

ALGAL PRODUCTIVITY AND NITRATE ASSIMILATION IN AN
EFFLUENT DOMINATED CONCRETE LINED STREAM¹*Robert Kent, Kenneth Belitz, and Carmen A. Burton²*

ABSTRACT: This study examined algal productivity and nitrate assimilation in a 2.85 km reach of Cucamonga Creek, California, a concrete lined channel receiving treated municipal wastewater. Stream nitrate concentrations observed at two stations indicated nearly continuous loss throughout the diel study. Nitrate loss in the reach was approximately 11 mg/L/d or 1.0 g/m²/d as N, most of which occurred during daylight. The peak rate of nitrate loss (1.13 mg/l/hr) occurred just prior to an afternoon total CO₂ depletion. Gross primary productivity, as estimated by a model using the observed differences in dissolved oxygen between the two stations, was 228 mg/L/d, or 21 g/m²/d as O₂. The observed diel variations in productivity, nitrate loss, pH, dissolved oxygen, and CO₂ indicate that nitrate loss was primarily due to algal assimilation. The observed levels of productivity and nitrate assimilation were exceptionally high on a mass per volume basis compared to studies on other streams; these rates occurred because of the shallow stream depth. This study suggests that concrete-lined channels can provide an important environmental service: lowering of nitrate concentrations similar to rates observed in biological treatment systems.

(KEY TERMS: aquatic ecosystems; algae; effluent dominated streams; nutrient assimilation; productivity; periphyton; wastewater; water quality.)

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INTRODUCTION

High nitrate in drinking water has long been linked to health concerns and eutrophication in receiving waters (Mueller *et al.*, 1995). However, recent studies suggest that nitrate contamination may be an even greater threat to drinking water and aquatic life than previously believed. Weyer *et al.* (2001) found an increased risk for certain types of

cancer in older women from even low level nitrate exposure in drinking water over many years. Marco *et al.* (1999) reported toxic responses by several amphibians to nitrate concentrations below limits recommended by the U.S. Environmental Protection Agency (USEPA, 2004) for drinking water and water inhabited by warm water fishes. The health and environmental issues associated with elevated nitrate concentrations are magnified in rivers and streams receiving large volumes of treated wastewater discharges, such as the Santa Ana River in California. Nitrate concentrations in the Santa Ana Basin are of particular concern because Santa Ana River water is used for recharging aquifers that provide supply for more than two million people in the southern California coastal plain.

The Santa Ana River is the largest river in southern California, and most base flow in the river is maintained by discharges of treated municipal sewage (Izbicki *et al.*, 2000; Mendez and Belitz, 2002). Although most of this effluent is tertiary treated (Burton *et al.*, 1998), it often has residual nitrate concentrations greater than 5 mg NO₃⁻ as N/L. Most of the river flow is diverted to spreading grounds, in the lower part of the watershed (Orange County Water District, 1996). As a result, nitrate loading is one of the most significant water quality issues in the Santa Ana Basin (Burton *et al.*, 1998; Hamlin *et al.*, 1999; Belitz *et al.*, 2004).

The purpose of this study is to evaluate the hypothesis that algal productivity during the day (photosynthesis) is responsible for the substantial nitrate loss observed along a reach of Cucamonga Creek, a tributary of the Santa Ana River (Figure 1). The work was

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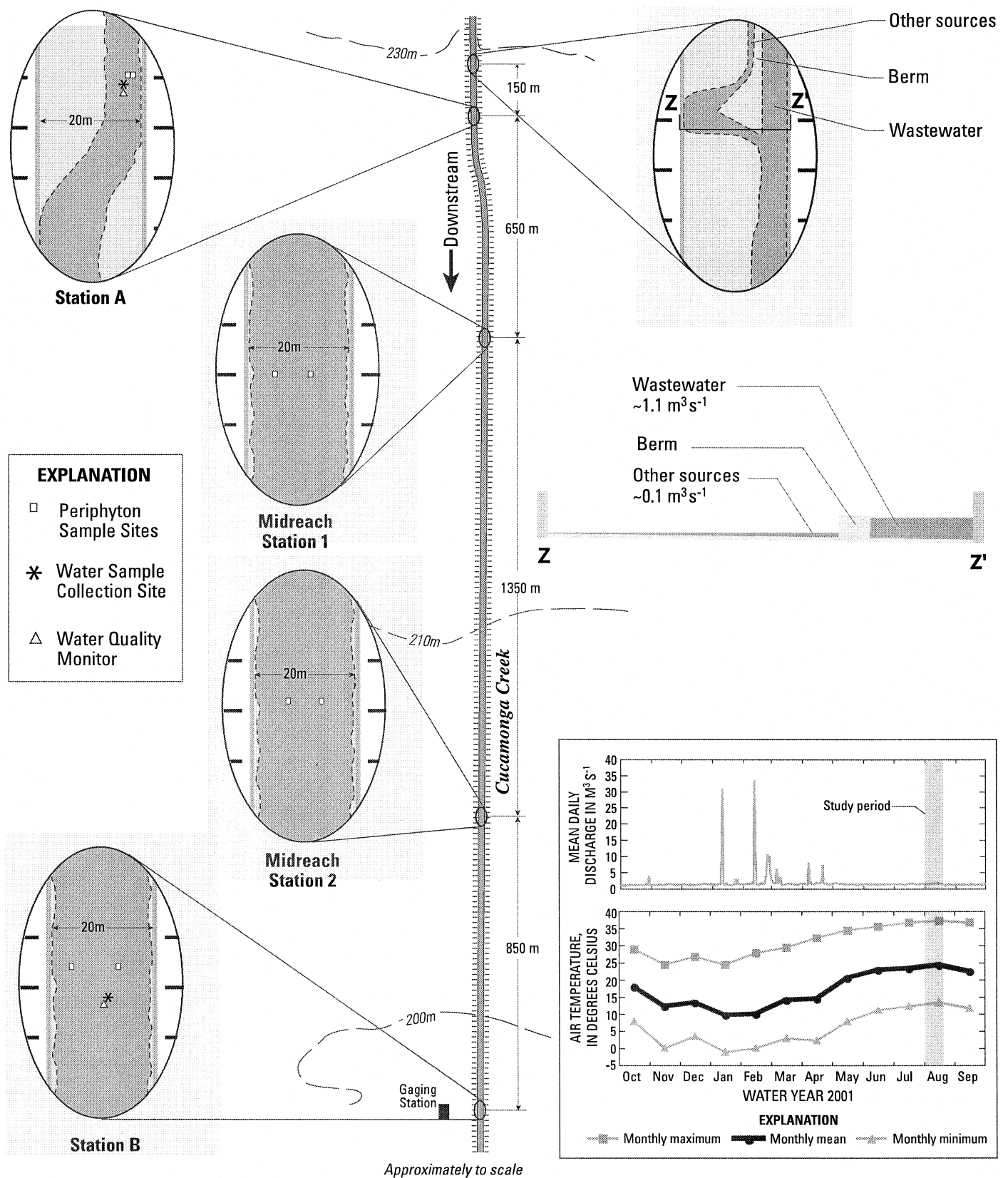


Figure 1. Study Reach Diagram Including Sampling Locations, Stream Cross Section at Confluence, and Plots of Discharge and Air Temperatures Around the Time of the Study.

motivated by a general need to better understand the processes affecting nitrate concentrations in Santa Ana Basin streams. In addition, there is a need to better understand the ecosystem function of altered streams in semi-arid environments.

Cucamonga Creek has been straightened and concrete lined to provide flood control, and base flow consists primarily of discharge from a municipal wastewater treatment plant, with a minor contribution from local runoff. The wastewater discharge provides a steady, nutrient rich water source to the stream. Due to the channel slope and the concrete lining, little sediment accumulates on the stream bottom. Most biochemical oxygen demand is removed from the wastewater in the treatment process. The drainage area for the relatively small contribution of local runoff is about 200 km², and is mostly urban street runoff with, perhaps, small inputs originating in the relatively undeveloped San Gabriel Mountains. Previous research, conducted as part of the U.S. Geological Survey's National Water Quality Assessment Program (NAWQA), indicated nitrate loss of about 1 mg/L (as N) between the outfall of the treatment plant and a NAWQA monitoring site approximately 4 km downstream.

In the present study, water quality and algal biomass data were collected to test the hypothesis that algal assimilation was the dominant instream process responsible for the high observed nitrate losses. Changes in stream concentrations of dissolved oxygen (DO) and nitrate were incorporated into a simple model that treats the stream reach as an equivalent volume of water. Algal photosynthesis, community respiration, and stream reaeration were considered the dominant processes in the model. If the proposed hypothesis can be substantiated, then there is some ecosystem benefit associated with concrete lined channels. Such channels, despite their prevalence, have been understudied from an ecosystem perspective.

Previous Studies

A number of authors have evaluated the dynamics of benthic algae and water quality in perturbed settings. Some of these have noted that benthic algae affect stream hydrodynamics, creating heterogeneous conditions, such as chemical gradients and zones of relatively low velocity (Dodds, 1991; Mulholland *et al.*, 1994; Chételat *et al.*, 1999). Some recent studies have examined benthic algal responses to conditions common in urban settings, such as impervious substrates and steady, nutrient rich flows (Ferreira *et al.*, 1999; Murdock *et al.*, 2004; Taylor *et al.*, 2004).

