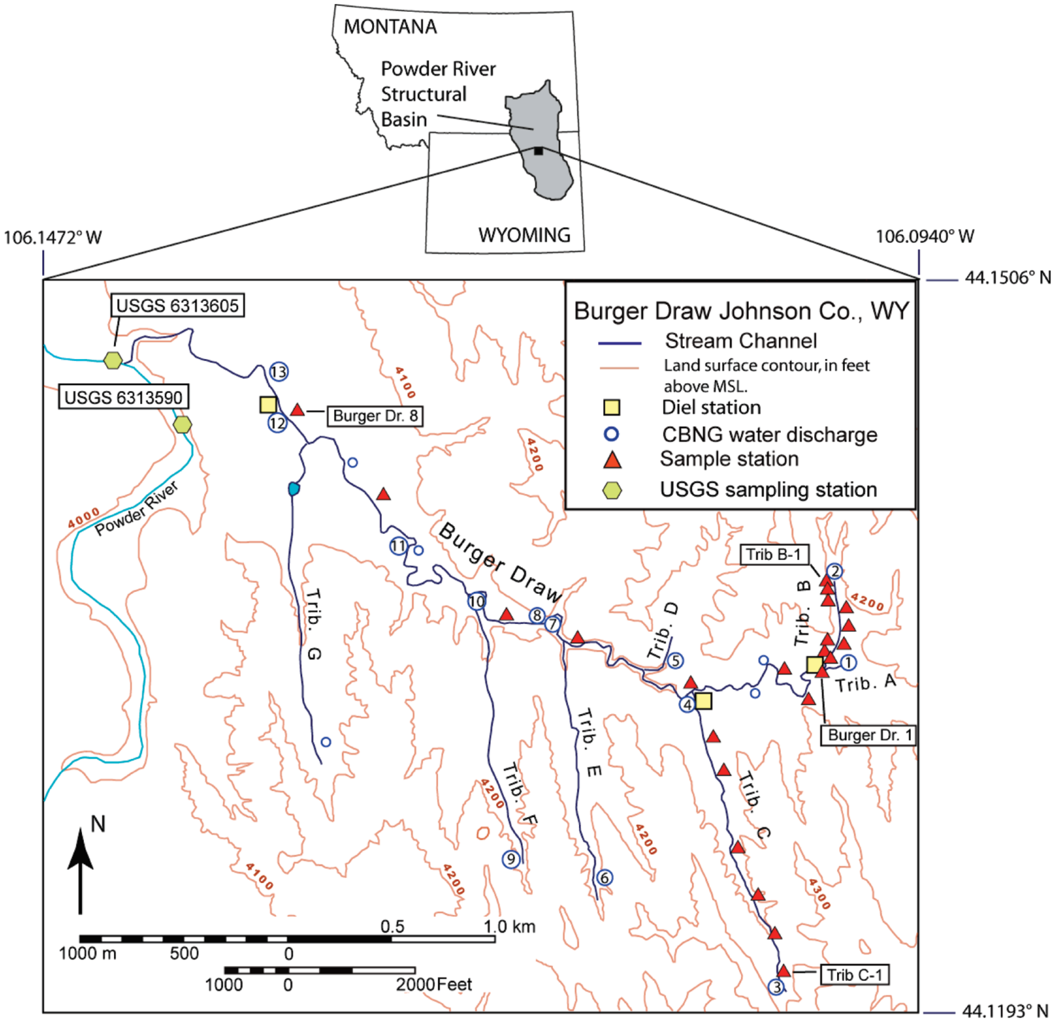

FIGURE 1. Map of the Burger Draw study site in Johnson County, WY. Sampling stations for each channel start at 1, as indicated, and consecutively increase in the downstream direction. Unnumbered discharge locations were not sampled.

concentration decrease in the water. For ammonium, this could be due to sorption, volatilization, assimilation into biomass, or dissimilatory reactions, such as oxidation to nitrite and nitrate by nitrification or oxidation to nitrogen gas by anammox-type reactions. Likewise, DIN uptake could be the result of both assimilatory and dissimilatory processes, but would not include nitrification, which does not result in a net concentration change in the water. Nitrate reduction is used to mean any dissimilatory process that decreases the nitrate concentration, including denitrification. The latter is presumed to be a dominant nitrate-reducing process, but was not specifically assessed in this study.

