

**Rapid #: -2612503**

**Ariel**  
**IP: 129.219.247.60**

---

**CALL #:** [http://condor.library.colostate.edu/sfxicl3?url%5Fver=Z39.88 ...](http://condor.library.colostate.edu/sfxicl3?url%5Fver=Z39.88...)  
**LOCATION:** **COF :: EJournals :: Highwire Press American Society of Agronomy:Full Text**  
TYPE: Article CC:CCG  
JOURNAL TITLE: Journal of environmental quality  
USER JOURNAL TITLE: journal of environmental quality  
COF CATALOG TITLE: Journal of environmental quality  
ARTICLE TITLE: Nutrient variation in an urban lake chain and its consequences for phytoplankton production  
ARTICLE AUTHOR:  
VOLUME: 38  
ISSUE:  
MONTH:  
YEAR: 2009  
PAGES: 1429-1440  
ISSN: 0047-2425  
OCLC #:   
CROSS REFERENCE ID: 603646  
VERIFIED:

**BORROWER:** **AZS :: Main Library**  
**PATRON:** **Nation,Marcia**  
PATRON ID:  
PATRON ADDRESS:  
PATRON PHONE:  
PATRON FAX:  
PATRON E-MAIL: [marcia.nation@asu.edu](mailto:marcia.nation@asu.edu)  
PATRON DEPT: Hayden Interlibrary Loan Counter, Tempe Campus  
PATRON STATUS: Academic Profes  
PATRON NOTES:



This material may be protected by copyright law (Title 17 U.S. Code)  
System Date/Time: 6/16/2009 9:43:10 AM MST

---

## Nutrient Variation in an Urban Lake Chain and its Consequences for Phytoplankton Production

W. John Roach SimBiotic Software

Nancy B. Grimm\* Arizona State University

In the Central Arizona–Phoenix (CAP) ecosystem, managers divert mixed stream water and groundwater to maintain an artificial lake chain in Indian Bend Wash (IBW), a historically flashy, ephemeral, desert stream. Nutrient concentrations in the CAP ecosystem's groundwater, stream water, and floodwater differ: stream water has low concentrations of both inorganic N and P, while groundwater is low in inorganic P but rich in nitrate ( $\text{NO}_3^-$ ). Consequently, groundwater contribution drives inorganic N concentrations in the lake chain. In contrast, floodwater typically has high P concentrations while remaining low in N. Thus we expected N and P concentrations in IBW lakes to vary with the mix of water flowing through them. Elevated  $\text{NO}_3^-$  and low inorganic P concentrations were predicted when groundwater pumping was pronounced and this prediction was supported. We hypothesized that these predictable changes in water chemistry would affect nutrient limitation of phytoplankton. Laboratory nutrient-addition bioassays demonstrated that phytoplankton growth was P-limited throughout the summer of 2003 when N/P was high. However, after a late-season flood drove N/P below 31:1, the expected threshold between N and P limitation, N limitation was observed. Our results indicate that effects of floods, the preeminent historic drivers of Sonoran Desert stream biogeochemistry, are mitigated in urban ecosystems by decisions about which spigots to turn. Consequently, nutrient limitation of urban streams is driven as much by management decisions as by natural hydrologic variation.

URBANIZATION affects both hydrologic and biogeochemical cycles through the deliberate human modification of fluvial ecosystems (Paul and Meyer, 2001) and through intentional and inadvertent nutrient enrichment of urban landscapes (Baker et al., 2001; Grimm et al., 2008). Cities grow as pristine forest, desert or grassland ecosystems are developed, or as agricultural fields are replaced with housing. Invariably such land-use and land-cover changes produce myriad effects on ecosystem processes (Foley et al., 2005), including altered nutrient cycling in aquatic ecosystems (Groffman et al., 2004; Williams et al., 2004). Streams and lakes are particularly vulnerable to land-use changes that result in increased nutrient loading (Carpenter et al., 1998). Because of this vulnerability, Williamson et al. (2008) argue that aquatic ecosystems are good sentinels of both terrestrial and aquatic environmental change. They contend that ecosystem metabolism of lakes and streams, which is influenced by external nutrient loadings that integrate catchment sources, provides critical information on the functioning of the broader landscape. This paper reports a study of how the extensive hydrologic engineering that accompanied growth in a catchment of the CAP ecosystem has affected temporal patterns of a key limnological phenomenon, nutrient limitation of primary production. We investigated temporal patterns of nutrient limitation in a string of artificial urban lakes in IBW, a historically ephemeral desert stream that once drained most of what is now Scottsdale, AZ. Today, IBW lakes are maintained at baseflow by additions of water from groundwater wells and from canals that supply a mixture of groundwater and surface water. During storms, the system experiences flash floods similar to those of unaltered desert streams (Roach et al., 2008).

We focused on N and P, the macronutrients that most frequently limit primary production in aquatic ecosystems (Downing and McCauley, 1992). Recent meta-analyses and empirical studies

Copyright © 2009 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Published in *J. Environ. Qual.* 38:1429–1440 (2009).  
doi:10.2134/jeq2008.0191

Received 24 Apr. 2008.

\*Corresponding author (nbgrimm@asu.edu).

© ASA, CSSA, SSSA

677 S. Segoe Rd., Madison, WI 53711 USA

W.J. Roach, SimBiotic Software, 407 E. Main St., Missoula, MT 59802; N.B. Grimm, School of Life Sciences, Arizona State Univ., P.O. Box 874501, Tempe, AZ 85287. Research was performed at Arizona State University.

