Controls on pH and Ammonia Toxicity in Rivers of the Colorado Plains

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Executive Summary

1) Temperature directly affects the numeric standards for ammonia in warm-water streams of Colorado, but temperature also can affect ammonia standards indirectly through interactions that link climate, metabolic processes, and pH. Recent monitoring data for Plains rivers, in combination with results of studies of oxygen metabolism, suggest that the balance between photosynthesis and respiration favors high pH when temperature is high.

2) Samples and field measurements were collected between July 2010 and May 2011 at four stations, in order to determine the relative importance of temperature, hydrologic variables, and biomass of benthic algae in controlling pH in Plains streams and rivers.

3) Across the sampling stations, biomass of benthic algae (as chlorophyll a) remained low when depth was greater than ~0.35 m; below this depth threshold, algal biomass was able to accumulate when other factors were not limiting to growth. For a given location, the depth threshold of ~0.35 m can be translated into a discharge threshold for removal of algal biomass, thus providing a basis for analysis of historical records or for modeling.

4) The potential for metabolic control of pH is highest at low discharge and especially after extended periods of low discharge.

5) Neural-network modeling showed, for a given location, a strong relationship between discharge and pH. Temperature, time of day, and recovery (time since a critical flow for removal of periphyton biomass) affect pH at low discharge, but not when discharge is high. Although neural network modeling will be improved by additional field studies over several years, these relationships demonstrate strong potential for predictions of the effects of climate variation or changes in water management on pH in Plains rivers.

6) Preliminary modeling suggests that climate warming may lead to a modest increase in pH for Plains rivers. The most important factors affecting pH, however, are related to hydrologic variation and changes in water management, both of which can affect the patterns of accumulation for periphyton biomass.

Introduction

For permitted discharges to warm-water streams in Colorado, application of the current (AMMTOX modeling) ammonia standards for protection of aquatic life results in stricter chronic ammonia limits compared with limits consistent with the previous (CAM modeling) standards. At low temperatures (< 15°C when early life stages are present, < 7°C when early life stages are absent), the chronic ammonia standard is determined largely by pH; at higher temperatures, temperature has an increasing role in determination of the chronic standard (Figure 1). For a given value of pH, an increase in temperature results in a decrease in the numeric ammonia standard, at least for warm temperatures. Thus, climate variation (including climate warming) directly affects the numeric standards for ammonia, particularly in warm waters (e.g., Plains rivers).

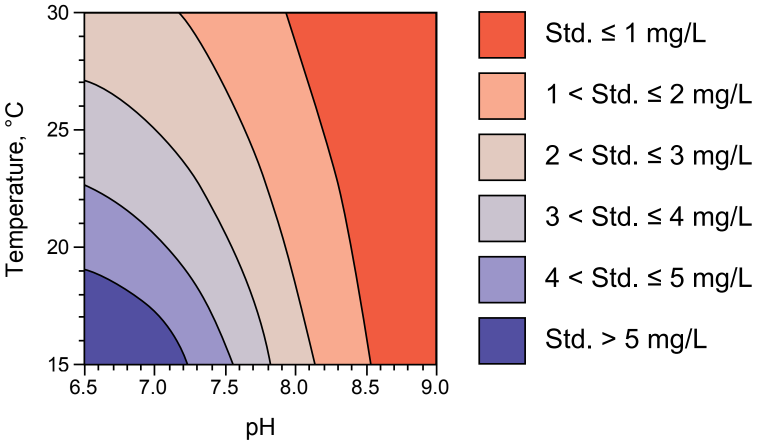

Figure 1. Variation in the chronic AMMTOX standard (early life stages present) with temperature an pH.

In addition to the direct effects of temperature variation on numeric standards for ammonia, climate variation affects ammonia standards indirectly through interactions that link climate, metabolic processes, and pH. Due to high treatment costs associated with ammonia removal, adoption of the new ammonia standards has already led to considerable interest in pH and processes affecting pH. Recent monitoring data for the South Platte River and Boulder Creek also draw attention to processes affecting pH in Plains rivers and streams and raise questions about potential effects of climate variation on pH[1]. Interactions among factors affecting pH in running

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[1] Concurrent observations of high temperature and high pH in Boulder Creek suggest a link between climate and processes affecting pH. Such a link also is suggested by similarities in temporal patterns of pH across multiple locations on the South Platte main stem and tributaries between Denver and the confluence with the St. Vrain.

waters are complex and not well quantified. Thus, predicting the effects of climate variation on numeric standards for ammonia will require a better understanding of the factors controlling pH.

In aquatic ecosystems, photosynthesis and respiration often are the most important metabolic processes affecting pH. Photosynthesis produces oxygen and raises pH; aerobic respiration consumes oxygen and lowers pH. Temperature regulates rates of photosynthesis, community respiration, and other metabolic processes, and these rates are strongly influenced by inter-annual climate variation and also changes in climate over longer periods of time. Rates of photosynthesis and respiration in running waters also are influenced by hydrologic changes, including those associated with climate variation or water management (Cronin et al. 2007).

As with other biogeochemical processes, rates of photosynthesis and respiration typically increase with increasing temperature, up to an optimal range of temperature; beyond the optimal range, rates decline. Because temperature-response curves for different metabolic processes are not the same, the balance between photosynthesis and respiration may change with seasonal or long-term variations in temperature. Metabolism data for a site on the South Platte River show that the upper bounds for both photosynthesis and respiration increase with temperature between 5°C and 25°C, but the rate of photosynthesis increases faster than the rate of respiration; thus, the upper bound for net metabolism (the sum of photosynthesis and ecosystem respiration) may increase with temperature in Plains rivers, and the probability of positive net metabolism (i.e., a shift in the metabolic balance that leads to high pH) may increase above 20°C (Figure 2). There are many values of net metabolism that fall below the upper boundary shown in Figure 2, which suggests that factors other than temperature often control the balance between metabolic processes. Nonetheless, temperature appears to be an important factor controlling net metabolism under conditions that could lead to extreme values of pH in Plains rivers and streams.