Experimental Section

Study Site. The study was conducted in the Powder River Structural Basin, a sedimentary basin located primarily in northeastern Wyoming, which features late Cretaceous to early Tertiary age coal and shale deposits that are currently the focus of intensive development for CBNG recovery. The basin is a semiarid, high-plain rangeland environment characterized by sagebrush, grasses, and ephemeral drainage channels. CBNG discharge water samples were collected mostly within Johnson County, WY (see the Supporting Information). Stream channel studies were conducted in Burger Draw, an ephemeral channel, which drains into the Powder River, a perennial channel, near Buffalo, WY (Figure 1). In 2005, Burger Draw received year-round discharge from an estimated 50−200 CBNG production wells. The number of wells in operation at any given time varied. Water was pumped from a production well into an open-air tank at a discharge location, where it was combined with water from several other wells. The residence time in the tank was estimated to be 10−20 min. The water exited the tank through an overflow pipe by gravity and was discharged within a few meters into a drainage channel via a standpipe. Discharge near the mouth of Burger Draw was 0.036 $m^3 s^{-1}$ on June 25, 2005, all of which was attributable to CBNG production.

Sample Collection. Water samples for synoptic or regional collection events were collected from stream channels or directly from the discharge standpipes. Whole water samples were measured on-site for temperature, pH, dissolved oxygen (DO), and specific conductance with a portable field meter. Water samples were filtered through a Gelman 0.45 μm capsule filter and preserved by (1) freezing (anions), (2) acidification with H_2SO_4 (pH $\approx$ 2; cations), or (3) acidification with H_3PO_4 (pH $\approx$ 2) and chilled at 4 °C for dissolved organic carbon (DOC). Diel sampling stations consisted of a programmable, automated water sampler, a Hydrolab miniSonde with dissolved oxygen, pH, temperature, and specific conductance probes, and a terrestrial pyranometer connected to a data recorder. Diel water samples were stored on ice until processing, which occurred within 0−8 h after collection. Stream channel travel times were determined using rhodamine as a tracer. Samples were collected at the diel sampling station.

TABLE 1. Range of Selected Constituents in CBNG Well Water and Production Water Point Source Discharges in the Powder River Basin, Wyoming

	CBNG wells[a]		CBNG water discharge point[b]	
constituent	range	mean	range	mean
specific conductance (μS cm^{-1})	470–3020	1300	1502–4470	3400
pH	6.8–7.7	7.3	6.9–8.2	7.4
alkalinity (mequiv L^{-1})	5–38	16	9–26	20
sulfate concn (μM)	<0.1–125	25	<5–225	35
chloride concn (μM)	150–1800	370	227–1287	820
ammonium concn (μM)	60–290	130	95–527	360

[a] Data from ref *7* for 47 individual wells in the Powder River Basin. [b] Data from this study for 19 discharge locations in the Powder River Basin. Discharge sources comprise water from several permitted CBNG wells (typically 5−10, but in some cases (Beaver Creek) substantially more than that). Details of discharge locations and sampling dates can be found in the Supporting Information.

Analyses. Anions (including nitrate and nitrite) and cations (including ammonium) were analyzed by ion chromatography (*10*). DOC was analyzed by oxidation with ammonium persulfate and conductometric detection (*11*). Quality assurance/quality control was monitored by including sample duplicates, blanks, and reference standards for all analyses and reference samples for DIN species (nitrate, nitrite, and ammonium). Rhodamine concentrations were determined with fluorescence spectroscopy.

Results and Discussion

DIN in CBNG Water. A survey of DIN concentrations in CBNG production water is shown in the Supporting Information (Table 1A); the ammonium data are summarized in Table 1. Included in the table are results from Rice et al. (*7*) for water collected directly from individual CBNG wellheads and water samples collected for this study from 19 CBNG discharge pipes in the Powder River Basin. Each discharge sample is a mixture of water from several CBNG wells; in one case it is a composite from a large number of wells. Chemical composition of the CBNG water was variable, with specific conductance and alkalinity ranging from about 470 to 4500 μS cm^{-1} and from 5 to 38 mequiv L^{-1}, respectively, though pH and DOC were more uniform, from 6.8 to 8.2 and from 133 to 439 μM C, respectively. SAR values for the discharge waters were 18.2−35.3, illustrating the high sodium concentrations relative to calcium and magnesium concentrations that are typical of CBNG production water (*7, 12*). SAR values >18 are considered to be a high sodium hazard and harmful to soil structure (*5*).