**Abbreviations:** CAP, Central Arizona–Phoenix; DIN, dissolved inorganic nitrogen, which is the sum of ammonium and nitrate; IBW, Indian Bend Wash; L-1, L-2, L-3, L-4, L-5, L-6, L-7, & L-8, consecutive artificial lakes along Indian Bend Wash (from upstream to downstream); N, nitrogen;  $\text{NH}_4^+$ , ammonium;  $\text{NO}_3^-$ , combined nitrate and nitrite; N/P, molar ratio of dissolved inorganic nitrogen to soluble reactive phosphorus;  $N_0$  and  $N_t$ , in-vivo fluorescence of phytoplankton incubation at time 0 and time  $t$ ;  $r$ , exponential growth rate;  $Q_{\max}$ , maximum average daily discharge during flood event; Roos. Well, a groundwater well located on Roosevelt Street delivering water directly to Indian Bend Wash; SRP, soluble reactive phosphorus; TDP, total dissolved phosphorus.

challenge the conventional wisdom that P limits all freshwater ecosystems and N limits all coastal marine ecosystems (Elser et al., 1990, 2007). Stoichiometric theory posits that, all else being equal, when the N/P ratio of a nutrient source is higher than that of algae, P should be limiting; conversely, when the N/P ratio of the nutrient supply is lower than that of algae, N should limit growth (Downing and McCauley, 1992). Downing and McCauley (1992) examined the relationship between total N and total P concentrations in 221 lakes from 14 countries in an attempt to empirically determine where the threshold between N and P limitation lies. They concluded that lakes with molar N/P ratios <31 were more likely to be N limited than those with higher N/P ratios, especially if total P concentration was >1.0  $\mu\text{mol L}^{-1}$ . If total P concentration was <1.0  $\mu\text{mol L}^{-1}$ , growth tended to be P limited regardless of the N/P ratio.

How then does urbanization affect the relative availability of N and P in aquatic ecosystems? Numerous studies have documented that urban streams experience elevated loading of N and, to a lesser extent, of P. High loading has been ascribed to changes in land use and associated elevated inputs from fertilization (Bernhardt et al., 2008), as well as increased atmospheric deposition (Lovett et al., 2000). Increases in impervious surface area result in rapid transport of stormwater and its nutrient load to streams without any intervening uptake or transformation, compounding the effects of elevated inputs (Walsh et al., 2005). Finally, a host of direct modifications of hydrologic systems influences their capacity to retain or transform nutrient inputs. Urban stream channels are frequently simplified by both channel straightening and a reduction in input of coarse woody debris, compromising their ability to retain increased nutrient loads (Bernhardt et al., 2008; Groffman et al., 2005). Consequently, the proportion of nutrients entering urban catchments that is exported to recipient ecosystems has increased (Groffman et al., 2004; Wollheim et al., 2005).

As these studies suggest, land-use patterns contribute to the elevated nutrient loads observed in urban streams. What is less well understood is how specific management decisions contribute to nutrient loading. People not only alter the physical structure of urban ecosystems, but they also are active agents within the city, continually making decisions about when and where resources are made available. In many cities, especially those of the arid and semiarid western United States, water has been diverted from distant surface streams (Libecap, 2005) or pumped from aquifers to maintain numerous artificial lakes constructed as amenities to urban parks, golf courses, and developments (Roach et al., 2008). Studies that link the effects of management decisions with historic drivers of biogeochemical processes in urban ecosystems are needed (Kaye et al., 2006; Pickett et al., 1997). Here we report the first study, to our knowledge, which explicitly considers how ecosystem function is affected by decisions regarding how municipal water supplies are managed. We hypothesize that choices about which water sources are tapped to maintain artificial lakes in the CAP ecosystem will affect concentrations of both N and P in the lake water, which, in turn, will affect which nutrient limits phytoplankton primary production in the lakes.

In the CAP ecosystem, stream-water chemistry is affected by the legacies of past farming practices as well as present-day agriculture. Agricultural practices, especially fertilizer use, have vastly increased agricultural yields (Matson et al., 1997), but unfortunately, not all of this fertilizer is retained on the land. Instead, some of the highly soluble  $\text{NO}_3^-$  is transported from agricultural fields (and urban lawns, which also are heavily fertilized) to aquifers and surface waters (Howarth et al., 1996; Spalding and Exner, 1993; Xu et al., 2007). Historic fertilizer use contributed to  $\text{NO}_3^-$  pollution of the Salt River Aquifer underlying CAP ecosystem, in which average groundwater  $\text{NO}_3^-$  concentration in the 1990s reached 860  $\mu\text{mol L}^{-1}$  under urban areas and 1280  $\mu\text{mol L}^{-1}$  under agricultural areas (Xu et al., 2007), concentrations that are well above the Environmental Protection Agency's limit of 714  $\mu\text{mol L}^{-1}$  for drinking water (Spalding and Exner, 1993). Previous research demonstrated that  $\text{NO}_3^-$  concentration in a Phoenix-area canal increased steadily with the number of groundwater wells contributing to its flow (Roach et al., 2008). Given the high concentration of  $\text{NO}_3^-$  in groundwater, we expected  $\text{NO}_3^-$  concentration to increase when the proportion of groundwater diverted through the artificial lake string was high, whether it arrived indirectly from the canal system or directly from groundwater wells.

Regardless of modifications made to urban streams, precipitation remains an important driver of patterns in stream discharge, especially in ephemeral streams. Understanding how anthropogenic modification of urban hydrology interacts with natural variation in precipitation to affect ecosystem processes is a critical challenge for managers of urban aquatic ecosystems, particularly those working in arid and semiarid climates. In comparatively pristine Sonoran Desert streams, floods flush nutrients from the surrounding landscape into the surface stream and strongly influence stream nutrient concentrations. Nutrient controls on periphyton growth thus are tightly linked to the hydrologic regime (Grimm and Fisher, 1986). Although floods increase concentrations of both N and P in pristine desert streams, in the urban IBW system we expected floods to dilute the high  $\text{NO}_3^-$  concentrations in lakes receiving groundwater inputs. Conversely, because accumulated P tends to be washed from urban surfaces like parking lots (Hope et al., 2004) and golf courses (King et al., 2007) during storms, we expected floods to increase P concentration.

To meet our objective of showing how management and climate variability interact to determine temporal variation in nutrient limitation, we tested the predictions outlined above that nutrient concentrations would vary with water source (groundwater via wells or canals vs. floodwater). Further, based on the work of Downing and McCauley (1992), we hypothesized that P limitation would occur when  $\text{N/P} > 31:1$  or P concentration was <1.0  $\mu\text{mol L}^{-1}$  and that N limitation would occur when P concentration was >1.0  $\mu\text{mol L}^{-1}$  and  $\text{N/P} < 31:1$ .