Although temperature can affect metabolic processes and pH, hydrologic changes associated with climate variation also can affect rates of ecosystem metabolism and pH. Flows of sufficient magnitude to mobilize sediments across the entire stream bed remove algal biomass and reduce rates of benthic photosynthesis to near zero. Flows of lower magnitude also can affect

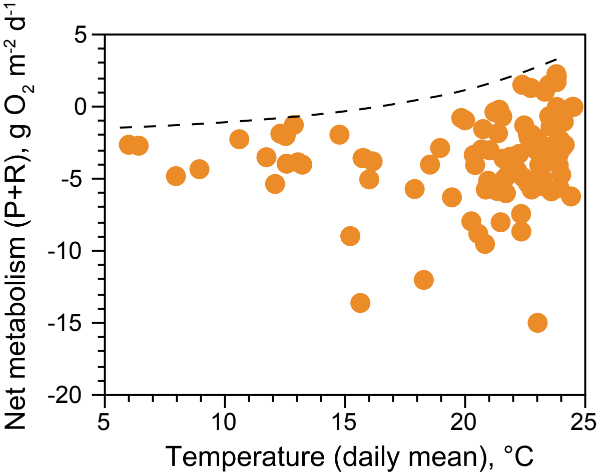

Figure 2. Net metabolism (the sum of photosynthesis and ecosystem respiration) as a function of daily mean temperature, for a site on the South Platte River near County Rd. 24.5 (G. Cronin and J. McCutchan, unpublished data).

rates of photosynthesis in running waters because some bed movement can occur even at modest flows and also because sloughing of algal cells may occur at flows below the threshold for bed movement (Segura et al. 2010, Cronin et al. 2007, Horner and Welch 1981). Once in transport, most algal cells sloughed from periphyton communities probably do not persist over long distances, but transported algae do account for a small fraction of net metabolism in the South Platte River (C. Baroch and J. McCutchan, unpublished data[2]).

Objectives: The main objective of this study of the South Platte River and Boulder Creek is to determine the relative importance of factors affecting pH in Colorado Plains rivers. Factors considered here include temperature, hydrologic variables, and biomass of benthic algae (as chlorophyll *a*). Some preliminary goals will be to determine for each sampling location the rate at which algal biomass accumulates, critical flows above which biomass of algae is lost, and relationships between algal biomass, hydrologic conditions (e.g., flow volume and time since a critical flow), and pH. Empirical (statistical) relationships developed from field studies will ultimately provide a basis for understanding and modeling how future changes in climate and water management may affect metabolic processes in Plains streams and rivers, water quality, and treatment costs for domestic wastewater. Empirical relationships developed from field studies

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[2] Photosynthetic rates for transported algae can approach 10% of the rates for the entire algal community (benthic plus transported algae) in the South Platte River below Denver. Most of the algal cells in transport near Denver, however, are planktonic forms rather than dislodged benthic algae.

also will make possible analyses of historical records of discharge, temperature, and pH.

Methods

Field sampling: Samples and field measurements were collected between July 2010 and May 2011 at three stations on the South Platte River and one station on Boulder Creek (Table 1). Sampling at one station on the South Plate (SP-64) was stopped in late 2010 after a construction project just downstream altered the hydrologic conditions at this station.

Station name	Station ID	# sampling dates
South Platte River at 64th. Ave.	SP-64	9
South Platte River at 88th. Ave.	SP-88	15
South Platte River near Co. Rd. 24.5	SP-RD24.5	9
Boulder Creek at 107th. Street.	BC-107	8

Table 1. List of sampling stations on the South Platte River and Boulder Creek.

On each sampling date, depth and mean velocity (i.e., velocity at 0.6 x depth) were measured at five points along each of three or more transects across the channel; normally, points along transects were spaced equally across the channel, but spacing of points was compressed and transects did not cover the full width of the channel on some dates with high flow. At each location where depth and velocity were measured, pH, temperature, dissolved oxygen, and specific conductance were measured at mid depth with a YSI sonde, and a core of surface sediments (upper 2-5 cm) was collected for analysis of benthic chlorophyll *a*. Sediment cores were held on ice and in darkness for transport to the laboratory.

Laboratory analyses: In the laboratory, cores of surface sediments were stored in darkness at -20°C prior to chlorophyll analysis. Samples were lyophyllized, and chlorophyll was analyzed by hot ethanol extraction (with sonication), followed by spectrophotometry (Marker et al. 1980, Nusch 1980, Lewis and McCutchan 2010).

Hydrologic records and channel geometry: Records of daily mean discharge for three gaging stations on the South Platte River are relevant to the present study: Commerce City (USGS 06714215 South Platte River at 64th. Ave), Henderson (DWR PLAHENCO South Platte River at Henderson), and Ft. Lupton (USGS 06721000 South Platte River at Ft. Lupton). For points along the South Platte below 64th. Avenue, records of discharge were derived from a flow-accounting model that includes gage records, additions from gaged tributaries and effluent discharge, ditch diversions, and ungaged flows (calculated from flow residuals between main stem gages). Records of daily mean discharge for points along Boulder Creek between the Boulder gage (USGS 06730200 Boulder Creek at N. 75th. Street) and BC-107 were derived by the same flow-accounting method.