These, and other authors, often find that such conditions result in shifts in community composition or increased stream algal biomass (Chételat *et al.*, 1999; Ferreira *et al.*, 1999).

Previous studies have generally focused either on well controlled conditions at a laboratory scale, or on less well controlled conditions at a stream scale. The present study differs from previous work in that it was carried out in a stream dominated by external controls. The concrete lining of Cucamonga Creek, the steady supply of high nutrient, treated wastewater, and the relatively small volume of other water sources provided an opportunity to conduct a study under well controlled conditions at a stream scale. The present study uses a very simple mathematical model to test the hypothesis that algal assimilation is responsible for the observed nitrate loss in Cucamonga Creek.

Several laboratory studies have contributed to the basic understanding of algal nitrogen uptake for potential wastewater treatment applications (Gersberg *et al.*, 1978; Kim *et al.*, 1990; Rectenwald and Drenner, 2000; Mariñelarena and Di Giorgi, 2001). These studies provide a context for comparing algal nitrate uptake values in Cucamonga Creek with values observed in systems designed for treatment. Other researchers have examined algal uptake in field settings. A number of these have examined algal nitrogen assimilation using nutrient amendments (Bushong and Bachmann, 1989; Triska *et al.*, 1989, 1993; Kim *et al.*, 1992; Davis and Minshall 1999; Dodds *et al.*, 2002), and others have examined algal assimilation of nitrogen in lakes and streams that have relatively high ambient nutrient concentrations (Crompton and Hersh, 1987; Grimm, 1987; Bachmann *et al.*, 1991). These papers provide a context for understanding stream ecosystem response to high nutrient concentrations.

Since Streeter and Phelps (1925) developed their model of the primary mechanisms controlling stream DO levels, a variety of increasingly sophisticated models have been used to examine processes affecting stream water quality. For example, the multiparameter Water Quality Analysis Simulation Program (WASP) (supported by the USEPA) has been used to model the stream water-quality impacts of various water sources (Warwick *et al.*, 1997, 1999; Wool *et al.*, 2003). Another simulation program maintained by the USEPA, the Enhanced Stream Water Quality Model (QUAL2E), simulates the major reactions of nutrient cycles, algal production, and benthic and carbonaceous oxygen demand to develop total maximum daily loads (TMDLs) (Brown and Barnwell, 1987). QUAL2E is presently the most widely used computer model for simulating stream water quality (Chapra, 1997).

In the present study, a very simple model is developed based on Odum's (1956) two-station approach for measuring stream primary productivity, and Redfield's (1958) molar stoichiometry for estimating nitrate uptake by algae. The simple model provides a simple test of the hypothesis that algal assimilation is responsible for the large changes in nitrate concentrations observed in Cucamonga Creek. A more complicated model is not needed to test this simple hypothesis.

Study Area

The diel study was conducted along a 2.85 km reach of Cucamonga Creek, which began 1.4 km downstream of a wastewater treatment plant outfall (Figure 1). Upstream of the study reach, a 50 cm high concrete berm separated the treated effluent from local runoff. During the study, the depth of flow was about 30 cm on the side containing effluent, and about 5 cm on the side containing local runoff. The discharge averaged about 1 m³/s on the effluent side and less than 0.1 m³/s on the local runoff side. The berm terminates about 200 m upstream of the study reach. Just before the berm terminates, the channel is contoured to divert the local runoff sharply away from, and then sharply back toward, the effluent (Figure 1). The two sources of water mixed for a distance of about 150 m before entering the study reach.

The study reach is concrete lined and receives nearly 100 percent sunlight exposure over its entire length. The reach consisted of an upstream site, Station A, and a downstream site, Station B (Figure 1). The channel slopes approximately 10 m per km. Along the reach, the stream channel transitions from box to trapezoidal shape, and averages about 20 m in width. The wetted stream bottom does not usually extend from bank to bank under base flow conditions, and center channel depth is typically 8 to 15 cm. The study reach has no tributary input under normal base flow conditions. The wetted concrete stream bottom is blanketed with filamentous macroalgae (periphyton), but little sediment accumulates on the stream bottom due to the concrete bottom, the relatively high and constant stream velocity (approximate mean = 0.7 m/s, Standard Error (SE) = 0.02 m/s) and periodic scouring events. Around the time of the diel study there was practically no sediment accumulation in the channel even though the last significant storm event had occurred three months prior to the study (Figure 1, inset).

METHODS

Sampling Design and Field Methods

The study began August 15, 2001, at 2100 h at Station A, and the last sample was collected at 2200 h on August 16 at Station B. Sampling at Station B was delayed one hour relative to Station A to account for the approximate travel time, as previously determined by dye and surface float tests. Chloride measurements during the study reconfirmed the approximate travel time. Each sample pair was labeled by the collection time at Station A.

Twenty-five paired samples were collected at the two stations over a 24-hour (diel) period, and were selectively analyzed (Table 1). Water temperature, pH, specific conductance, and DO were continuously monitored at each site using YSI® instream, multiparameter probes (Jarrell, 1999). Coreadings were taken approximately every 3.5 hours with separate calibrated multiparameter probes by deploying them in the stream for about one hour at approximately three-hour intervals. The coreadings were used to confirm measurements of pH, specific conductance, and water temperature, as well as to correct for measurement drift in the DO probes. Carbon dioxide and alkalinity were measured by field titration with Hach® digital titrators (American Public Health Association, 1995). Water samples for these titrations, as well as for laboratory analyses, were collected by mid-stream grab since the stream was too shallow for isokinetic sampling (Wilde *et al.*, 1999).

Samples were filtered in the field using a 0.45 µm membrane filter for most dissolved constituents, and a 0.7 µm glass fiber filter for dissolved organic carbon (DOC). Samples for DOC and unfiltered nutrient analyses were preserved with 4.5N sulfuric acid. All samples were put on ice immediately, and shipped to one of two U.S. Geological Survey (USGS) laboratories for analyses within 72 hours of collection (Table 1).

Periphyton samples were collected at four stations along the reach, during the study and the two weeks prior, to determine periphyton standing crop and growth rate. The time series of algal growth (measured by chlorophyll *a* and ash free dry mass) began on August 3. Standing crop samples were also collected that day. At each station, two 0.25 m² squares were scrubbed with steel and nylon brushes. The approximate locations of the stations and the scrubbed squares are shown in Figure 1. These were selected to be as representative as possible, based on visual inspection, of the study reach. In some cases, the exact location of the sampling squares had to be shifted a few meters to avoid rough areas of concrete that

TABLE 1. Summary of Observed Changes in Concentration of Selected Parameters Between Stations A and B.

	Daylight Hours				Hours of Darkness			
	No. of Samples	Mean Change	Direction of Mean Change	p-Value ⁶	No. of Samples	Mean Change	Direction of Mean Change	p-Value ⁶
Chloride ¹ (mg/l)	12	-1.8	decrease	0.021	10	-0.37	decrease	0.16
Dissolved Organic Nitrogen ² (mg/l as N)	6	0.16	increase	0.016	6	0.080	increase	0.031
Particulate Organic Nitrogen ² (mg/l as N)	6	0.17	increase	0.016	6	0.16	increase	0.031
Ammonia ³ (mg/l as N)	6	0.0010	increase	0.22	6	0.030	increase	0.016
Nitrite ³ (mg/l as N)	6	0.010	increase	0.016	6	0.0030	increase	0.22
Nitrate ³ (mg/l as N)	13	-0.65	decrease	<0.001	11	-0.28	decrease	0.0070
Total Nitrogen ^{2,3} (mg/l as N)	6	-0.44	decrease	0.16	6	0.010	increase	>0.22
Dissolved Phosphorus ² (mg/l as P)	3	-0.022	decrease	0.12	4	-0.022	decrease	0.12
Dissolved Orthophosphate ³ (mg/l as P)	3	-0.024	decrease	0.12	4	-0.0080	decrease	0.31
Particulate Phosphorus ² (mg/l as P)	3	0.045	increase	0.12	4	0.55	increase	0.062
Total Phosphorus ² (mg/l as P)	3	0.022	increase	0.12	4	0.030	increase	0.19
Dissolved Organic Carbon ⁴ (mg/l as C)	4	0.13	increase	0.19	4	0.20	increase	0.062
Particulate Organic Carbon ⁵ (mg/l as C)	4	1.8	increase	0.062	4	0.85	increase	0.062

Analytical Methods:

¹Determined at the USGS Geochemical Laboratory in San Diego by ion chromatography.²Determined at the National Water Quality Laboratory in Denver (Patton and Truitt, 1992).³Determined at the National Water Quality Laboratory in Denver (Fishman, 1993).⁴Determined at the National Water Quality Laboratory in Denver (Brenton and Arnett, 1993).⁵Determined at the National Water Quality Laboratory in Denver (USEPA, 1992).⁶Significance tests on observed differences between concentrations of selected parameters at Stations A and B using Wilcoxon (1945) Signed-Rank Test. Changes in concentrations were submitted to one-tailed tests on observed loss or gain of constituent. The "Direction of Mean Change" column indicates whether the concentration of each constituent is generally observed to increase or decrease in the reach. A p-value less than 0.05 provides statistical significance for the observed change with a greater than 95 percent degree of confidence. This degree of confidence cannot be achieved with this test when the number of sample pairs (n) is less than five.

would have been incompatible with the sampler described below. Periphyton was immediately collected from the scrubbed squares to provide zero-time standing crop estimates of biomass (ash free dry mass) and chlorophyll *a*. After this initial scrubbing, time series samples were collected at each station in a different location within one of the squares every three to four days until August 17.