## Study Site

Indian Bend Wash is an ephemeral desert stream that historically only flowed in direct response to precipitation, draining ap-

proximately 520 km<sup>2</sup> of desert, agricultural, and suburban lands in Scottsdale, AZ. Development of the IBW watershed began in the early 20th century near the confluence with the Salt River, with the entire lower 48 km<sup>2</sup> of the watershed under cultivation until ~1949 (Roach et al., 2008). Urban growth exploded in the 1970s and by 2003 all but ~20% of the former cropland had been converted to urban uses (Roach et al., 2008).

Because IBW was prone to flash flooding, as urbanization proceeded flood control became a pressing need. The City of Scottsdale responded by channelizing the floodplain and protecting it from development. As part of this flood-control project, a greenbelt with numerous shallow lakes was constructed in the lower portion of the watershed (Roach et al., 2008). Between floods, lake levels are maintained with water delivered from an extensive series of lateral canals that originate with the Arizona Canal (Fig. 1). In fact, the eight lakes (L-1 through L-8; Fig. 1) of our study site comprise an important link in the Salt River Project canal system, and water is returned to the larger canal system at the bottom of the chain. Thus engineering has transformed this stretch of an ephemeral wash into a perennial lake chain. The origin of the canal water is surface flow from the Salt River, which is diverted into the canal network upstream from the city, and Colorado River water transported to the CAP ecosystem via the Central Arizona Project canal. During periods of high municipal or agricultural demand, groundwater is used to supplement these surface sources. Groundwater wells discharge into the Arizona Canal, its lateral canals and, occasionally, directly into the lakes of IBW.

The hydrologic engineering in this reach is complex. The eight lakes in our study differ in their morphometry (Table 1) and position relative to the major water inputs (Fig. 1). Lateral canals deliver their mix of surface and groundwater directly to lakes L-1 and L-8 while additional groundwater from the Roosevelt Well (Roos. Well) is discharged directly to the stream between lakes L-6 and L-7 (Fig. 1). Complicating things further, water from the stream above L-1 is occasionally diverted around the lake and into the stream feeding L-2. Although the wash is technically a tributary to the Salt River, during baseflow all water from the lake chain is returned to the canal system through a drain in L-8. Only during floods when water overtops the southern edge of L-8 and flows due south is the hydrologic link between the wash and the Salt River restored.

## Materials and Methods

We quantified how spatial patterns in water chemistry and nutrient limitation of phytoplankton varied over time. Because flows through IBW were historically ephemeral, we focused on how these attributes changed immediately after and for several days following floods. Floods were operationally defined as precipitation-driven surface flows recorded on flow gages in the otherwise dry channel below L-8 (Fig. 1).

## Lake Chemistry

With the exception of L-1, which was not sampled on five dates in 2002 when flows were diverted around the lake, we sampled all lakes on 24 dates in 2002 and 19 dates in 2003. Surveys

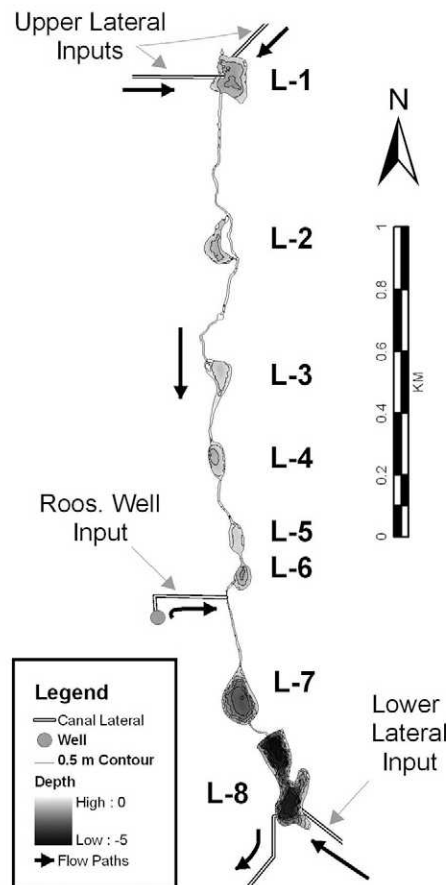


Fig. 1. Map of lake chain (L-1 through L-8) running through the lower IBW greenbelt. A mix of surface water from the Salt, Verde, and Colorado Rivers is delivered to the chain via the upper-lateral inputs to L-1 and the lower-lateral input to L-8. The Roosevelt Well (Roos. Well input) delivers water directly to the channel between L-6 and L-7. A drain along the SW edge of L-8 diverts water back into the irrigation system. Dark arrows indicate dominant flowpaths. Bathymetry is indicated by shading and 0.5-m contour lines.

Table 1. Morphometric data for the lakes of Indian Bend Wash. Data were collected during baseflow.

Lake name	Perimeter	Distance between inlet and outlet	Surface area	Volume	Maximum depth
		m	m <sup>2</sup>	m <sup>3</sup>	m
L-1	552	186	12,018	12,909	1.72
L-2	443	218	5947	4865	1.54
L-3	455	182	6222	3460	0.96
L-4	308	134	4899	3751	1.30
L-5	318	141	3999	2256	1.12
L-6	267	117	3546	3634	1.80
L-7	490	209	13,665	25,286	3.08
L-8	950	291	25,719	64,144	4.96

were conducted approximately monthly during winter and more frequently in summer, with survey frequency increasing directly after floods. Samples were collected from the outlet of each lake (Fig. 1) and coarse estimates of discharge through the lakes were made using timed flotation at select locations along the chain. In addition, we opportunistically sampled a subset of lakes during five floods for a total of 48 sampling dates. Water was collected for nutrient analyses during all sampling efforts.