Estimates of mean flow velocity and mean channel depth for each station are available from velocity-depth profiles across multiple transects, as described above; because transects did not extend across the full width of the channel on some dates when flow was high, estimates of mean channel depth used for statistical analyses were calculated from records of discharge and channel geometry equations derived from calibration data for gages (Figure 3).

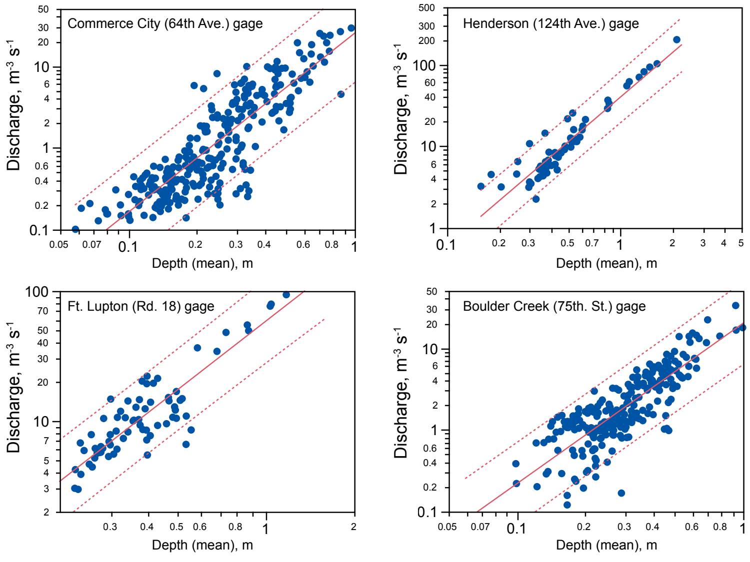

Figure 3. Relationships between mean depth and discharge for gages on the South Platte River and Boulder Creek.

Statistical analyses: Stepwise linear regression often can be used successfully for development of empirical (statistical) relationships for use in simulation modeling, but other approaches sometimes are necessary when responses are strongly non-linear and cannot easily be linearized (e.g., through log transfomation). Artificial neural network modeling provides a highly flexible alternative to linear approaches and is useful for finding patterns in complex data sets. The Neural Net platform in JMP ver. 9 (SAS, Cary, NC) was used to develop empirical models to predict pH in Plains rivers.

Results

At each sampling location, paired measurements of benthic chlorophyll and flow velocity identified a threshold for velocity above which chlorophyll concentration was consistently low; for velocities below the threshold, measurements of benthic chlorophyll spanned a range of values from high to low (Figure 4). If mean velocity over the water column is above the threshold, algal growth is inhibited by flow conditions that lead to sloughing of algal cells, bed movement, or abrasion of cells by transported sediment; below the threshold, algal biomass can accumulate if other requirements for growth (e.g., light, temperature, nutrients) are met. Because it can take weeks for benthic algal communities in the South Platte River to reach peak photosynthetic rates (Cronin et al. 2007), and presumably peak biomass, benthic chlorophyll can be low even when velocity is well below the threshold for biomass removal and other requirements for algal growth are met. Biomass may be removed almost instantaneously by spates, but recovery is not instantaneous. During this study, velocity thresholds across the sites ranged from ~0.4 m/s at BC-107 to ~0.9 m/s at SP-64. The threshold value for biomass removal was not as clearly defined at SP-64 as for the other sites, and the most clearly defined threshold was observed at SP-RD24.5. These differences in response to changes in velocity probably are related to differences in sediment grain size across sites. SP-RD24.5 has the finest sediment grain size and SP-64 has the coarsest sediment.

At each station, the chlorophyll concentration was low when depth was greater than ~0.35 m; below the depth threshold, benthic chlorophyll varied over a wide range (Figure 5).

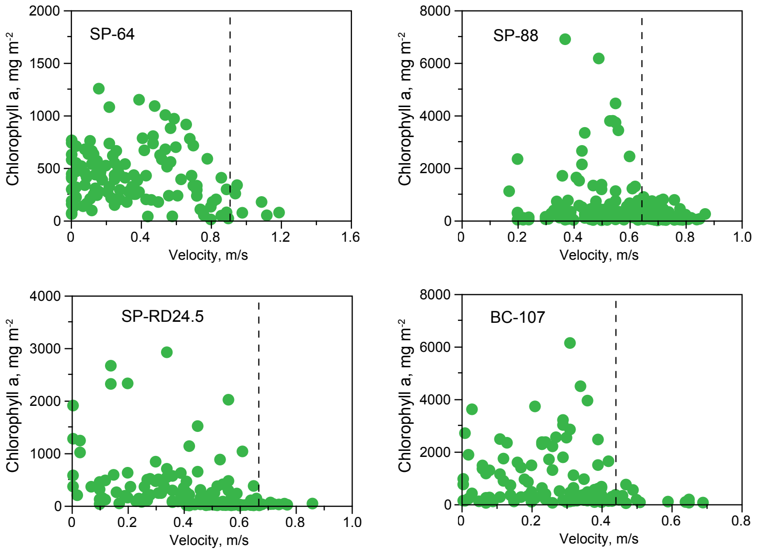

Figure 4. Relationships between benthic chlorophyll and flow velocity for each of the four sampling stations. Dashed lines show the approximate thresholds for removal of algal biomass.