Periphyton was collected using a 10 cm diameter sampler, which is an enlarged version of the syringe microalgae samplers described in Cushing *et al.* (1983), Britton and Greeson (1989), Aloï (1990), and Porter *et al.* (1993). The large diameter sampler was necessary to adequately represent the filamentous macroalgae that dominated the reach. After removal of the sampler, the diameter of the cleaned area was measured. Water column samples were also collected periodically to determine the seston contribution to stream productivity.

Three aliquots of the periphyton suspensions and water samples for seston were filtered in the field, and frozen until analyzed for chlorophyll *a* and ash free dry mass. Analytical results were averaged from

results of the three aliquots. Chlorophyll *a* was determined in the USGS Geochemical Laboratory in San Diego using the USEPA fluorometric method (Arar and Collins, 1992; American Public Health Association, 1995) with a phaeophytin correction. All chlorophyll *a* analyses were performed on August 29, 2001, so that the maximum holding time for the frozen samples was 26 days. Ash free dry mass was determined in the USGS California District Laboratory in Sacramento using the USEPA standard method (American Public Health Association, 1995).

Three additional types of data were collected: sunlight availability (percent), stream discharge (m³/s), and stream surface area (m²). The percentage of sunlight availability for an average day during the time of the study was obtained using a Solar Pathfinder® (Platts *et al.*, 1987) at the same four sites in the reach where periphyton was periodically collected. Canopy and other local topographic shading features are reflected by the plastic dome of the device and quantified in relation to stream latitude and the month of sample collection. Downstream discharge (Station B) is continuously monitored by the USGS (Agajanian *et*

al., 2002). Additional discharge measurements were made periodically near Station A. The Inland Empire Utilities Agency provided hourly discharge data for the municipal wastewater treatment plant effluent.

Method for Estimating Primary Productivity

Primary productivity was estimated using the two-station open system approach introduced by Odum (1956). This approach was used because DO measurements are easily made, and the study channel characteristics provide a well controlled environment for making these measurements. In the two-station approach, the change in DO along a stream reach is related to primary productivity, reaeration, and respiration. For a study utilizing discrete measurements, a mass balance for DO at any time, t_i , can be written

$$X(t_i) = GP(t_i) + k_a(t_i)Sd(t_i) - R(t_i) \quad (1)$$

where t_i is the time increment i (dimensionless); $X(t_i)$ is the change in DO in the reach at t_i (mg O₂/L/hr); $GP(t_i)$ is the gross primary productivity at t_i (mg O₂/L/hr); $k_a(t_i)$ is the reaeration coefficient operative at t_i (hr⁻¹); $Sd(t_i)$ is the stream DO saturation deficit at t_i (mg/L); $R(t_i)$ is the community respiration at t_i (mg O₂/L/hr). Equation (1) can also be expressed in terms of the net primary productivity

$$X(t_i) = NP(t_i) + k_a(t_i)Sd(t_i) \quad (2)$$

where $NP(t_i)$ is the net primary productivity at t_i (mg O₂/L/hr).

It has been shown that the reaeration coefficient, k_a , varies with stream depth and velocity and that both k_a and respiration vary with temperature (McDonnell and Kountz, 1966; McDonnell, 1971; Bowie *et al.*, 1985; Wright and McDonnell, 1986; Rathbun, 1998). For shallow stream depths comparable to Cucamonga Creek (see Rathbun, 1998:35), the reaeration coefficient can be calculated relative to reference values.

$$k_a(t_i) = k_{ref}(1.0241^{T_i - T_{ref}}) (U_i/U_{ref})^{0.73} (Y_i/Y_{ref})^{-1.75} \quad (3a)$$

where $k_a(t_i)$ is the reaeration coefficient at t_i ; k_{ref} is the reaeration coefficient at the reference temperature, reference velocity, and reference depth; T_i is the water temperature at t_i (°C); T_{ref} is the reference water temperature (°C); U_i is the velocity at t_i (m/s); U_{ref} is the reference velocity (m/s); Y_i is the stream depth at t_i (m); and Y_{ref} is the reference stream depth (m).

Discrete values of depth are based on direct measurements of stage. Values for stream velocity are based on measured values of discharge (a function of stage), depth, and width. The reference values for depth and velocity are taken as the average for the diel study. The value of k_{ref} is a calibration variable.

Respiration, $R(t_i)$, can be calculated as a function of temperature

$$R(t_i) = R_{ref}(1.047^{T_i - T_{ref}}) \quad (3b)$$

where R_{ref} is the respiration at the reference temperature (mg O₂/L/hr).

Equations (1) and (2) can be rearranged to derive expressions for $GP(t_i)$ and $NP(t_i)$, which allows for computation given values of the other terms.

$$GP(t_i) = X(t_i) - k_a(t_i)Sd(t_i) + R(t_i) \quad (4a)$$

$$NP(t_i) = X(t_i) - k_a(t_i)Sd(t_i) \quad (4b)$$

Two of these terms, changes in DO, $X(t_i)$, and the DO saturation deficit, $Sd(t_i)$, are easily measured. The other parameters, however, need to be estimated.

The value for respiration can be estimated using nighttime data, because no primary productivity occurs during darkness. For nighttime measurements, values of respiration ($R_N(t_i)$) can be calculated

$$R_N(t_i) = k_a(t_i)Sd(t_i) - X(t_i) \quad (5)$$

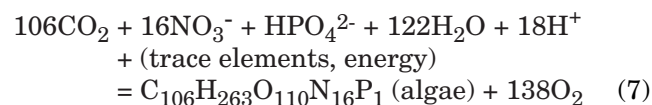
(for $t_i < t_{\text{sunrise}}$ and $t_i > t_{\text{sunset}}$)

A reference value for respiration (R_{ref}) can then be calculated as the average of the nighttime values

$$R_{ref} = \overline{R_N(t_i)} \quad (6)$$

It is further assumed that the reference value, R_{ref} , occurs at the average temperature for the night.

The reference value for k_{ref} , a calibration variable, was based on matching predicted average nitrate uptake during daylight to observed average nitrate loss during daylight. The nitrogen assimilated was presumed to be in the form of nitrate because this was the predominant form of nitrogen in the stream. Predicted nitrate uptake was based on Redfield's (1958) molar stoichiometry (Drever, 1997)



Redfield's stoichiometry, on a mass basis, requires 0.05 mg of nitrate uptake (as N) for each mg of net primary productivity (as O₂)

$$N(t_i) = 0.05 * NP(t_i) \quad (8)$$

where $N(t_i)$ is the predicted rate of nitrate uptake at time t_i (mg N-NO₃⁻/L/hr).

The model calibration proceeded as follows. A value of k_{ref} was assumed, and then a value of R_{ref} was calculated from Equations (3a), (5), and (6) using observed values of T_i , $Sd(t_i)$, and $X(t_i)$. Given these values of k_{ref} and R_{ref} , values of $NP(t_i)$ were calculated from Equations (3a), (3b), and (4b) using observed values of T_i , $Sd(t_i)$, and $X(t_i)$. Values of $N(t_i)$ were then calculated using Equation (8), and the daytime values were averaged. The average predicted daytime value was then compared to the average daytime observed nitrate loss. The value of k_{ref} was adjusted, by trial and error, to obtain a match between the predicted and observed average daytime nitrate loss. Once the model was calibrated, values of $GP(t_i)$, $NP(t_i)$, and $N(t_i)$ were calculated for the entire diel period using Equations (4a), (4b), and (8), respectively. Productivity (change in O₂) and predicted nitrate assimilation (change in NO₃⁻ as N) are expressed as mg/L/hr. Productivity is also expressed as g O₂/m²/d for the purpose of comparison with previous studies in the aquatic ecology literature.

Potential Limitations

The present study has a number of potential limitations. This study uses a two-station open system method as the basis for modeling primary productivity, and is therefore sensitive to the estimated value of the reaeration coefficient (Bott *et al.*, 1978; Bowie *et al.*, 1985; Owens, 1969). This limitation is addressed using observed changes in nitrate concentrations to calibrate for values of the reaeration coefficient (Bowie *et al.*, 1985).

The model relies on some relatively simple assumptions. One of these assumptions is that the observed changes in stream DO concentrations result only from net primary productivity (NP) and reaeration, as expressed in Equation (2). Equation (2) is only applicable if carbonaceous biochemical oxygen demand (CBOD) and sediment oxygen demand are negligible. The waste-water treatment plant is required to limit CBOD, and estimates this using an equation (G. Meinzer, Inland Empire Utilities Agency, written communication, September 11, 2001)

$$CBOD \text{ (mg/L)} \approx 1.57 \text{ TOC} - 23.5 \quad (9)$$

where TOC is the total organic carbon (mg/L). Based on concentrations of TOC and the small amount of sediment observed during this study, CBOD was negligible at all times.

The model also assumes that nitrate uptake will follow Redfield stoichiometry, which predicts a nitrogen uptake rate of 0.05 mg per mg of net oxygen production. Several studies have used ratios other than Redfield ranging from approximately 0.02 to 0.05 (Warwick and McDonnell, 1985a; Grimm *et al.*, 1981, after Wong and Clark, 1976). Since the Redfield ratio is in the upper end of these values, its application to predicting nitrate uptake would lead to a relatively large value of nitrogen loss for a given value of primary productivity. Conversely, if the Redfield ratio is used to predict productivity from observed nitrate losses, then its application would lead to a relatively low value of predicted primary productivity. Regardless of the ratio used, a characteristic of any model that predicts nitrogen uptake based on net primary productivity is that it will predict negative uptake (N release) at night when NP is negative.