We collected triplicate samples into new polyethylene centrifuge tubes and stored them at 4°C until processed at the Goldwater Environmental Laboratory (GEL) of Arizona State University. We report solute concentrations as the mean of these triplicates. Samples were analyzed colorimetrically on a Lachat QC8000 (Lachat Instruments, Loveland, CO) autoanalyzer for nitrite + nitrate (hereafter  $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and soluble reactive phosphorus (SRP). The N/P ratio was calculated as the ratio of dissolved inorganic nitrogen ( $\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$ ) to SRP. Before analysis, samples were centrifuged at  $10^4$  RPM for 10 min. Colorimetric methods for quantification were the phenol-hypochlorite method for  $\text{NH}_4^+$ , the cadmium-copper reduction method for  $\text{NO}_3^-$ , and the ascorbic acid reduction method for SRP. SRP was chosen to indicate P availability based on analysis of both SRP and total dissolved phosphorus (TDP) in samples from four different dates. TDP was measured as above for SRP, after an inline persulfate digestion. Linear regression analysis indicated that the TDP pool was predominantly SRP, with a slope  $\approx 1$  and an intercept not significantly different than zero ( $F = 525$ ;  $df = 1, 49$ ;  $P < 0.001$ ;  $R^2 = 0.91$ ;  $b_1 = 0.95$ ;  $b_0 = \text{NS}$ ). With the exception of four dates in 2002, analyses were typically conducted within 24 h and always within 72 h. On those four dates in 2002, laboratory difficulties necessitated that samples be centrifuged, decanted, and frozen before analysis for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and SRP.

Discharge data of floods were obtained from a stream gauge maintained by the Flood Control District of Maricopa County, located approximately 400 m south of L-8 and, during one flood when this gauge failed (13–16 Feb. 2003), from a USGS gauge approximately 1400 m further south (Fig. 1). Gages were located in an ephemeral reach and thus only recorded discharge during flood events. There were 13 distinct floods in 2002 and 13 in 2003. When discharge through the ephemeral channel lasted more than 1 d, the flood was considered to occur on the day with the highest average daily discharge. Thus successive floods had to be separated by at least 1 d of reduced flows to be considered distinct. Water chemistry was compared to flood size as indicated by the maximum daily (24 h) discharge ( $Q_{\text{max}}$ ) measured during any single precipitation-driven flow event and, in the case of  $\text{NO}_3^-$  and N/P, monthly  $\text{NO}_3^-$  loading from the upper-lateral wells, from the Roos. well, and from the lower-lateral wells. Monthly pumping totals for groundwater wells contributing water to the laterals feeding the wash were taken from reports prepared for the USEPA as part of a Superfund remediation project (North Indian Bend Wash Participating Companies, 2002, 2003). Additional data on  $\text{NO}_3^-$  in the Arizona Canal and in groundwater wells were provided directly by G. Elliott of the Salt River Project, which has analyzed  $\text{NO}_3^-$  since the mid-1980s by ion chromatography.

## Nutrient Limitation of Phytoplankton Growth

Nutrient-addition bioassays with dilution were used to assess the potential for phytoplankton growth limitation by N and/or P. These bioassays assess limitation by determining which nutrient or combination of nutrients, when supplied in excess, stimulates phytoplankton growth. Dilution is used to reduce effects of crowding and to minimize consumption by microconsumer grazers, thereby improving estimates of phytoplankton growth rates (Sommer,

1989). To characterize how changes in chemical characteristics of water affected temporal and spatial variation in nutrient limitation of phytoplankton, we conducted assays on samples collected on 13 dates between 30 May and 3 Dec. 2003. On each date, 2 L of lake water were collected from the outlet of each of eight lakes and immediately returned to the laboratory where incubations were initiated within 8 h. Experimental vials (acid-washed, clear 250-mL vials) were filled with  $\sim 130$  mL filtered lake water (Whatman GF/F) and inoculated with 20 mL of unfiltered water. Experimental enrichment concentrations were approximately  $500 \mu\text{mol L}^{-1}\text{N}$  and/or  $32 \mu\text{mol L}^{-1}\text{P}$  (as  $\text{KNO}_3$  and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , respectively) in a fully factorial set of treatments (Control, +N, +P, +N&P), except on 30 May, when the  $500 \mu\text{mol L}^{-1}\text{N}$  was added as  $\text{NH}_4\text{NO}_3$ . Experimental enrichments were chosen to ensure that added nutrients were available in excess. Each treatment was replicated three times. After enrichment, vials were covered with Petri dishes and incubated for 3 d in a growth chamber (PAR 120– $150 \mu\text{mol s}^{-1}\text{m}^{-2}$ ). To more closely reflect field conditions, temperature and light regimes were varied slightly for summer and fall samples (14:10 light/dark and 27°C for samples from May to August; 10.5:13.5 light/dark and 25°C for samples from November to December).

Bulbs located in the door supplied light within the chamber. As a result, irradiance experienced by the vials varied with distance from the door. Samples were staggered to limit shading. To avoid confounding the effects of distance from the door and nutrient treatment, samples were arrayed in three rows parallel to the door, with one replicate of each treatment from each lake in each row. Growth was assessed as change in *in vivo* fluorescence and measured on a Turner Design TD700 fluorometer, calibrated to a solid-state standard.

## Data Analyses

All statistical analyses were performed using SYSTAT (SYSTAT Software, Inc., 2002). A forward stepwise multiple linear regression procedure was used to analyze the effects of  $Q_{\text{max}}$  and days postflood on SRP and  $\text{NH}_4^+$  concentrations as well as the effects of  $Q_{\text{max}}$ , days postflood, and monthly groundwater  $\text{NO}_3^-$  loading rates on  $\text{NO}_3^-$  concentration and N/P in the outlets of the eight lakes. Predictor variables were selected sequentially in order of their relative reduction of sum of squares if their partial *F* statistics were significant at the  $P \leq 0.10$  level. After insertion, variables were dropped if they ceased to remain significant at the  $P \leq 0.10$  level. We estimated groundwater  $\text{NO}_3^-$  loading rates from data on monthly pumping rates and mean  $\text{NO}_3^-$  concentration of the seven wells that either pumped directly to the study reach or to the canal laterals that maintained baseflow through the lake chain. We divided the wells into three groups: the three upper-lateral wells which discharged to the laterals above lake L-1; the Roos. Well, which discharged to the stream between lakes L-6 and L-7; and the three lower-lateral wells, which discharged to the lateral above lake L-8 (Fig. 1).