Ammonium was present in all CBNG production waters tested, ranging from 60 to 527 μM, and was the dominant inorganic nitrogen species. Nitrate and nitrite concentrations, when present, were less than 8 and 1 μM, respectively. At least part of the variability in ammonium concentration may have been related to the length of time a well had been pumped. For example, at one discharge location (trib B) ammonium concentrations were determined for nearly a 3.5 year period (Figure 2). Ammonium concentrations were highest when CBNG production first commenced and subsequently decreased with time of withdrawal. The concentration ranged from 450 to 140 μM with a steady decrease of about 18% per year. This contrasts with chloride, which increased about 7% per year over the same time interval.

Coal, which is the product of a depositional environment, generally contains from 0.5% to 3% (dry weight) nitrogen, most of it organic (*13−15*). Ammonia gas production from organic nitrogen has long been known as an unwanted byproduct of coal gasification technology (*15*). In coal deposits, coalification (coal formation), coal weathering, and anaerobic microbial degradation of coal can all result in mineralization of organic nitrogen to ammonium (*13*). Hence, coal can contain relatively high amounts of exchangeable ammonium (*16*). The gradual decrease in ammonium concentration may have been due to long-term depletion of sorbed ammonium that was associated with the coal, continued pumping causing a decrease in the pool of sorbed ammonium in the vicinity of the well bore. A similar decreasing concentration trend with time is observed with methane, which also sorbs to the coal matrix (*17*).

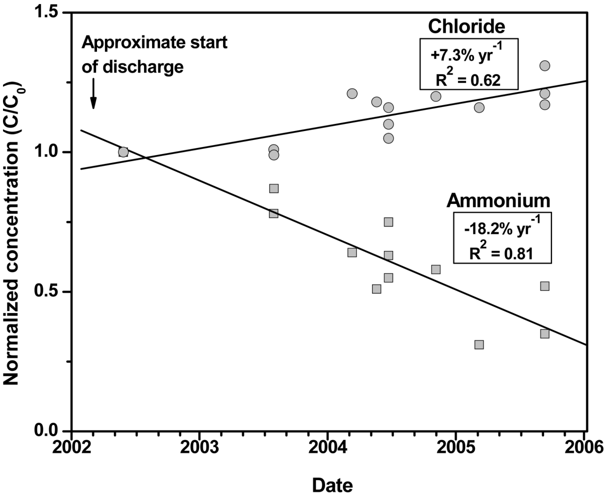

FIGURE 2. Changes in normalized concentration of ammonium and chloride in water collected from the tributary B discharge pipe over a 3.5 year period. The first sample collected (C_0, May 2002) contained 978 and 453 μM chloride and ammonium, respectively.

Assuming the mean ammonium concentration from this study (Table 1) is a reasonable approximation of CBNG production water in the PRB, the average PRB CBNG well discharges 12−34 kg of ammonium N per year (using the 2006 Wyoming average annual pumping rate of 6.7 × 10^6 L). The basin-wide total discharge for 2007 (17 300 producing wells) would be approximately 200−500 t of N in 1.1 × 10^8 m^3 of water. For comparison, the annual average discharge for the Powder River near Moorhead, MT (1930−2008) was 3.9 × 10^8 m^3 (*4*). If the average DIN concentration at that location before CBM production began was 0.5−1.0 mg of N L^{-1} (only very sparse data are available), that corresponds to an annual load of 200−400 t of N. The implication is that DIN in CBM production water could represent a substantial contribution to nitrogen export via the Powder River, depending upon the extent of removal during transport through the PRB watershed.

Synoptic Stream Channel Study. The fate of ammonium when CBNG water was discharged into ephemeral channels