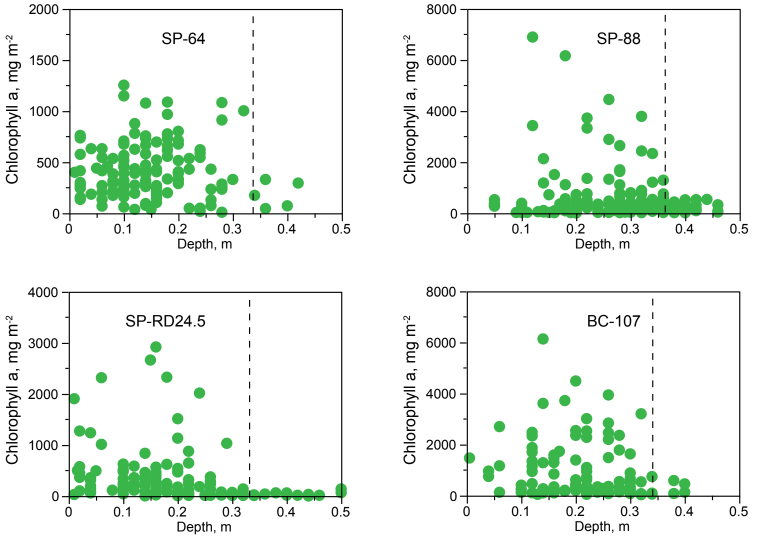

Figure 5. Relationships between benthic chlorophyll and depth for each of the four sampling stations. Dashed lines show the approximate thresholds for removal of algal biomass.

Although the relationships between benthic chlorophyll concentration and depth are generally similar to those between benthic chlorophyll and mean velocity (Figure 4), the depth thresholds for biomass removal are more consistent across sites (~0.34-0.36 m) than are the corresponding velocity thresholds.

For comparisons across sites or generalized modeling of periphyton accrual in Plains streams, depth is a more consistent predictor of the potential for periphyton accrual than is mean velocity over the water column; this consistency holds even across a wide range of sediment grain size. From channel-geometry equations relating depth and discharge (Figure 3), it is possible to equate depth thresholds for periphyton accrual to equivalent thresholds of discharge (Table 2). Thus, gage records in combination with channel-geometry equations relating depth and discharge provide essentially continuous records of the potential for periphyton accrual, during the study period or for other periods of time.

Station ID	Depth threshold, m	Discharge threshold, cfs	Discharge threshold, $m^3 s^{-1}$
SP-64	0.34	95	2.7
SP-88	0.36	223	6.3
SP-RD24.5	0.33	343	9.7
BC-107	0.34	113	3.2

Table 2. Thresholds (depth and discharge) for periphyton removal at sampling stations on the South Platte River and Boulder Creek.

When sampling began in 2010 after peak snowmelt runoff, mean benthic chlorophyll was low at each of the four stations. The maximum concentration of benthic chlorophyll over the study period was <1000 mg m^{-2} at SP-64 and SP-RD24.5 and >2000 mg m^{-2} at SP-88 and BC-107 (Figure 6). At SP-64, the mean chlorophyll concentration increased rapidly through August and September when discharge was near the threshold for biomass removal, and benthic chlorophyll concentration was lower in autumn after brief periods of higher discharge (Figure 6). Sampling at SP-64 was discontinued in late 2010 due to a construction project downstream that altered hydrologic conditions at this station. At SP-88, benthic chlorophyll did not show a substantial increase until fall and increased slowly over the winter and early spring, during which time discharge remained near the threshold for biomass removal; chlorophyll increased rapidly just before snowmelt runoff. At SP-RD24.5, periphyton biomass fluctuated over the year; discharge fell below the threshold for biomass removal in September but rose above the threshold in November. At BC-107, benthic chlorophyll increased sharply between December