This study does not account for asynchrony between photosynthesis and its associated metabolic costs, including nutrient uptake, which can introduce error (Bott, 1996). The two-station approach used here treats the stream reach as an equivalent volume of water with an equivalent (average) velocity. Such an approach does not take into account localized zones of relatively low velocity flow or chemical gradients that may arise in these localized zones (Dodds, 1991; Mulholland *et al.*, 1994; Mallin *et al.*, 2004; Taylor *et al.*, 2004).

Daytime supersaturation of DO may result in loss to the atmosphere as bubbles, resulting in an underestimation of primary productivity (Odum, 1956; Owens, 1969). On the other hand, if instream nitrate removal processes, other than algal assimilation, are significant, modeled productivity will be overestimated, since the model relies partially on the assumption that algae are responsible for the loss.

The present study took place over the period of a single summer day (August 15 to 16, 2001). Area mean monthly air temperatures were relatively constant from June through September 2001, ranging from 22.6 to 24.6°C (Figure 1) (San Bernardino County Water Resources Division, 2003), suggesting that the diel study was representative of summer conditions. In contrast, the diel study is unlikely to be representative of winter conditions.

Nutrient uptake rates, using instream measurements, cannot separate algal uptake from uptake by other organisms, such as heterotrophs (Webster *et al.*, 2003). In addition, simultaneous remineralization also masks nutrient assimilation, resulting in a conservative estimate of uptake (Mulholland, 1996), since the observed nitrate uptake values result from net loss in the reach rather than attempting to separate the processes of uptake and recycling. However, this error should be small when most of the stream

nitrogen is in the form of nitrate, as is the case in Cucamonga Creek. The nitrogen products of remineralization are organic nitrogen and ammonium, requiring additional nitrification to convert ammonium to nitrate (Davis and Minshall, 1999).

Finally, since shallow stream conditions did not permit isokinetic sample collection, the grab sampling technique left open the possibility that water samples were not representative of the entire stream transect at Station A if the wastewater and urban runoff components of flow were not completely mixed there. The wastewater component dominates stream flow, so it is likely that any incomplete mixing at the Station A sampling site would result in an under-representation of the urban runoff component in a grab sample collected at mid-stream. Unfortunately, no stream profiles to determine water quality variation in the cross sections were performed at either sampling station. Stream flow data from the separate wastewater and urban runoff components are presented to help estimate the magnitude of potential errors introduced by the sample collection technique.

RESULTS

Environmental Conditions and Selected Analytes

On August 16, 2001, sunrise over Cucamonga Creek was at approximately 0600 h, and sunset was at approximately 1900 h. The 13 sample pairs for which the upstream samples (Station A samples) were collected between 0600 h and 1800 h are considered daylight samples, and the remaining 12 pairs, night samples. A complete dataset for the water quality parameters sampled for during the diel study can be publicly accessed through the USGS National Water Information System (NWIS) database (USGS, 2001) using the site numbers for Stations A and B (340041117355701 and 11073495, respectively).

Stream discharge in the study reach averaged 1.3 m³/s, with a range from 0.5 to 2.1 m³/s (Figure 2A). The extremes in flow shown in Figure 2A are likely exaggerated because of inaccuracies in the stage/discharge rating curve. Stream stage averaged 0.11 m, with a range from 0.08 to 1.4 m. During the study, the discharge consisted of more than 90 percent wastewater and less than 10 percent urban runoff, based on discrete measurements of each source in the upstream channel where a berm separates the two sources (Figure 2B). Samples for three nonnutrient anions were collected hourly (bromide, sulfate, and chloride). Fluctuations in chloride concentrations

observed at Station A were generally observed at Station B one hour later, confirming the use of the one-hour travel time (Figure 2I).

Stream TOC concentrations were consistently below 10 mg/L. Use of Equation (9) results in negative values for CBOD for all stream measurements of organic carbon made during the diel period suggesting that CBOD was, at all times, negligible. Negligible CBOD, along with low sediment accumulation, justified the use of Equation (2), which attributes DO changes only to net primary productivity and stream reaeration. Both particulate and dissolved organic carbon generally increased within the reach (Table 1), and increases in particulate organic carbon were greater during the day than at night, likely due to algal sloughing.

Observed changes in pH between Stations A and B were small during the night (usually less than 0.5 pH units) but generally large during the day (Figure 2D). The values during the night were consistent with the pH values of the wastewater effluent (G. Meinzer, Inland Empire Utilities Agency, written communication, September 11, 2001); the reported mean daily pH of the effluent was 7.50 on August 15 and 7.65 on August 16. During the night at Station A, there is a strong inverse correlation between changes in discharge and changes in pH that is not clear cut during daylight. The decreased correlation may be related to photosynthesis, fluctuating proportions of wastewater treatment plant effluent to higher pH urban runoff, or incomplete mixing at Station A.

Phosphorus concentrations were below 1 mg/L as P throughout the study. The mean total phosphorus concentration was 0.34 mg/L at Station A and 0.37 mg/L at Station B (Figure 2G). Dissolved orthophosphate, the predominant species at both stations, usually decreased within the reach (Table 1, Figure 2H), resulting in a net diel loss of 0.037 g PO₄³⁻-P/m². The mean loss rates for dissolved orthophosphate were three times higher during hours of daylight than during the night (Table 1). When other forms of dissolved phosphorus are included, the net diel loss was 0.05 g P/m², and the mean loss rates for dissolved phosphorus were the same for samples collected during hours of darkness as for hours of daylight (Table 1). In contrast to the consistent loss observed for the dissolved species of phosphorus, particulate phosphorus concentrations increased in the reach throughout the diel study, with a net diel gain of 0.094 g P/m². As a result of these gains in particulate phosphorus, total phosphorus concentrations increased in six out of seven sample pairs between Stations A and B (Figure 2G), and the increases were similar for the daytime and nighttime periods (Table 1).

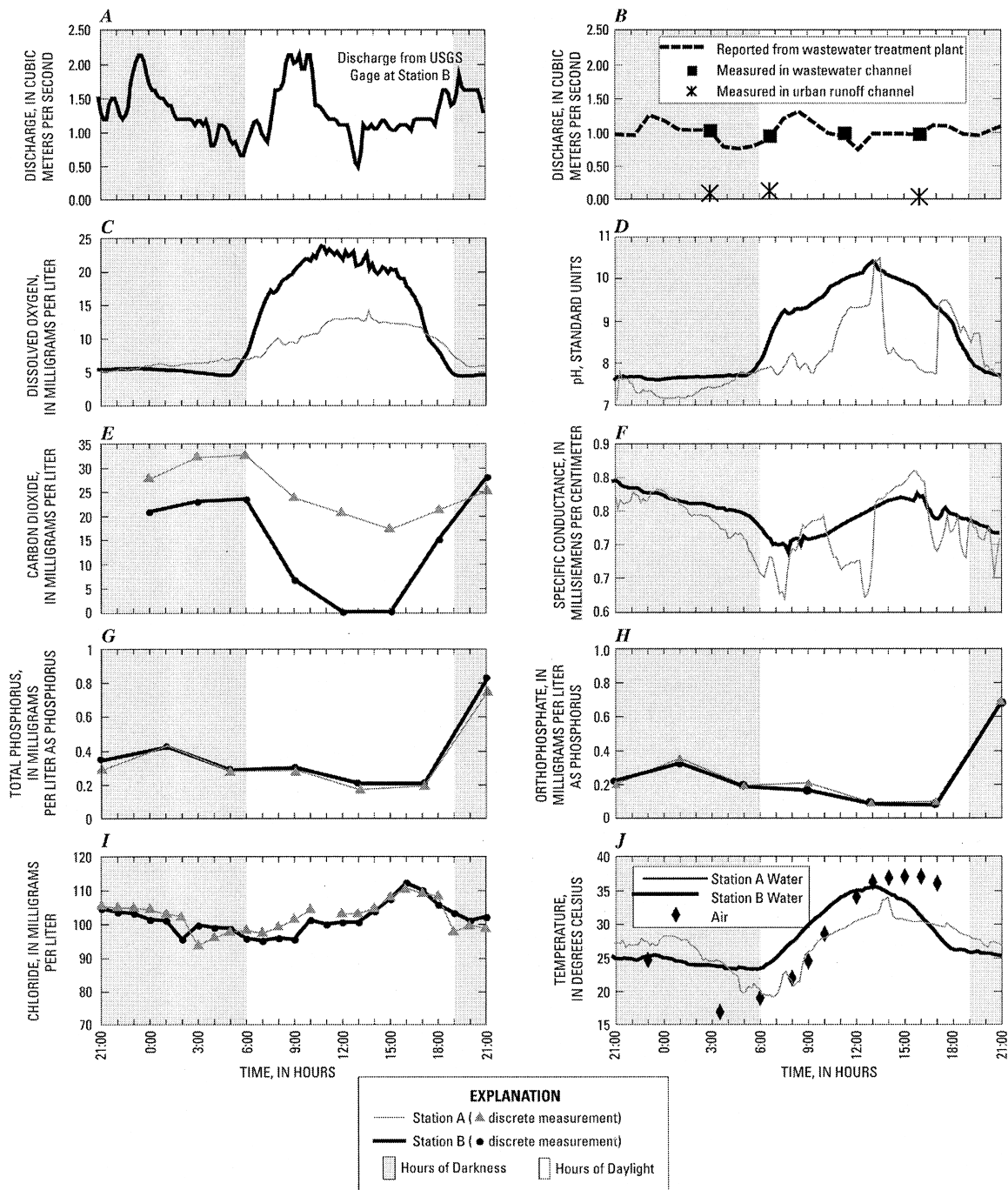


Figure 2. Diel Changes in Selected Parameters at the Two Sampling Stations. Sample collection times at the Downstream Station (Station B) are offset by one Hour (approximate travel time in stream reach).