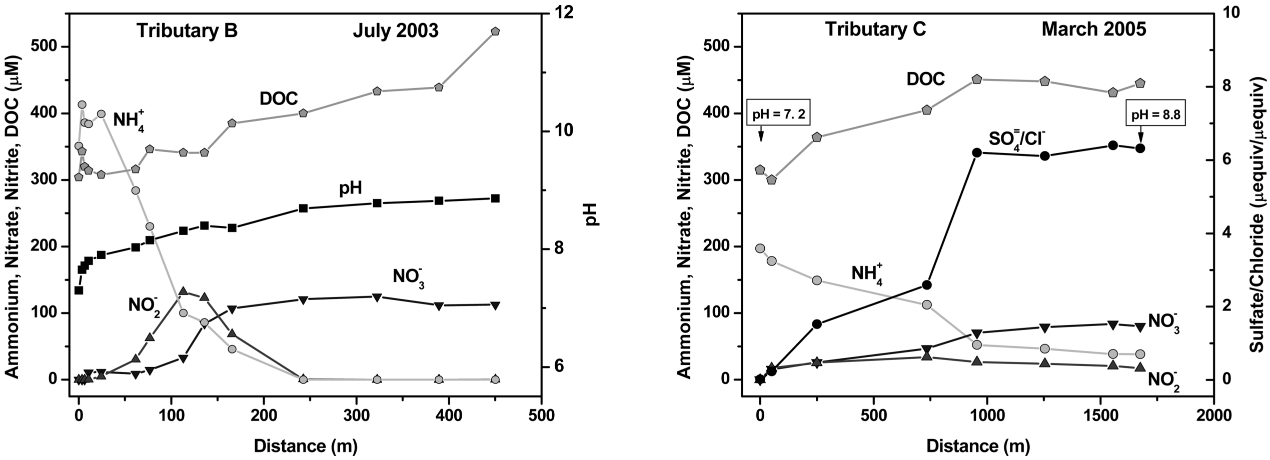

FIGURE 3. Changes in concentration of ammonium, nitrate, nitrite, DOC, and pH along tributary B of the Burger Draw channel in July 2003 and tributary C in March 2005. Also shown is the ratio of sulfate to chloride concentrations in tributary C.

was determined using synoptic studies along two channels receiving discharge from individual outfalls as compared to the Burger Draw main channel that received discharge from several separate discharge locations. The two individual channels, or "tributaries", differed in that trib B was a heavily vegetated (with grasses), gentle slope with a south-facing aspect, while trib C was a deeply incised, steeper slope that was sparsely vegetated, with a north-facing aspect. Trib B's reach is 0.45 km long; water takes $\sim$6 h to travel from the discharge pipe to the confluence with trib A. Trib C's reach is 1.7 km, with $\sim$3 h travel time. Complete results for the synoptic sampling events for trib B, trib C, and the main channel are shown in the Supporting Information, Tables 2A and 3A.

The dissolved ammonium concentration in trib B source water for a synoptic sampling event in July 2003 was 350 μM, with no detectable nitrate or nitrite (Figure 3). Down gradient from the outfall pipe, the ammonium concentration dropped markedly with distance and was undetectable 0.24 km downstream with subsequent nitrate and nitrite production within the same interval (Figure 3). Nitrite concentrations increased to slightly greater than 130 μM about 0.1 km downstream from the outfall, but then decreased with subsequent downstream distance. By the end of the trib B reach the DIN was essentially 100% nitrate. The total DIN concentration decreased throughout the reach and was $\sim$25% of the initial ammonium concentration in the outfall water just above the confluence with trib A (Figure 3). DOC increased from 300 to 520 μM along the reach, while the pH increased from 7.3 to 8.9. Sulfate and chloride concentrations, however, remained constant throughout the reach (Supporting Information, Table 2A).

In the trib C source water, ammonium concentrations were somewhat lower than in the trib B outfall, but also variable, ranging from 445 to 200 μM for May 2004 to September 2005 (data not shown). When released into the trib C channel, ammonium decreased in concentration downstream, with a concomitant increase in nitrite and nitrate (Figure 3). Unlike trib B, ammonium was transported the entire length of the trib C channel (1.7 km). However, in September nitrification within the reach was more complete than in March, with less ammonium and more nitrate and nitrite present (data not shown). Total DIN concentrations decreased along trib C by only 25% in March and not at all in September. DOC and pH increased along the reach, in similar proportion to the increases in trib B, but in contrast to trib B, sulfate concentrations increased substantially along the trib C reach relative to chloride concentrations (Figure 3). This is likely due to gypsum dissolution, similar to the observation by Healy et al. (*9*) during CBNG water infiltration from an impoundment located near the trib C discharge.