Data were transformed before regression analysis. All nutrient data were  $\log_{10}$  transformed to linearize the data and to ensure that the residuals were normally distributed, as indicated by normal-probability plots and Kolmogorov-Smirnov tests on the

residuals. Log<sub>10</sub> transformations of the predictor variables  $Q_{\max}$  and days postflood and square-root transformation of loading rates further linearized the relationships between the predictor variables and the transformed nutrient concentrations, as indicated by examination of plots of residuals vs. predictor variables. Examinations of the plots of the residuals of the final models against the predictor values indicated that the residuals were homoscedastic. Both examination of normal probability plots and Kolmogorov-Smirnov tests indicated that the residuals of the final models for all regressions were normally distributed.

Phytoplankton growth was quantified by calculating the average daily exponential growth rate ( $r$ ; d<sup>-1</sup>) in each vial:

$$r = [\ln(N_t/N_0)]/t$$

where  $N_t$  is the in-vivo fluorescence at the end of the incubation,  $N_0$  is the initial in-vivo fluorescence, and  $t$  is incubation duration. Treatment means ( $r$ ) from each lake on each date were compared using a two-way ANOVA:

$$r = b_0 + \text{ROW} + \text{N} + \text{P} + \text{N} \times \text{P}$$

where nutrient treatments (N and P) were considered fixed factors and ROW was a blocking variable indicating the distance of the incubation vials from the light source. A hierarchical series of decision rules modified from Maberly et al. (2002) was used to distinguish between different types of nutrient limitation that were suggested by a significant treatment effect (Table 2). When the interaction was significant, all nutrient treatment means were compared using Bonferroni tests to control the family-wise error associated with conducting all possible comparisons.

## Results

There were 26 floods recorded between 1 Jan. 2002 and 31 Dec. 2003 in the ephemeral channel below Lake L-8 (Fig. 2A). The maximum average daily discharge of these floods, as measured in the channel below the lake chain, ranged from 3.4 to 1100 m<sup>3</sup> min<sup>-1</sup> and averaged 81 m<sup>3</sup> min<sup>-1</sup>. When not flooding, baseflow through the lake chain ranged between 0 and 25 m<sup>3</sup> min<sup>-1</sup>. Although loading from all three well groupings was lowest during winter, there were striking differences between the groups (Fig. 2B). The highest loading rates of the upper-lateral wells were seen from April to October of 2003 and in early 2002. Conversely, loading rates from the lower-lateral wells were highest from April to November of 2002 and from September to December of 2003. Loading from the Roos. well was greatest during the summer and early fall of 2002; it was inactive during 2003 (Fig. 2B).

## Lake Chemistry

Lake water chemistry varied more or less synchronously in all eight lakes. As a result, patterns observed in lake L-6 (Fig. 3) are typical. Below we detail how the concentrations of SRP, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> as well as N/P varied in response to floods and NO<sub>3</sub><sup>-</sup> loading from groundwater wells. We focus our presentation on patterns observed in L-6, but highlight where patterns observed in other lakes differed.

Soluble reactive phosphorus concentration varied more than 25-fold over the course of this study, ranging from 0.16 to 4.17 μmol L<sup>-1</sup> (mean = 0.76, SE = 0.04,  $n$  = 349). Fluctuations in SRP concentration were driven largely by floods: floodwaters delivered P-rich water to the lake chain, with SRP concentration increasing with  $Q_{\max}$  (e.g., Fig. 3A) and decreasing with days postflood (e.g., Fig. 3B). Together these two factors combined to explain between 17 and 49% of the variation (as indicated by  $R^2_{\text{adj}}$ ) in SRP concentration in lake outlets (Table 3). The SRP concentration was better predicted in the upper lakes than in the downstream lakes, as indicated by the steady and consistent decline in  $R^2_{\text{adj}}$  of the models from the eight lakes (Table 3).

Ammonium concentration also was highly variable, ranging from 0.4 to 31.7 μmol L<sup>-1</sup> (mean = 5.1, SE = 0.29,  $n$  = 356). Like SRP, NH<sub>4</sub><sup>+</sup> concentration in lake outlets declined after floods (e.g., Fig. 3C). Unlike SRP, in six of eight lakes NH<sub>4</sub><sup>+</sup> concentration declined with  $Q_{\max}$  (e.g., Fig. 3D). Linear regression analysis indicated that  $Q_{\max}$  and days postflood, either together or alone, explained between 12 and 30% of the variation in NH<sub>4</sub><sup>+</sup> concentration (Table 3).

During the course of the study, NO<sub>3</sub><sup>-</sup> concentration varied over three orders of magnitude, ranging from 0.2 to 521 μmol L<sup>-1</sup> (mean = 117, SE = 6.6,  $n$  = 356). Much of this variation could be explained by flood characteristics and groundwater contributions. Regression analysis indicated that lake NO<sub>3</sub><sup>-</sup> concentrations increased with increased NO<sub>3</sub><sup>-</sup> loading (e.g., Fig. 3G) and, with the exception of L-5 and L-8, decreased with days postflood (e.g., Fig. 3F; Table 3). Regression models explained between 41 and 66% of the observed variation in NO<sub>3</sub><sup>-</sup> concentration in the eight lakes (Table 3).

Primarily because of the large variation in NO<sub>3</sub><sup>-</sup> concentration, N/P also varied dramatically over the course of the study ranging from 0.2 to 1541. Multiple linear regressions showed that N/P increased with NO<sub>3</sub><sup>-</sup> loading (e.g., Fig. 3J; Table 3). Although N/P concentration declined as  $Q_{\max}$  increased in the lower four lakes (e.g., Fig. 3H; Table 3), there was not significant relationship between these two variables in the upper four lakes (Table 3). Final regression models explained between 36 and 63% of the observed variation in N/P. However, even though NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and SRP varied with days postflood in virtually all lakes, with the exception of Lake L-8 in which N/P increased significantly after floods, N/P showed no significant relationship with days postflood in the other seven lakes (Table 3). This suggests that in the days following the floods, both inorganic N and SRP declined at rates that were roughly proportional and that as a result N/P did not change over time.