TABLE 2. Model Input Reference Parameters and Observed Daytime Nitrate Loss (values from 0600 h to 1800 h).

T_{ref}	25°C
k_{ref}	0.91/hr
R_{ref}	3.5 mg O_2 /L/h
Mean nitrate loss (observed)*	0.65 mg NO_3^- -N/L/h
Mean nitrate loss (modeled)*	0.65 mg NO_3^- -N/L/h

Nitrogen

Observed concentrations of the various nitrogen species are graphed in Figure 3. The sample collected at 0300 h at Station A had anomalous concentrations for most nitrogen species. The nitrate value for this sample (confirmed by replicate analysis at a separate laboratory) appears low, while ammonia and

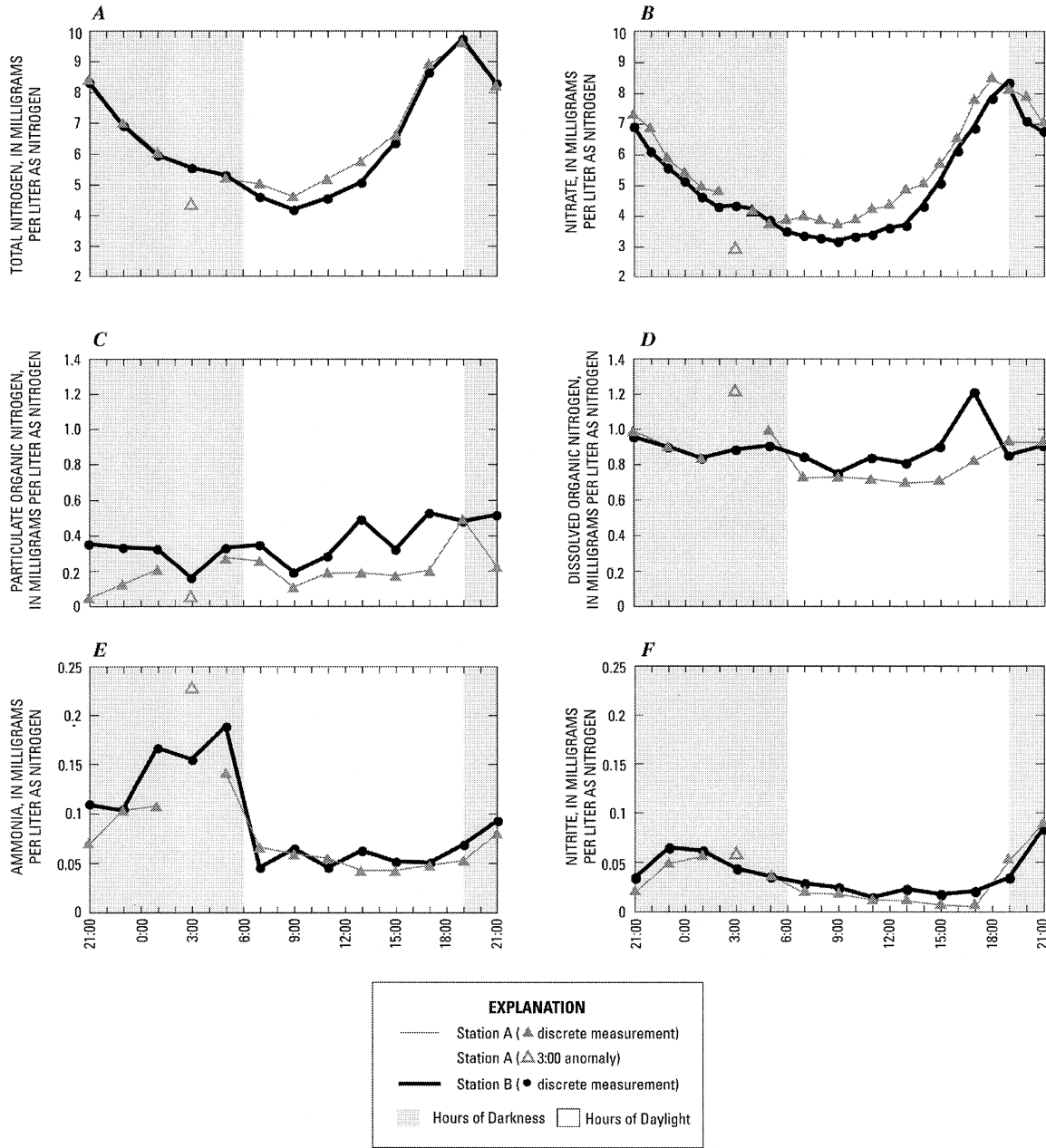


Figure 3. Diel Changes in the Various Nitrogen Species at the Two Sampling Stations. Sample collection times at the Downstream Station (Station B) are offset by one Hour (approximate travel time in stream reach).

dissolved organic nitrogen appear elevated. It is likely that the sample was compromised during collection and field processing. This outlier was excluded from all calculations involving the constituents for which the anomalous sample was analyzed. For completeness, the anomalous concentrations appear in Figure 3, but they are disconnected from the time series in each plot.

Approximately 80 percent of the nitrogen present in the stream was in the form of nitrate. The remainder was primarily organic nitrogen. The concentrations of all nitrogen species except nitrate generally

increased in the study reach, and the increases were statistically significant ($p < 0.05$) during the periods of day and night for all species except for ammonia during daylight hours and nitrite during hours of darkness (Table 1). The mean increase for particulate organic nitrogen during hours of daylight was similar to the mean increase at night. Consistent increases in particulate organic nitrogen suggest that algal sloughing varied little during the diel study. Dissolved organic nitrogen and nitrite tended to increase more during hours of daylight than at night. More dissolved organic nitrogen may have entered the stream during

the day as a result of higher rates of algal metabolism during daylight hours. However, ammonia (another product likely to be released through algal metabolism) tended to increase more in the study reach at night. The net diel gains of particulate organic nitrogen, dissolved organic nitrogen, nitrite, and ammonia were 0.31, 0.066, 0.012, and 0.019 g N/m² respectively. The total net diel gain was 0.41 g N/m²/d for the nonnitrate species.

In contrast to these other nitrogen species, concentrations of nitrate generally decreased in the study reach. Throughout the 24-hour period (21 of 24 samples excluding the 0300 h anomaly), the concentrations at Station B were lower than at Station A (Table 1). This difference was statistically significant for both the night and daylight periods, but more so for daylight. The greatest observed loss rate (1.1 mg/L/hr) was observed during peak sunlight at 1300 h. Mean nitrate loss in the study reach during daylight hours was 0.65 mg NO³-N/L/hr (Tables 1 and 2). At night, nitrate loss continued, but slowed to a mean of 0.25 mg NO³-N/L/hr, so that nitrate loss for the 24-hour study was approximately 11 mg NO³-N/L/d. Computed on a per unit area basis, total NO³- loss was 1.0 g NO³-N/m²/d; 0.77 g NO³-N/m² for the daylight hours, and 0.25 g NO³-N/m² for hours of darkness. In terms of total nitrogen mass balance, the net diel gains described above for the other nitrogen species were offset by this net diel nitrate loss of 1.0 g NO³-N/m²/d by 0.59 g N/m²/d.

TABLE 3. Modeled Productivity and Respiration for the Daylight and Diel Periods.

	Mg O ₂ /l	g O ₂ /m ²
GP for 13-Hour Daylight Period	228	21
R for 13-Hour Daylight Period	56	5.1
NP for 13-Hour Daylight Period	172	15.8
R for 24-Hour Diel Period	96	8.7
NP for 24-Hour Diel Period	133	12.0

Productivity

The spatial and temporal changes in dissolved oxygen and carbon dioxide concentrations, along with observed algal accumulation and standing crops, indicate high algal productivity in Cucamonga Creek. The time series curves show relatively low oxygen and high carbon dioxide concentrations at night, and relatively high oxygen and low carbon dioxide during daylight (Figures 2C and 2E). The early afternoon CO₂ minima and O₂ maxima were far more extreme at the

downstream Station B than at the upstream Station A. The decline in CO₂ was accompanied by a decline in bicarbonate and an increase in carbonate (Figure 4). These changes in carbonate speciation are consistent with the changes in pH (Figure 4).