The main channel of Burger Draw receives CBNG water from multiple sources, some directly discharging into the main channel, others from tributary channels having varying flow rates, travel lengths, and duration of operation. Consequently, the patterns of DIN concentrations within the main channel were rather variable from one sampling event to another, but some general trends were evident. First, total DIN concentrations were relatively constant along the main channel reach but gradually decreased with time. For example, in May 2002, the mean reach DIN was 370 μM, which had decreased to 170 μM by March 2005 (Figure 4). Most commonly, the concentration order was nitrate > ammonium > nitrite, indicating that ammonium oxidation was typically incomplete, but examples of all other sequence orders also were evident, including situations where nitrite concentrations exceeded 100 μM. The temporal decrease in DIN load likely reflects a similar pattern seen in the trib B source water (Figure 2); however, it could also be the result of increased DIN removal rates within Burger Draw. Second, ammonium was always present near the mouth into the Powder River (station 8, Figure 1); concentrations ranged from 68 to 210 μM. Third, the pH in the main channel was always >8, ranging up to 8.7 at station 8.

The dynamics of ammonium and DIN uptake in the Burger Draw tributaries can be determined, at least in part, from the synoptic sampling results. Downstream concentration profiles for reactive nitrogen from a point source discharge were compared to those of chloride, a conservative solute, to determine the channel uptake length (S_w), mass transfer velocity (v_f), and first-order rate constant (k_1) for ammonium and DIN in the section of the channel in which the concentrations were decreasing (Table 2; see refs *18* and *19*). The ratio of S_{w,NH_4} for trib C to trib B is >16, indicating that ammonium on average traveled nearly 20× further in trib C than in trib B. Tracer studies in headwater streams across the United States attributed depth and velocity as primary factors related to differences in S_{w,NH_4} and v_{f,NH_4} (*20*). As noted, the trib C channel is more incised and steeper than that of trib B, which fits the observed correlation. However, in-stream processes also accounted for some of the uptake variability in headwater streams (*20*) and in Burger Draw (Figure 3, Table 2). Nitrification was a primary ammonium uptake process in both channels, but there was also substantial non-nitrifying uptake in trib B. Nitrification does not result in a net loss of DIN. Thus, relatively short DIN uptake lengths indicate DIN uptake by processes other than nitrification, such as assimilation. For trib C, $S_{w,DIN} > S_{w,NH_4} \gg$ reach length,

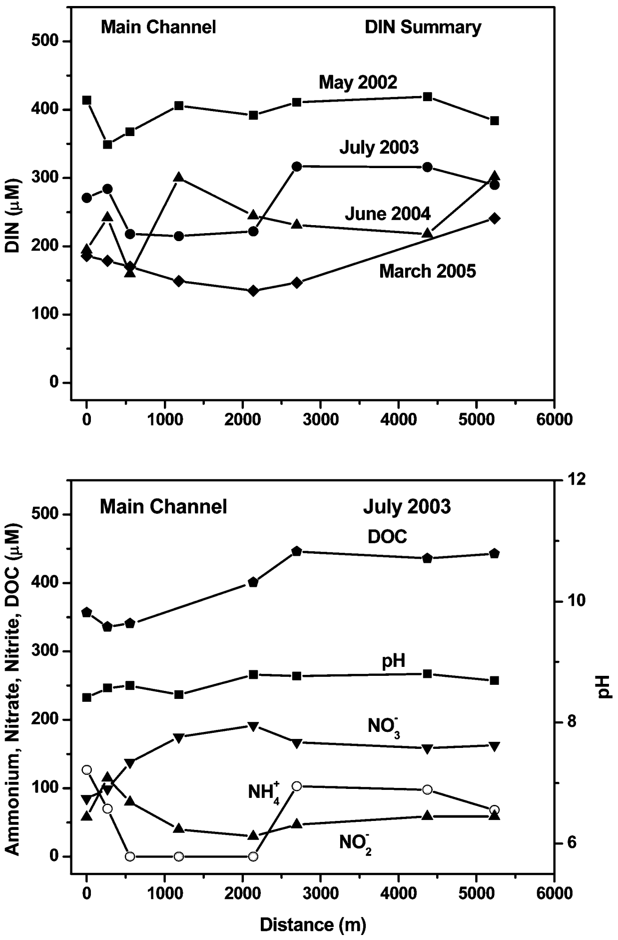

FIGURE 4. Changes in (top) DIN concentration along the main stem of the Burger Draw channel in May 2002, July 2003, June 2004, and March 2005 and (bottom) distribution of DIN species in July 2003.