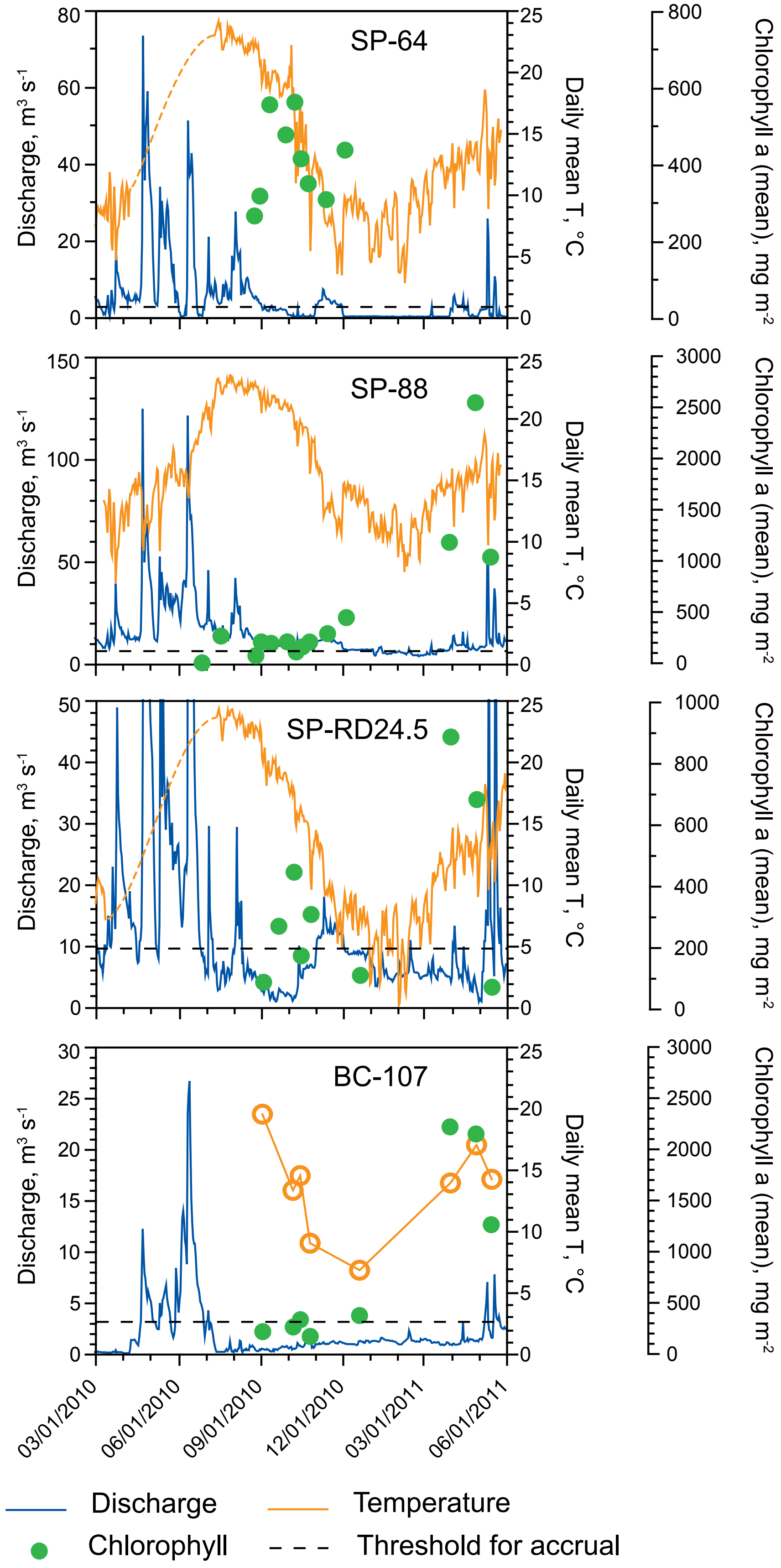

Figure 6. Temporal changes in benthic chlorophyll *a* (mean), discharge, and temperature at each of the study locations. On each panel, the threshold for removal of algal biomass is shown by a dashed line. No samples for chlorophyll analysis were collected where depth was greater than 0.5 m; especially during times of high discharge, sampling over the entire reach would have produced lower values for mean benthic chlorophyll.

and April. It is important to note that no samples were collected at depths greater than 0.5 m; thus, mean chlorophyll concentrations shown in Figure 6 underestimate means across the entire channel, especially at high discharge.

Across the four sampling stations, temporal variations in pH were closely related to seasonal changes in temperature (Figure 7). At each station, the highest pH values during the year occurred when temperature was high, and the lowest pH values occurred during winter. Examination of previous monitoring data collected by Metro District staff indicate that the maximum pH over the year often occurs shortly after the date of maximum temperature. The pH values presented in Figure 7 reflect means over the period of sampling (typically between 9:00 and 16:00) rather than daily means, so the patterns reported here are affected somewhat by variations in the time of sampling.

Analysis of historical flow records: Analysis of historical flow records (January 2001 - May 2011) for the four sampling stations shows differences among the sites in the frequency of flows below the threshold for biomass removal (Figure 8). Over this ten-year period, the median flows for SP-64 and SP-RD24.5 were below the corresponding thresholds for biomass removal, but flow exceeded the threshold on many dates at each location. At SP-88, discharge exceeded the threshold for biomass removal on >75% of dates. At BC-107, discharge rarely exceed the threshold for biomass removal.

Time-series plots of recovery duration illustrate the temporal patterns of hydrologic control over periphyton accrual at each location (Figure 9). Recovery is defined here as the time in days since discharge last exceeded the flow threshold for biomass removal (see Table 2); each time discharge exceeds the flow threshold, the duration of recovery is reset to zero. Over this 10-year record, SP-64 and SP-RD24.5 experienced a wide diversity in the length of recovery periods, including many brief periods of two weeks or less but also periods of 60 days or more. Recovery periods of 60 days or more were more frequent during years of low discharge (e.g., the drought of 2002-2003) but also occurred in years with higher discharge. At SP-88, there were typically two or three periods of recovery longer than ten days in a given year, but the duration of