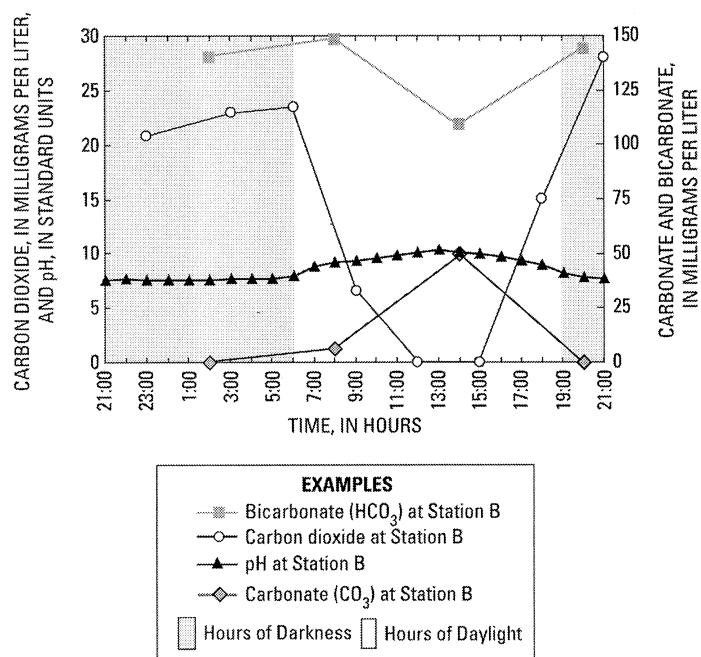


Figure 4. Diel Changes in Bicarbonate, Carbon Dioxide, pH, and Carbonate at the Downstream Station (Station B).

Bicarbonate concentrations remained constant during the diel study, except for the 1400 h sample pair when the concentration decreased by 40 mg/L. This significant decrease occurred at the same time that CO₂ was totally depleted at Station B, suggesting that algae began to utilize bicarbonate in the absence of CO₂. Also in this 1400 h sample pair, the carbonate concentration at Station B increased in response to the high pH. The simultaneous rise in pH, depletion of CO₂, decline in bicarbonate, and increase in carbonate are consistent with algal utilization of bicarbonate (Figure 4).

The dominant periphyton was *Cladophora* sp. (S.D. Porter, USGS, oral communication, August 30, 2001). Other algal taxa included *Scenedesmus dimorphus*, *Lyngbia* sp. or *Oscillatoria limnetica*, *Pediastrum* sp., and *Fragillaria* sp. The chlorophyll *a* of the periphyton standing crop, measured at four sites at the beginning of the study, averaged 178 mg/m² (SE = 23 mg/m²). This level falls in the range (>150 to 200 mg/m²) characterized by Biggs (2000) as unnaturally high for streams, and is well above the 100 mg/m² described as “nuisance level” by Murdock *et al.* (2004).

Sample data from the chlorophyll *a* time series of algal accumulation were highly variable and, therefore, not considered reliable. Periphyton ash free dry mass standing crop, measured at two sites at the beginning of the study, averaged 70 g/m² (SE = 10 g/m²) (Figure 5). Standing crop ash free dry mass samples for two sampling sites were lost during analysis. Algal biomass accumulation, measured at three sites, on cleaned areas of channel bottom equaled or exceeded these ash free dry mass standing crop values within three to six days. Then, values alternated between

decreases (presumed sloughing) and growth (Figure 5). The mean, presloughing, accumulation rate was 13.2 g dry mass m²/d (SE = 1.6 g/m²/d), and agrees reasonably well with algal accumulation predicted by the model based on net primary productivity (Table 4).

From visual inspection of the filters used to process the algal samples, the seston appeared to be predominantly broken periphyton filaments (*Cladophora*). The stream seston samples had a mean chlorophyll *a* concentration of 18 mg/L (SE = 1.5 µg/L), and a mean

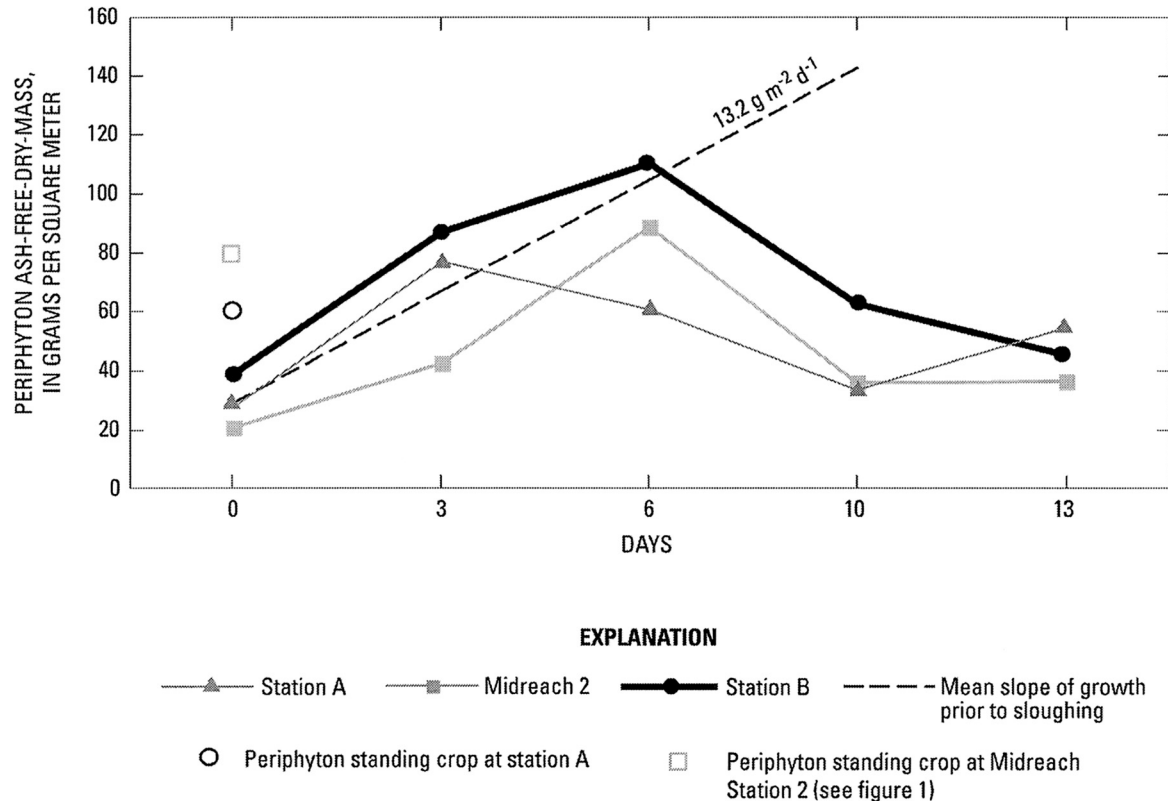


Figure 5. Periphyton Growth (at three locations) and Standing Crop (at two locations) Measured by Ash Free Dry Mass. The mean growth rate prior to initial sloughing was 13.2 g/m/d.

TABLE 4. Comparison of Observed and Modeled Algal Accumulation, Nitrate Loss, and Orthophosphate Loss for All Periods.

	Observed	Modeled
Algal Biomass g/m ² /d, Dry Weight	13.2	12.5
Nitrate Loss During Daylight g NO ³ -N/m ² /d	0.77	0.78
Nitrate Loss During Darkness g NO ³ -N/m ² /d	0.25	-0.16
Nitrate Loss During Diel Period g NO ³ -N/m ² /d	1.0	0.62
Orthophosphate Loss During Daylight g PO ₄ ³ -P/m ² /d	0.03	0.11
Orthophosphate Loss During Darkness g PO ₄ ³ -P/m ² /d	0.01	-0.02
Orthophosphate Loss During Diel Period g PO ₄ ³ -P/m ² /d	0.04	0.09

ash free dry mass of .066 g/L (SE = 0.007 g/L). These concentrations, when normalized for discharge and stream area, suggest that the seston contribution to stream primary productivity is small. As chlorophyll *a*, seston represents less than 1 percent of the standing crop, and by ash free dry mass, less than 10 percent of the standing crop.

Modeling of Gross Primary Productivity

Estimates of gross primary productivity and nitrate uptake were based on modeling of DO and observed changes in nitrate concentration. The reference parameters for the model are compiled in Table 2. The observed differences in DO concentrations, and the mean saturation deficit for dissolved oxygen in the stream reach, are shown in Figure 6A. Figure 6B shows the temperature dependent respiration parameter, $R(t_i)$, and the temperature, flow, and depth dependent reaeration coefficient, $k_a(t_i)$. The average $k_a(t_i)$ for the diel period was 0.96/hr, and ranged from 0.79 to 1.2/hr (Figure 6B). Average $R(t_i)$ for the night was 3.5 mg O₂/L/hr, ranging from 3.0 to 3.9 mg O₂/L/hr. During daylight, $R(t_i)$ ranged from 3.0 to 5.5 mg O₂/L/hr (Figure 6B).

Once the model was calibrated, values of GP and NP were calculated using Equations (4a) and (4b) respectively. Figure 6C shows a steep rise in both GP and NP starting at sunrise (about 0600 h). These reach their peaks at about midday, with the maximum for NP (22.6 mg O₂/L/hr) occurring at 1050 h,

and the maximum for GP (27.4 mg O₂/L/hr) occurring two hours later at 1250 h. Both GP and NP begin to decline steeply at about 1530 h, leveling off again at sunset (about 1900 h). During hours of darkness, photosynthesis ceases and respiration continues. As expected, NP is negative at night. Integrated values for GP, NP, and R during daylight hours and the diel period are tabulated in Table 3. Values are expressed in terms of both mg O₂/L, and g O₂/m² for consistency with the engineering and ecological literature, respectively.