TABLE 2. Summary of Mean Values for Ammonium and DIN Uptake Parameters from Burger Draw Tributaries B and C Synoptic Sampling Events[a]

	NH_4^+ uptake[b]			DIN uptake[b]	
channel	S_w (m)	v_f (m h^{-1})	k_1 (day^{-1})	S_w (m)	k_1 (day^{-1})
tributary B ($n = 7$)	48	0.165	56.6	195	14.4
tributary C ($n = 2$)	812	0.035	16.8	−10000	1.1

[a] Details of sampling events, calculations, and error estimates can be found in the Supporting Information, Table 5A. Terms defined as S_w = uptake length, or average distance traveled by a solute molecule before being removed or reacted, v_f = mass transfer coefficient, or velocity of solute removal or reaction from the water column, and DIN = total dissolved inorganic nitrogen, or $[NO_3^-] + [NO_2^-] + [NH_4^+]$. [b] Uptake calculated for stream interval where $[NH_4^+] > 50$ μM; see Figure 3.

suggesting that net removal of ammonium from the production water discharge was minimal (indeed, in one sampling event there was a net DIN gain within trib C (Supporting Information, Table 5A)). In trib B, once $[NH_4^+] < 50$ μM, $S_{w,DIN}$ increased 8×, suggesting that nitrate uptake processes (including nitrate reduction) were less active than processes responsible for ammonium uptake and thus required a longer transport interval to remove an equivalent amount of DIN. Other factors not considered here may also contribute to the differences in ammonium and DIN uptake that were evident between tribs B and C.

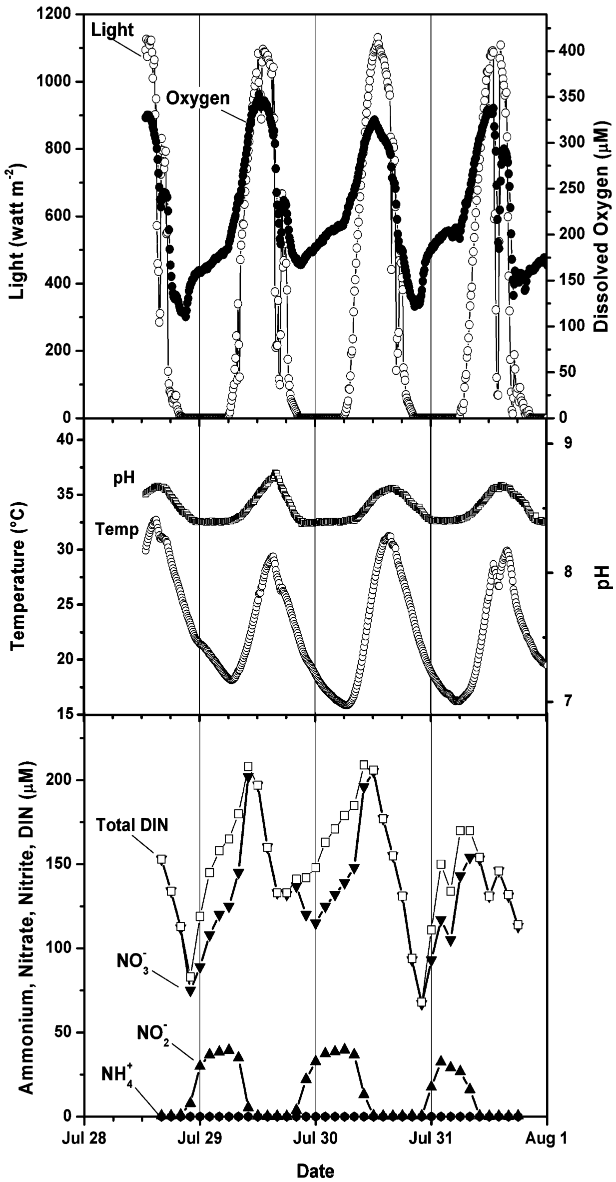

FIGURE 5. Diel changes in incident light, dissolved oxygen concentration, temperature, pH, and concentrations of inorganic nitrogen species in the downstream end of tributary B of Burger Draw (see Figure 1 for location) in July 2003.