On a number of dates over the course of the study, floods (Fig. 2A) and changes in groundwater loading (Fig. 2B) combined to drive N/P back and forth across the predicted threshold (31:1) for N vs. P limitation (Fig. 2C). In part because of their smaller volumes (Table 1), N/P of the upper six lakes varied more between sampling dates than did N/P of L-7 and L-8. Day to day variation of the upper lakes was comparatively synchronous, as indicated by small standard error associated with mean N/P of these six lakes (Fig. 2C). While N/P was most frequently >> 31:1, average N/P of the upper lakes dipped below 31:1 on more than 40% of sam-

Table 2. Hierarchical logic sequence to distinguish forms of nutrient limitation. Differences in growth rates,  $r$ , estimated under four different treatment combinations: control (C), nitrogen addition (N), phosphorus addition (P), combined nitrogen and phosphorus addition (NP) were evaluated using the general linear model  $r = b_0 + \text{ROW} + \text{N} + \text{P} + \text{N} \times \text{P}$ . ROW was a blocking variable indicating an incubation bottle's distance from the light source in the growth chamber. Cell means were compared using Bonferroni tests. Adapted from Maberly et al. (2002).

Effect	Logic	Decision
Sig. N×P Interaction	If $N \leq C$ and $P \leq C$ and $NP > C$	Co-limitation
	If $N \leq C$ and $P > C$ and $NP > P$	Primarily P limited; Secondarily N limited
	If $P \leq C$ and $N > C$ and $NP > N$	Primarily N limited; Secondarily P limited
Sig. P and Sig. N	If $P > C$ and $N > C$ and $NP > C$	Both nutrients limiting
Sig. P only	If $(NP \sim P) > (N \sim C)$	P limited
Sig. N only	If $(NP \sim N) > (P \sim C)$	N limited
No Sig. Effects	$P \leq C$ and $N \leq C$ and $NP \leq N$ and $NP \leq P$	Not N or P limited

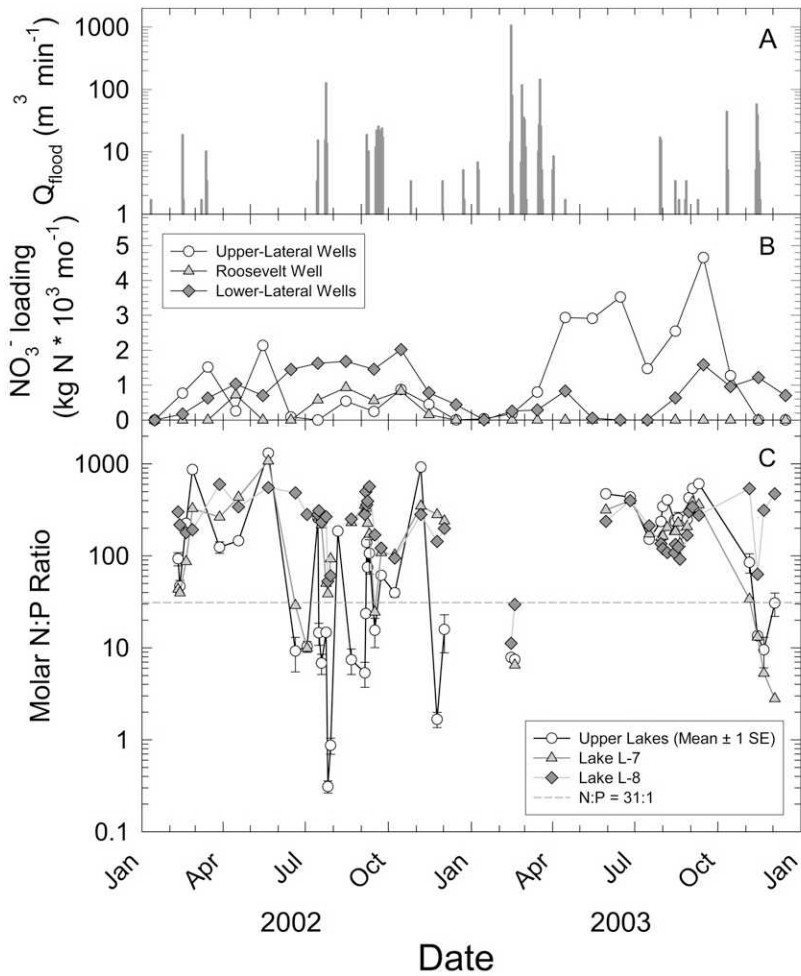


Fig. 2. Average daily discharge during 26 floods (Panel A). Combined monthly loading rates by upper-lateral wells, the Roosevelt well, and lower-lateral wells (Panel B). Mean N/P in outlets of the upper six lakes (open circles) compared to N/P in water from the outlets of L-7 (closed triangles) and L-8 (closed diamonds) across 48 sampling dates in 2002 and 2003. Error bars represent  $\pm 1$  SE about the mean of lakes L-1 through L-6. The expected cutoff between N and P limitation (dashed line; N/P = 31:1) is plotted for reference.

pling dates (12 of 28) in 2002, with low N/P being most common in late summer and early fall (Fig. 2C). Low N/P ratios were most often observed in the upper lakes after floods during periods when loading rates for the upper-lateral wells were low (Fig. 2). Because of their comparatively large size, N/P did not vary as frequently or as widely in L-7 and L-8 as it did in the upper lakes. Moreover, the inputs from the Roos. well above L-7 and from the lower lateral to L-8 further contributed to the consistent and comparatively high N/P ratios observed in these two lakes (Fig. 2).