Figure 6D contrasts nitrate loss observed during the diel study with that predicted by the model. During daylight hours, there was reasonably good agreement in terms of the magnitude and timing of the observed and predicted losses. The maximum loss rate observed (1.1 mg NO₃-N/L/hr) agreed well with the maximum loss rate predicted by the model. This peak loss rate at 1300 h was followed by a three-hour decline that coincided with CO₂ depletion at Station B (Figures 2E, 4, and 6D). When stream CO₂ levels recovered in the late afternoon, observed nitrate loss increased for two hours before sunset. Since NP is negative at night, the simple model put forth in this paper predicts that nitrate assimilation will also be negative at night, which would have resulted in nitrate increases in the reach during hours of darkness. Such increases were not observed. Nitrate loss generally continued during hours of darkness, but at a lower rate than during hours of daylight.

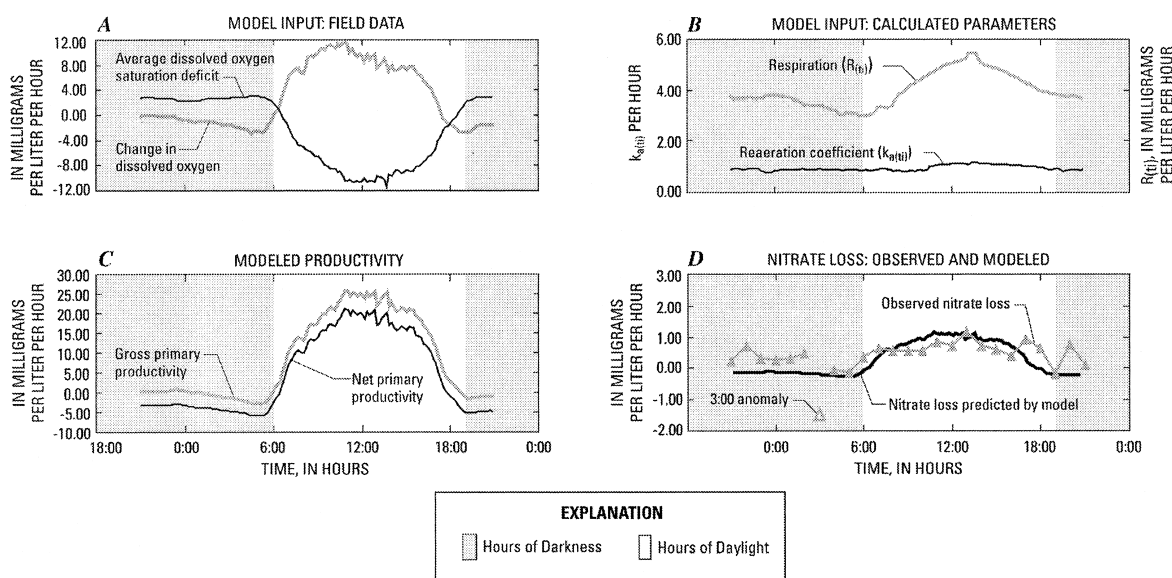


Figure 6. Diel Changes in Model Inputs (A and B) (additional input parameters included flow velocity, average depth, and water temperature); (C) Model Output Productivity; and (D) Nitrate Loss Observed and Modeled.

DISCUSSION

In stream ecology studies, nitrate loss and primary productivity are generally expressed in terms of mass per unit area, reflecting a focus on the benthic community (life on the stream bottom). In these terms the nitrate loss rate observed in Cucamonga Creek ($1.0 \text{ g/m}^2/\text{d}$) is high relative to many natural streams (Grimm, 1987; Triska *et al.*, 1989; Bachmann *et al.*, 1991), but is comparable to some agricultural streams (Isenhardt and Crumpton, 1989), and streams receiving treated wastewater (Crumpton and Isenhardt, 1987). The estimated GP for this study ($21 \text{ g O}_2/\text{m}^2/\text{d}$) is in the upper range of values found in the literature (Odum, 1956; O'Connell and Thomas, 1965; McDiffett *et al.*, 1972; Bott *et al.*, 1978; Erdmann, 1979; Sumner and Fisher, 1979; Bowie *et al.*, 1985; Warwick and McDonnell 1985b; Grimm, 1987; Lamberti and Steinman, 1997; Uehlinger *et al.*, 2002). The highest productivity of any study found (Crumpton and Isenhardt, 1987), was reported GP values for a stream in Iowa receiving treated wastewater equivalent to 23 to $64 \text{ g O}_2/\text{m}^2/\text{d}$.

Gross primary productivity observed in the present study of $21 \text{ g O}_2/\text{m}^2/\text{d}$, and the resulting nitrate uptake of $1.0 \text{ g N/m}^2/\text{d}$, does not appear to be exceptional on a mass per area basis. However, it is high on a mass per volume basis; $228 \text{ mg O}_2/\text{L}/\text{d}$ and $9.7 \text{ mg N/L}/\text{d}$, respectively. Reported values for GP in streams typically range from less than 1 to $175 \text{ mg O}_2/\text{L}/\text{d}$ (Erdmann, 1979; Warwick and McDonnell, 1985b; Grimm, 1987). Values for nitrogen uptake in natural and artificial streams typically range from negative (Triska *et al.*, 1993, observed small increases in stream nitrate concentrations in their study reaches) to about $6 \text{ mg N/L}/\text{d}$ (Van Kessel, 1977; Grimm, 1987; Bushong and Bachmann, 1989; Mariñelarena and Di Giorgi, 2001).

The rate of periphyton productivity in Cucamonga Creek was comparable to those of biological treatment systems that use algal and other biological processes, despite not being a system designed for this purpose. Biomass production values for biological systems typically range from 5 to $60 \text{ g dry weight/m}^2/\text{d}$. Therefore, the mean accumulation rate observed in Cucamonga Creek ($13.2 \text{ g dry weight/m}^2/\text{d}$) is in the range reported for these treatment systems. Such biological treatment systems include wetlands (Gersberg *et al.*, 1983; Phipps and Crumpton, 1994; Van Oostrom and Russell, 1994; Van Oostrom, 1995; Eriksson and Weisner, 1997; Stober *et al.*, 1997), tank mesocosms (Drenner *et al.*, 1997; Rectenwald and Drenner, 2000), artificial streams (Adey *et al.*, 1993, 1996; Craggs *et al.*, 1996; Mariñelarena and Di Giorgi, 2001), high rate algal ponds (Gianelli, 1971; Nurdogan and Oswald, 1995;

Green, *et al.*, 1996; Hoffmann, 1998; Mulbry and Wilkie, 2001; Wilkie and Mulbry, 2002), and wastewater treatment lagoons (Reed, 1984; Silva *et al.*, 1995; Green *et al.*, 1996; Hurse and Connor, 1999; Maynard *et al.*, 1999).

Similar to primary productivity, the nitrate loss rate observed in Cucamonga Creek was comparable to nitrogen loss rates observed in biological treatment systems. On a mass per area basis, the removal rates for these systems typically range from 0.001 to $4.56 \text{ g N/m}^2/\text{d}$, and in the Santa Ana Basin nitrogen removal rates range from 0 to $3 \text{ g N/m}^2/\text{d}$ (Reilly, 1994; Wildermuth Environmental Inc., 1998). The nitrate loss rate of $1.0 \text{ g NO}_3\text{-N/m}^2/\text{d}$ observed in Cucamonga Creek is higher than many of these treatment systems.

In Cucamonga Creek, the high rate of GP, on a per unit volume basis, results from the shallow stream depth. The high rate of GP caused daytime stream pH values as high as 10.5 standard units, complete CO_2 depletion for several hours, DO concentrations that exceeded 23 mg/L (greater than 300 percent saturation), and a diurnal variation in DO concentration of more than 19 mg/L . Such a diurnal variation in stream DO concentrations is as high as any ever reported. Another result of the shallow stream depth was that nighttime DO concentrations were not lowered as much as daytime values were raised (relative to saturation). Minimum DO concentrations during the diel study never reached levels considered to be anoxic (Mallin *et al.*, 2004).

Primary productivity and nitrate assimilation in Cucamonga Creek may have been affected by the availability of CO_2 . The time series graphs showing nitrate loss (Figures 3B and 6D) and DO (Figure 2C) concentrations seem to indicate a slowdown in both productivity and nitrate assimilation in the early afternoon. This slowdown in nitrate assimilation follows CO_2 depletion and a bicarbonate decline at Station B (Figure 4). Wood (1975, after Raven 1970) lists *Cladophora* as being capable of utilizing bicarbonates. However, switching to this alternate source of inorganic carbon might have slowed the rate of photosynthesis. In any case, the brief late afternoon recovery in nitrate loss rates appears to coincide with the reappearance of CO_2 and the recovery of bicarbonate concentrations at Station B (Figure 4).

In Cucamonga Creek, daytime nitrate loss rates were substantially greater than nighttime rates. However, observed nitrate loss continued during hours of darkness (Table 1, Figures 3B and 6D). This contrasts with what is predicted by the present simple model, which predicts uptake based on NP. Since NP is negative during hours of darkness, the model predicts nitrate gains (release) at night. In reality, metabolic release of nitrogen by algal mineralization would initially be in the forms of organic nitrogen,

and ammonia (Davis and Minshall, 1999; Warwick *et al.*, 1999), requiring the additional step of nitrification for nitrate to be added to the stream. The concentrations of organic nitrogen and ammonia generally did increase within the study reach (Table 1, Figure 3).