Diel Stream Channel Study. The synoptic sampling events in the Burger Draw watershed were primarily conducted during daytime. However, in small stream channels, there could be shifts in redox reactions if DO concentrations fluctuate substantially on a diel basis. Thus, to fully characterize the geochemistry of the discharged CBNG water on a 24 h basis, diel sampling stations were installed in Burger Draw (Figure 1). There was a diel fluctuation in DO concentration at each station during each deployment (Supporting Information, Table 4A). The greatest change was evident for trib B with a summertime diel range of 122−352 μM O_2 (55−169% air saturation) at the downstream end (Figure 5). In contrast, the main channel summertime DO concentration was lower, ranging from 102 to 193 μM O_2 (47−88% air saturation). During March, the DO fluctuations were attenuated for trib B but enhanced for the main channel, with nighttime low values for each near air saturation concentrations (data not shown). There were also large fluctuations in DIN concentration and speciation, which directly correlated with the DO fluctuations in Burger Draw (Figure 5). At the downstream end of Trib B, DIN concentra-

TABLE 3. DIN Loads (kg of N day^{-1}) in Burger Draw at the Source and Mouth of Two Tributaries Receiving a Single CBNG Discharge and near the Mouth of the Main Channel

nitrogen species	tributary B[a]		tributary C[b]		main channel[a]
	source	downstream[c]	source	downstream[c]	downstream[c]
nitrate	0.00	0.62	0.03	0.36	7.34
nitrite	0.00	0.07	0.00	0.05	3.18
ammonium	1.71	0.00	0.42	0.07	12.08
total	1.71	0.69	0.45	0.48	22.60

[a] Results from July 2003. [b] Results from September 2005. [c] Based on mean values of samples collected at 2 h intervals for at least a 76 h period and instantaneous discharge measurements (3.8, 1.8, and 48.1 L s^{-1} for trib B, trib C, and the main channel, respectively) made near the beginning or end of the sampling period. Downstream sites are diel sampling stations for each channel (see Figure 1).

tions were highest during peaks of DO and incident light and were composed entirely of nitrate. As DO concentrations decreased, nitrate and DIN concentrations decreased, reaching low values in the early dark period, when DO concentrations were lowest. The change in DIN concentration was up to 130 μM in a 12 h period, or 65% of the maximum value (Figure 5). Also evident was the appearance of nitrite, up to 40 μM, which persisted for about 12 h, starting in the dark at the nitrate minimum. The presence of nitrite, coupled with the continued absence of ammonium, clearly suggested that nitrate reduction rates were substantially increased at night, when oxygen production had ceased. Similar trends were evident at the downstream end of trib C (September 2005, data not shown), though the concentration changes were much smaller. Nitrate decreased after the midday peak by ~16% (maximum value 195 μM), while nitrite approximately doubled in concentration during the night from daytime low values of ~15 μM.

At the Burger Draw main channel diel station there was some indication of diel cycling, but concentration fluctuations were small compared to absolute values, and the trends were not always consistent with DO concentrations or time of day. Ammonium concentrations in the main channel varied from 140 to 270 μM (mean 210 μM, July 2003) but with no discernible periodic pattern. The same was true for total DIN, which ranged from 340 to 440 μM (mean 390 μM, July 2003).

Nitrogen Loads and Implications for CBNG Discharge. The results of the diel sampling clearly indicate that calculations of DIN loads in stream channels from CBNG production waters (and probably all other redox-sensitive species) must take into account daily fluctuations of nitrogen speciation and concentration. The mean daily contribution of DIN to the Burger Draw main channel was approximately the same for trib B and trib C. Each represented 2−3% of the total DIN load near the mouth of the main channel (Table 3). The load calculations further emphasize that a substantial amount of the source ammonium N was removed during transport through the trib B channel but virtually none was removed in the longer trib C channel. This difference is attributed primarily to the presence of dense stands of grasses in the trib B channel. Nitrification, ammonium assimilation, and nitrate reduction all appear to be more active in the trib B channel. This is likely assisted by oxygen and DOC production by the plants and associated epiphytes, which generally are lacking in trib C. In-stream chamber incubations confirmed that nitrification and nitrate reduction were both active in trib B surface sediments, even in plant-free patches of the channel (*21*). Both processes demonstrated light vs dark related fluctuations in rates of activity during the chamber incubations. It appears that nitrification was quite efficient in trib B during daytime periods, oxidizing first ammonium and then nitrite in the first 200 m below the discharge point, but much less so in the dark when oxygen concentrations were lower (Figure 3) (*21*). In the distal 250 m of trib B, nitrification was essentially complete and nitrate reduction was the predominant process, but much more so in the dark than during daylight (*21*). This resulted in the nighttime nitrite peak seen at the trib B diel sampling station (Figure 5). In trib C, on the other hand, nitrification was much less efficient, requiring nearly the whole reach to oxidize the CBNG ammonium and thus providing any nitrate reducing activity much less opportunity to ultimately lower the DIN load.