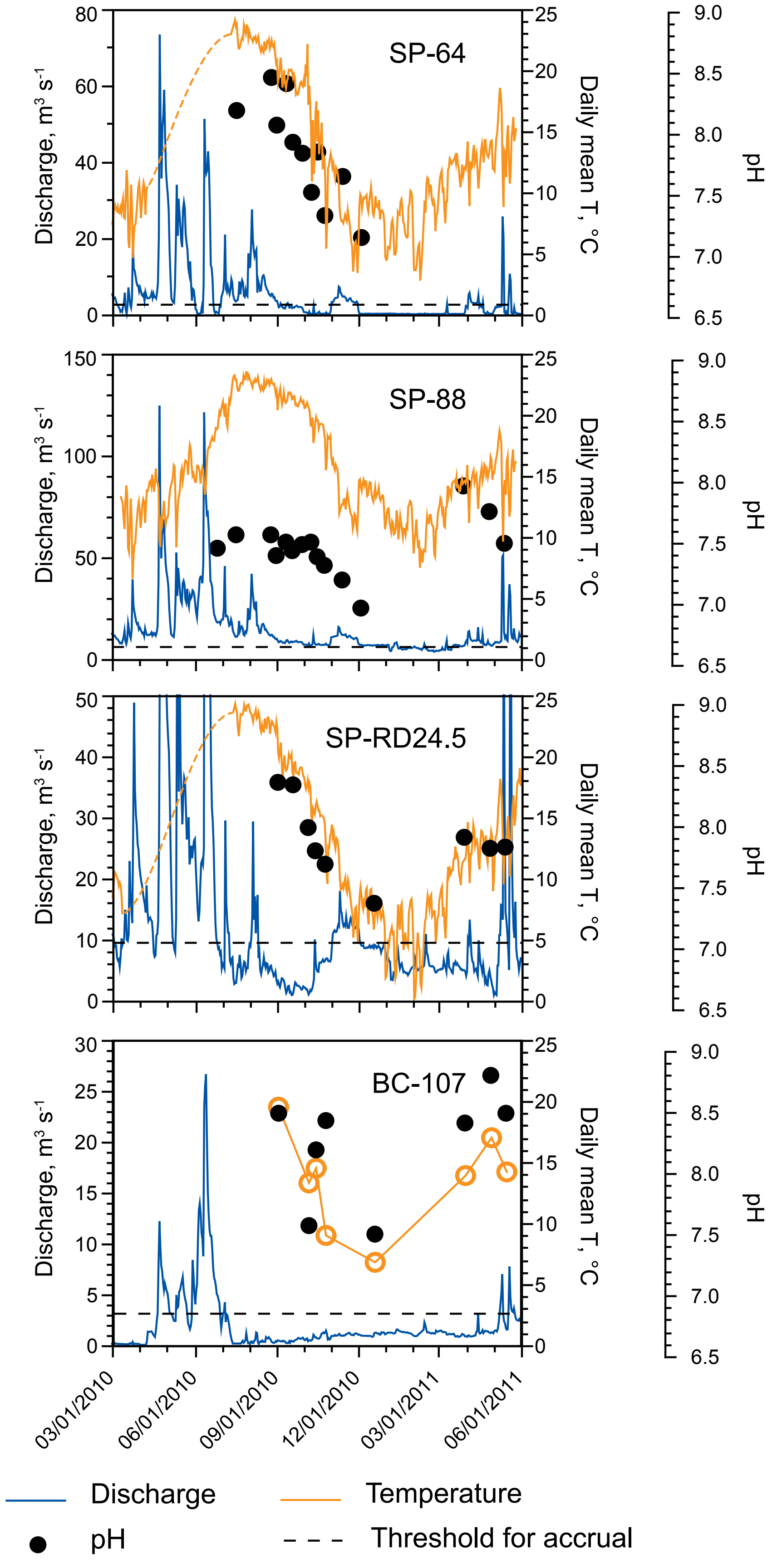

Figure 7. Temporal changes in pH (mean over the period of sampling), discharge, and temperature at each of the study locations. On each panel, the threshold for removal of algal biomass is shown by a dashed line.

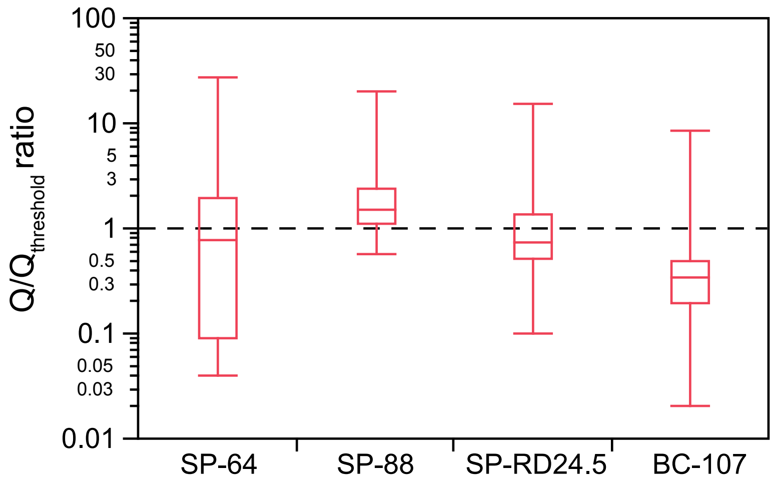

Figure 8. Box plots showing the distribution of $Q/Q_{threshold}$ (ratio of discharge to the discharge threshold for biomass removal) for each of the study sites. Biomass is removed at values of $Q/Q_{threshold} > 1$.