Nitrate losses in Cucamonga Creek during hours of darkness were probably not due to denitrification, although this is an important nitrate loss mechanism in many aquatic ecosystems (Van Kessel, 1977; Warwick and McDonnell, 1985b; Isenhardt and Crumpton, 1989; Bachmann *et al.*, 1991; Hinkle *et al.*, 2001; Webster *et al.*, 2003). Conditions in Cucamonga Creek, which include relatively high stream velocity, shallow depth, high DO minimum concentrations, and, especially, the lack of sediment, are not conducive to denitrification. Although a study on stream periphyton found that a modest amount of denitrifying activity can be performed by bacterial communities existing above the sediment within the *Cladophora sp.* mats themselves (Duff *et al.*, 1984a), the estimated maximum denitrification potential by those mat bacterial communities was equivalent to the consumption of less than 0.02 g NO³-N/m²/d. Grimm *et al.* (1981) also concluded that denitrification is generally not a significant nitrogen sink in Southwestern streams, partly due to the lack of nonalgal organic matter in these systems, a characteristic that these streams share with Cucamonga Creek.

Nitrate losses in Cucamonga Creek during hours of darkness may have been due to some delay between processes controlling these losses and the effects of these processes on nitrate concentrations at Station B. For example, there may have been a lag between photosynthesis and nitrate assimilation within the algal cells. Sciandra *et al.* (1997) found evidence of such a time lag between declines in algal nitrate assimilation rates and the extinction of a light source, and it has been suggested that continued assimilation after dark occurs through production and storage of adenosine triphosphate by photophosphorylation during hours of light (Thacker and Syrett, 1972).

The prolongation of observed nitrate losses until well after sunset may also have been due to variations in stream velocity caused by a spatial heterogeneity on the stream bottom (Dodds, 1991; Taylor *et al.*, 2004). Such heterogeneity, caused by the presence of the algal mats, may have lowered flow velocities in the areas of the mats, and delayed the arrival of some water at the downstream Station B. Some modelers account for such variations in stream velocity and their effects on stream nutrient cycling by using advection dispersion equations (Mulholland *et al.*, 1994). If a delay mechanism did exist between daytime processes controlling nitrate loss, and the observation of the loss, then one would expect the effects of this delay to decline throughout the night. Figure 6D

does appear to show a general pattern of decline in observed nitrate loss rates between the onset of darkness and early morning. Models that include a hydrodynamic component, like WASP6 (Wool *et al.*, 2003) or QUAL2E (Brown and Barnwell, 1987), could be used to test the hypothesis that a phase lag in flow is responsible for delays in observing nitrate loss at Station B.

To address continuous nitrate loss in streams, some models have used a two-equation approach which assumes a constant positive nitrogen assimilation rate at night, and a variable assimilation rate directly proportional to NP during daylight (Warwick and McDonnell, 1985a, 1985b). The two-equation approach is based on empirical data from several studies (some cited by Warwick and McDonnell, 1985a). The nighttime assimilation rate is related to algal processes since it is a function of the maximum rate of photosynthesis during the day.

Since this paper focuses on daytime processes, the nighttime values are not as of great concern. Observed nitrate loss was substantially greater during daylight hours than at night (Figures 3B and 6D), and the timing of daylight losses was in general agreement with nitrate uptake predicted by NP (Figure 6D). However, since the model did not predict the nitrate loss that occurred at night, the observed nitrate loss over the diel period (11 mg NO³-N/L/d, or 1.0 g NO³-N/m²/d) exceeded the loss predicted by the model (Table 4). If nitrate loss at night resulted from daytime productivity, then the average nitrate loss attributable to daytime processes value may have been underestimated. Since GP and NP were related to average daytime nitrate loss, then productivity may also have been underestimated.

Nevertheless, the rates of observed daytime nitrate uptake and algal accumulation are in reasonably good agreement, by Redfield stoichiometry, with the rates predicted by the model (Table 4). The model predicts that nitrate uptake rates will increase in the morning, remain steady during midday, and decline in the afternoon and evening. The observed nitrate loss rates follow a similar, but not as distinctive, pattern (Figure 6D). This is probably due to factors not considered in the model, such as those contributing to the observed nitrate loss during hours of darkness. In addition, the afternoon slowdown and subsequent recovery in nitrate loss rates, which may have been caused by the depletion and then return of carbon dioxide, could not have been predicted by this model.

In contrast to what was observed with nitrate, orthophosphate loss in the reach was substantially less than what the model predicted for phosphorus uptake. This might be expected since the model was calibrated for nitrate. However, a lack of correlation between phosphorus uptake and primary productivity

has been observed in other studies (Grimm *et al.*, 1981; Mulholland *et al.*, 1994), and this lack of correlation is not well understood. *Cladophora*, the dominant algae genus in the study reach, produces phosphatase, which may allow it to take up dissolved organic phosphorus (Lin, 1977), as well as orthophosphate. Spiraling, internal recycling, luxury uptake (Mantai, 1978), and intracellular storage (Wong and Clark, 1976) may also supply the P necessary for the observed productivity.

Relatively high nitrate and orthophosphate observed at both sampling stations make it unlikely that algal growth was nutrient limited in Cucamonga Creek at the time of this study. Nutrient concentrations were consistently above levels that would indicate eutrophic conditions, as well as levels of saturation for periphyton (Dodds *et al.*, 2002; Davis and Minshall, 1999).

The productivity observed during this diel study was probably close to the annual maxima for the stream reach. The study was limited to a single 24-hour period representing a relatively productive summer day. The variable thickness of periphyton on the channel bottom at Cucamonga Creek throughout the year likely affects the productivity and assimilative capacities of the algae. Short duration storm flows remove much of the standing crop at times, and the thick growth observed at other times may result in self-shading and reduced rates of photosynthesis (Dodds and Gudder, 1992). However, the nitrate loss observed in this study was not an isolated event. Prior sampling activities carried out on 10 different days throughout the year also showed that samples collected at Station B were consistently lower in nitrate concentrations than samples collected from locations upstream.

CONCLUSIONS

Cucamonga Creek is a concrete lined channel receiving discharges of treated wastewater. On a mass per volume basis, algal productivity and nitrate loss are exceptionally high there. The study used a simple model of primary productivity that related extraordinarily high observed daytime increases in dissolved oxygen concentrations to algal nitrate assimilation in the stream. A positive correlation between the elevated daytime concentrations of dissolved oxygen and pH, along with simultaneous decreases in bicarbonate and a temporary depletion of carbon dioxide, suggests that extraordinarily high primary productivity was controlling these stream conditions (Dodds *et al.*, 1991). The present study puts forth that this high primary productivity was responsible for the observed

instream nitrate loss rates. A number of previous studies have shown that algal assimilation can significantly contribute to nitrogen transformation in streams (Grimm *et al.*, 1981; Duff *et al.*, 1984b; Grimm, 1987; Crumpton and Isenhardt, 1987; Isenhardt and Crumpton, 1989; Kim *et al.*, 1992). Results from the model used here support the hypothesis that algal assimilation can account for nearly all of the observed nitrate loss in Cucamonga Creek. Nitrate loss rates there are comparable to biological systems designed to remove nitrate.

Algal mediated nitrate loss in Cucamonga Creek, a major tributary to the Santa Ana River, has important implications for water managers in the Santa Ana Basin. The Santa Ana River is used for recharging aquifers that provide water supply for more than two million people. Base flow in the Santa Ana River consists primarily of treated wastewater and, under base flow conditions, the river is almost entirely diverted to artificial recharge operations. Currently (2004), a regulatory framework is being developed to control nitrate in the basin (Wildermuth Environmental, Inc., 1998; California Regional Water Quality Control Board, Santa Ana Region, 2003). An important aspect of this regulatory framework considers the nitrate assimilative capacity of streams and aquifers in the Basin. The present study shows that nitrate assimilative capacity taking place in concrete lined channels can be significant.

The observed diurnal variability in nitrate assimilation has implications for monitoring programs, such as those used to evaluate TMDLs. If a single discrete value is used as representative of stream conditions, then loads can be underestimated or overestimated depending on the time of day when the sample was collected. Since monitoring programs generally collect samples during the day, the nitrate TMDL in a stream such as Cucamonga Creek would likely be underestimated because daylight concentrations of nitrate are lower than nighttime concentrations due to algal assimilation.

Concrete lined channels are commonplace in urban environments. They have been poorly studied from an ecosystem perspective despite their prevalence and a generally accepted expectation that they would differ in function from natural streams. Odum (1956:112) observed: "It may be found eventually that the most productive communities in existence are those in polluted streams." Results from the present study suggest that concrete lined flood control channels with characteristics like those of the study reach (high light exposure, high nutrient water, and relatively high velocity flow) can exhibit productivity and nutrient assimilation at rates well above those found in natural streams. This finding is contrary to the widely held belief that urbanization reduces the capacity

of riverine biological communities to remove excess nutrients (McClain *et al.*, 1998). The results from this study suggest that radically altered channels can provide a valuable environmental service, the lowering of nitrate concentrations in treated wastewater. Such environmental services arise when systems self-organize to maximize available resources (Odum, 1996).

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