Overall, it appears that the Burger Draw daily summertime contribution to the Powder River was about 23 kg of DIN in 2003 (Table 3). This load is a substantial contribution to the entire Powder River DIN load at Burger Draw. For example, in September 2004 the Powder River DIN load for depth and width integrated water samples above and below Burger Draw was 3.76 and 51.81 kg of N day^{-1}, respectively (Supporting Information, Table 6A). Similarly, in July 2005 the DIN increase attributable to Burger Draw was 9.69 kg of N day^{-1} (9.82 to 19.51 kg of N day^{-1}). Although it is unknown at present whether Powder River DIN loads are increasing overall, the DIN increase from 2004 to 2005 upstream from Burger Draw does correspond with increased CBNG discharge in the Powder River watershed (*3*). It is important to note that while the Burger Draw nitrogen contribution to the Powder River was substantial, the amount of water was not. For example, in July 2003, discharge was 48 and 1135 L s^{-1} (monthly mean) for each, respectively (Table 3) (*4*).

Management strategies for disposal of CBNG-produced water rarely consider downstream nitrogen effects. The results of this study clearly indicate that CBNG-associated DIN was being delivered from Burger Draw to the Powder River. The net result is an increased potential for eutrophication, though relatively little is specifically known about in-stream nitrogen cycling in this semiarid region. The Burger Draw results suggest that certain types of drainage channels much more effectively remove DIN than do others. It appears that increased exposure to channel sediments and plant communities substantially increases the amount of nitrogen removed, particularly if the travel distance is several hundred meters long. In contrast, short travel distances, deeply incised channels, or multiple discharge points closely spaced together all appear to decrease the efficiency of DIN removal and to decrease the net oxidation of ammonium to nitrate. The latter is particularly important because the pH increased with transport in Burger Draw, often approaching the p*K* for ammonia−ammonium equilibrium (9.2). In this pH range, the EPA water-quality criterion for ammonia concentration decreases sharply due to increased toxicity of the unprotonated form to fish and other aquatic species (*22*). For example, water in the Burger Draw drainage entering the Powder River in June 2004 contained 131 μM ammonium (pH 8.53, temperature 28 °C), which corresponds to a midday, acute (1 h exposure) and chronic (30 day exposure) water quality criterion of 216 and 31 μM ammonia, respectively (*22*). Since both pH and temperature fluctuate in this channel on a diel basis, this study suggests that ammonia toxicity levels will similarly fluctuate and be greatest mid to late afternoon and least in the predawn period. Although seasonal differences might also be expected, in limited sampling (March and November) there was no obvious change during transport in pH or in the extent of ammonium oxidation in cold weather months. It appears that high-pH, ammonium-containing water entered the Powder River all year long.

More investigation is needed to optimize nitrogen removal strategies from CBNG waters. It is clear that, for direct channel discharge, choosing appropriate drainage channel locations a priori could maximize both the efficiency of ammonium oxidation to nitrate and the total amount of DIN removed during transport, at least for the short term (2−3 years). The vegetation in the ephemeral channels in the Burger Draw watershed is primarily terrestrial plants and grasses. The long-term effect of the CBNG discharge on these communities may affect the overall long-term efficiency of nitrogen removal. At the same time, it appears that DIN concentration in CBNG water decreases with time (Figure 2). Therefore, the long-term need for nitrogen removal and its overall effectiveness are largely unknown. Other key issues that need addressing include the cumulative fate and effect of CBNG nitrogen loads on the Powder River and other perennial streams and rivers. Increasingly, as CBNG development continues, other production water disposal practices are being used, including the use of impoundments and center pivot irrigation. Potential differences in nitrogen removal capacity and nitrogen-cycling processes from these other approaches, and the overall implications for CBNG water management strategies, remain to be considered.

Acknowledgments

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Supporting Information Available

Tables showing (1) CBNG discharge samples collected, location, dates, and selected dissolved constituents, (2) selected water chemistry for synoptic sample collection events, (3) selected water chemistry for diel sample collection events, (4) ammonium and DIN uptake parameters for tribs B and C, and (5) DIN load calculations for the Powder River at Burger Draw in September 2004 and July 2005. This information is available free of charge via the Internet at http://pubs.acs.org.

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