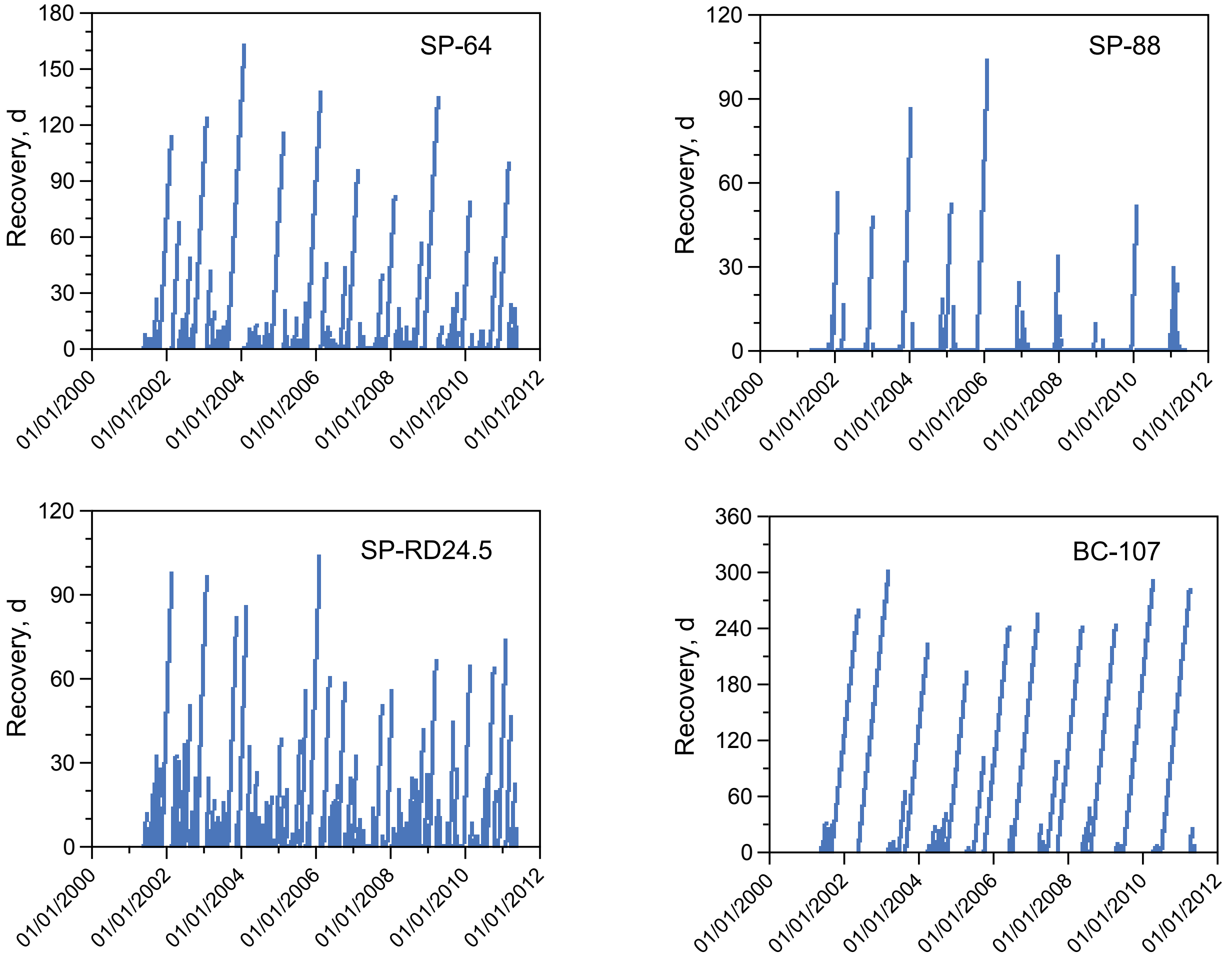

Figure 9. Ten-year reconstructions of recovery for the study locations. Uninterrupted lines show continuous periods of recovery for accumulation of periphyton biomass.

recovery rarely exceeded 60 days. At BC-107, periods of recovery lasted 180 days or more each year.

Neural network model: Models were developed with the Neural Net platform in JMP to predict pH from four variables: mean depth of the channel, mean daily temperature, time of day, and recovery. As explained above, recovery is defined here as the time in days since discharge exceeded the flow threshold for biomass removal, and duration of recovery is reset to zero each time discharge exceeds the flow threshold. The addition of other variables (i.e., hydrologic variables or benthic chlorophyll) to the models did not improve predictive capability. The best general models (i.e, models that do not include site designation as a variable) accounted for >70% of variance in pH. Some site-specific models accounted for an even greater proportion of variance, but site specific models are not useful for regional modeling.

Results of one general model are shown in Figure 10. Each row of panels shows the response curves for a particular combination of depth, temperature, time of day, and recovery. Mean depth of the channel has a large effect on pH. When depth or discharge is low (upper row of panels), pH increases with increasing temperature, and time of day also has a strong effect on pH. At intermediate depth or discharge (middle row of panels), pH is more responsive to

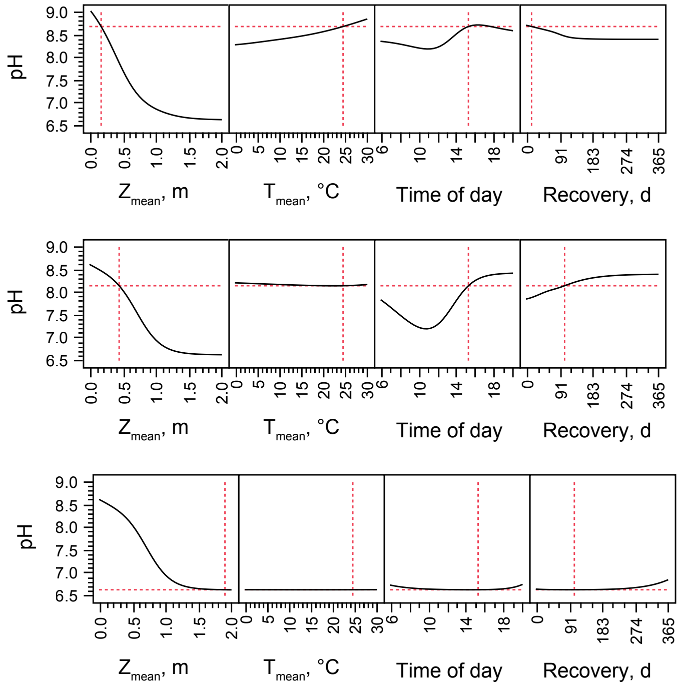

Figure 10. Results of neural network model to predict pH from depth, temperature, time of day, and recovery (time since discharge exceeded the flow threshold for biomass removal; when discharge exceeds the flow threshold, the duration of recovery is zero).

variation in time of day and recovery than to variation in temperature. When depth or discharge is high (bottom row of panels), variables other than depth have little effect on pH.

Discussion

Adoption of the new, stricter ammonia standards for warm waters in Colorado has led to strong interest in factors controlling pH, and standards may be even stricter in the future. Potential links between climate variation and pH also contribute to the need for a quantitative understanding of factors controlling pH in Plains streams and rivers. The factors directly affecting pH in running waters are generally well understood, but the complex and indirect relationships that link temperature and hydrology with pH have hampered attempts at quantitative modeling. Consequently, the potential effects of climate variation on pH in Plains rivers and streams have been difficult to predict under future climate scenarios or in response to changes in water management.