### Nutrient Limitation of Phytoplankton Growth

Nutrient limitation of phytoplankton was spatially and temporally variable and was well predicted by lake chemistry (Supplemental Table 1). Between 30 May and 28 Aug. 2003 N/P of the eight lakes remained  $>100:1$  (Fig. 2C) and phytoplankton growth in all lakes on all dates was initially P limited (Fig. 4, first circle). Indeed, only two instances of secondary N limitation (Table 2) were observed during this period with both occurring when DIN and SRP concentrations were relatively low. Changes in N/P caused

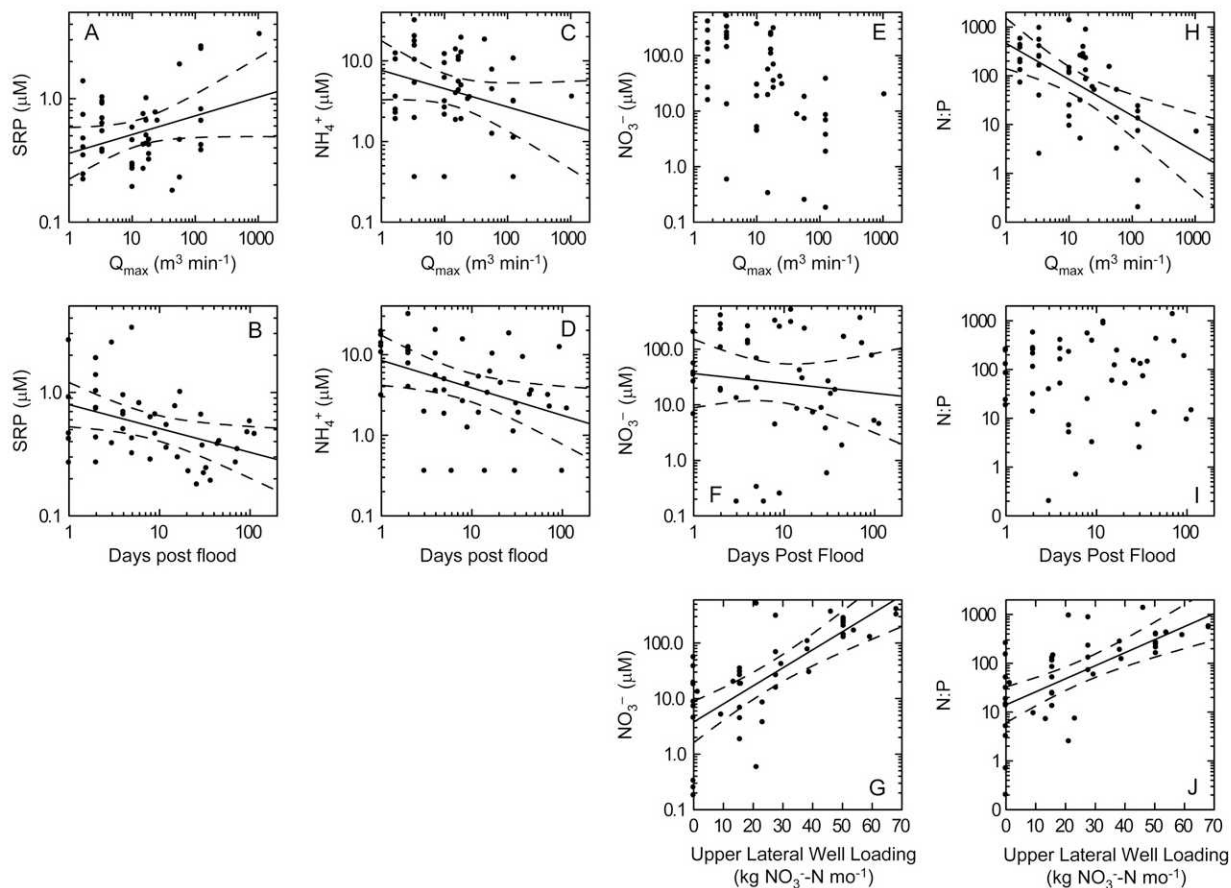


Fig. 3. Relationships between SRP,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and N:P in the outlet of L-6 and  $Q_{\text{max}}$  (top row), days since flood (middle row), and combined monthly  $\text{NO}_3^-$  loading rate of the upper-lateral wells ( $\text{NO}_3^-$  and N:P only) (bottom row). Simple regression and 95% confidence intervals are plotted. Monthly  $\text{NO}_3^-$  loading rates were square-root transformed.

predictable changes in nutrient limitation toward the end of 2003. By 5 November, DIN and SRP concentrations in the upper seven lakes had dropped dramatically though nutrient concentrations in L-8 remained relatively constant (Fig. 2C). Average DIN in lakes L-1 through L-7 declined from  $282 \pm 16 \mu\text{mol L}^{-1}$  on 28 August to  $16 \pm 3 \mu\text{mol L}^{-1}$  on 5 November while SRP dropped from  $1.17 \pm 0.07$  to  $0.23 \pm 0.02 \mu\text{mol L}^{-1}$  over the same period (means  $\pm 1$  SE). As a result, average N:P in these seven lakes dropped from  $282 \pm 16 \mu\text{mol L}^{-1}$  on 28 August to  $83 \pm 12$  on 5 November (means  $\pm 1$  SE). However, because N:P in all lakes remained at or above 31:1, all lakes were initially P limited with lakes L-1, L-2, and L-7, which had N:P ratios of 31, 32, and 34, respectively, displaying secondary N-limitation (Fig. 4, second circle). After a moderate flood ( $Q_{\text{max}} = 58 \text{ m}^3 \text{ min}^{-1}$ ) on 13 Nov. 2003, SRP concentration increased whereas DIN concentration remained relatively low, and on 14 November average N:P in the seven upper lakes was well below 31:1 at  $13 \pm 0.3$  (mean  $\pm 1$  SE). Bioassays conducted on samples from this date indicated that phytoplankton growth in L-2, L-4, and L-7 was not nutrient limited and that growth in lakes L-1, L-3, and L-5 was N limited (Fig. 4, third circle). In the days after the flood, SRP and DIN concentrations in lake water declined further, and by 21 November average SRP concentration in the upper seven lakes was  $0.55 \pm 0.04 \mu\text{mol L}^{-1}$  (mean  $\pm 1$  SE), well below the  $1 \mu\text{mol L}^{-1}$  threshold for P limitation. Bioassays on

this date indicated that the northern three lakes had returned to P limitation, with L-1 and L-2 exhibiting secondary N limitation, while lakes L-4 to L-7 were all co-limited (Fig. 4, fourth circle). Phosphorus concentrations continued to drop and on 3 December, when average SRP was  $0.24 \pm 0.1 \mu\text{mol L}^{-1}$  (mean  $\pm 1$  SE), lakes L-1 through L-6 were again P limited with L-1 exhibiting secondary N limitation and only L-7, the largest lake affected by the 14 November flood, was still exhibiting co-limitation (Fig. 4, fifth circle).