A recent study of the South Platte River (Cronin et al. 2007) showed that analyses based on calculation of Shield's stress and empirical measurements of ecosystem metabolism can be used to forecast metabolic change in rivers, and this approach could be applied to pH. However, the approach taken by Cronin and his colleagues depends on specialized survey equipment and cannot easily be applied to multiple locations. In contrast, the results presented here are based on simple methods that can be applied routinely and furthermore demonstrate potential for both site-specific and regional modeling. Neural network modeling is particularly well suited to the nonlinear relationships that control pH (Figure 10). Precision of modeling could be improved by additional field studies (e.g., 5 years of data for several sites instead of 1 year), but even the modest data set derived from this study was sufficient to characterize important mechanistic controls on pH.

In Plains rivers, net oxygen metabolism can increase rapidly when flows remain below the threshold for biomass removal (Cronin et al. 2007), and periphyton biomass can reach very high levels after extended periods of low flow (Figure 11). Thus, changes in climate that lead to lower flows and longer periods of low discharge are likely to result in higher biomass of benthic

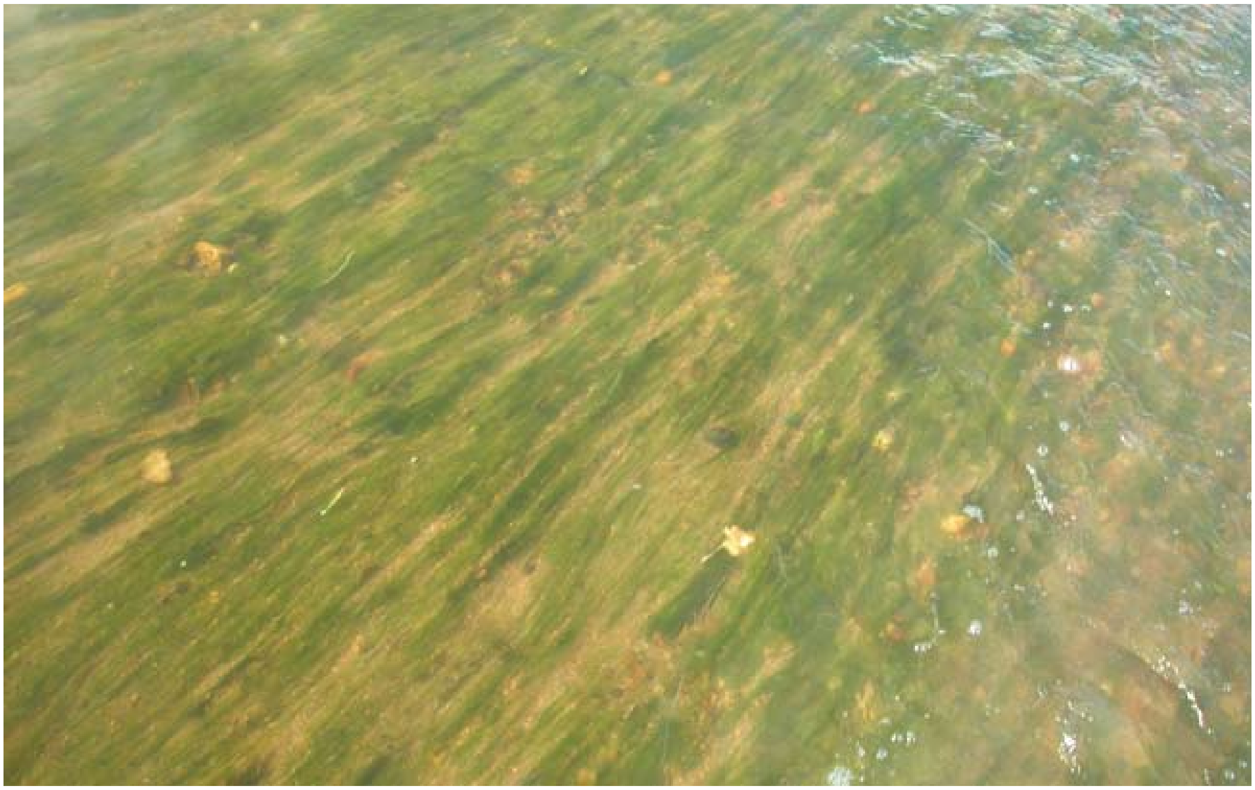

Figure 11. High biomass of benthic algae that is typical in many Plains rivers after extended periods of low discharge. Note cottonwood leaves for scale.

algae and higher pH in Plains rivers. The preliminary modeling presented here suggests that variation in pH for Plains rivers is controlled largely by hydrologic variables related to discharge (i.e., depth, velocity), duration of recovery, and temperature. At low to moderate depth or discharge, duration of recovery has an important effect on pH. Although modeling suggests that the effect of temperature on pH is trivial at moderate or high discharge (Figure 10, middle and lower panels), the direct effect of a temperature increase of 2-4°C (i.e., similar to the expected increase in summer temperatures by 2050; Ray et al. 2008) is consistent with an increase in pH of 0.10-0.15 units (Figure 10). The effect of temperature on pH is small in relation to the effect of hydrologic variables, but the effect of temperature is greatest under conditions when pH is already high. Changes in precipitation for the Colorado Plains over the next several decades are difficult to predict (Ray et al. 2008), and because population and water use in Colorado could nearly double by 2050 (CWCB 2010), changes in water management and population also must be considered. However, the analyses presented here provide a basis for modeling the effects of climate variation and changes in water management on pH for Plains rivers.

Acknowledgements

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