## Discussion

### Factors Affecting Spatial and Temporal Variation in Lake Chemistry

Concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and SRP varied both in space and in time, but drivers of that variation differed depending on the nutrient in question. Although floods explained much of the variation in all three constituents, mechanisms were likely different. The SRP increased directly after floods and in proportion to flood magnitude, suggesting that floodwaters were washing SRP that had accumulated in the surrounding watershed into the stream and that larger floods mobilized more SRP. Correll et al. (1999) hypothesize that a similar mechanism was responsible for the elevated P concentrations observed follow-



Table 3. Results of forward stepwise multiple linear regression analyses showing effects of maximum flood size ( $Q_{\max}$ ) and days postflood on soluble reactive phosphorus (SRP) and  $\text{NH}_4^+$  concentrations, and the effects of  $Q_{\max}$  and days postflood in addition to monthly loading rates (monthly pumping rate  $\times$   $\text{NO}_3^-$  concentration) on the concentration of  $\text{NO}_3^-$  and on N/P in the outlets of the eight lakes. Because only wells upstream of a lake could influence its chemistry only combined loading of the upper-lateral wells (UL well loading) was included as a potential variables in models for lakes L-1 through L-6. Models for L-7 included loading from the Roosevelt Well (Roos. Well loading) as well as the UL well loading. Models for L-8 included  $\text{NO}_3^-$  loading of the lower-lateral wells (LL well loading) as well as UL well loading and Roos. Well loading as potential variables. "NS" indicates explanatory variables that were included as potential variables but were not found significant during the stepwise regression while "—" indicates the variable was not predicted to affect the specific dependent variable and hence was not included in the set of potential model variables. Discharge, days postflood, SRP,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  were  $\log_{10}$  transformed before analysis. Loading rates were square-root transformed before analysis. Significance and magnitude of individual regression coefficients as well as the adjusted  $R^2$  are reported.

Lake	Variable	Chemical constituent											
		SRP			NH <sub>4</sub> <sup>+</sup>			NO <sub>3</sub> <sup>-</sup>			N/P		
		Slope	df	R <sup>2</sup> <sub>adj</sub>	Slope	df	R <sup>2</sup> <sub>adj</sub>	Slope	df	R <sup>2</sup> <sub>adj</sub>	Slope	df	R <sup>2</sup> <sub>adj</sub>
L-1	Q <sub>max</sub>	0.125*	2, 37	0.492	NS	1, 38	0.300	NS	2, 37	0.657	NS	1, 38	0.629
	Days postflood	-0.311***			-0.469***			-0.376**			NS		
	UL well loading	—			—			0.036***			0.033***		
L-2	Q <sub>max</sub>	0.098†	2, 39	0.446	-0.228*	2, 40	0.171	NS	2, 40	0.618	NS	1, 40	0.603
	Days postflood	-0.299***			-0.329**			-0.342†			NS		
	UL well loading	—			—			0.039***			0.034***		
L-3	Q <sub>max</sub>	0.091†	2, 39	0.372	-0.235†	2, 40	0.122	NS	2, 40	0.598	NS	1, 40	0.532
	Days postflood	-0.285***			-0.306*			-0.394*			NS		
	UL well loading	—			—			0.038***			0.032***		
L-4	Q <sub>max</sub>	0.098†	2, 41	0.326	-0.21*	2, 42	0.161	NS	2, 42	0.626	NS	1, 42	0.538
	Days postflood	-0.242***			-0.322**			-0.424*			NS		
	UL well loading	—			—			0.038***			0.031***		
L-5	Q <sub>max</sub>	0.104†	2, 41	0.325	-0.333**	2, 42	0.232	NS	1, 43	0.577	-0.317†	2, 41	0.541
	Days Postflood	-0.235***			-0.363**			NS			NS		
	UL well loading	—			—			0.033***			0.023***		
L-6	Q <sub>max</sub>	0.132*	2, 43	0.246	-0.259**	2, 44	0.263	NS	2, 44	0.557	-0.357*	2, 43	0.486
	Days postflood	-0.198**			-0.388**			-0.301†			NS		
	UL well loading	—			—			0.33***			0.02***		
L-7	Q <sub>max</sub>	0.095†	2, 41	0.180	-0.396**	2, 42	0.298	NS	3, 41	0.478	-0.223†	3, 40	0.483
	Days postflood	-0.137*			-0.431**			-0.238†			NS		
	UL well loading	—			—			0.248***			0.018***		
	Roos. Well loading	—			—			0.027***			0.025***		
L-8	Q <sub>max</sub>	0.097†	2, 44	0.168	NS	1, 46	0.264	-0.148***	3, 44	0.411	-0.229***	3, 43	0.361
	Days postflood	-0.132*			-0.479***			0.106*			0.214**		
	UL well loading	—			—			NS			NS		
	Roos. Well loading	—			—			NS			NS		
	LL well loading	—			—			0.117***			0.011**		

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

\*\*\* Significant at the 0.001 probability level.

† Significant at the 0.10 probability level.

ing floods in streams draining agricultural and forested watersheds. This hypothesis is consistent with previous research on streams draining desert shrubland (Grimm and Fisher, 1986), agricultural fields (Green et al., 2007), golf courses (King et al., 2007), and urban landscapes (Hope et al., 2004). In each case, P concentration of stream water (variously measured as total P or SRP) increased as a result of precipitation-driven overland flows. In Sycamore Creek, a Sonoran Desert stream near IBW, P is derived from weathering of P-rich volcanic rocks (Grimm and Fisher, 1986). Similarly, the source of SRP in runoff from parking lots in the CAP ecosystem has been hypothesized to be soil-derived dust from the surrounding desert (Hope et al., 2004). While geologic sources also may be important in IBW, application of P-rich fertilizers to parks and golf courses is an additional likely important source of P (King et al., 2007).

Control of P concentrations in streams has been ascribed to both adsorption to stream sediments (Meyer and Likens, 1979) and biotic uptake (Mulholland et al., 1985). In lakes, both mechanisms can be sinks for P, but redox state also controls availability. Under oxic conditions, inorganic P is bound to iron while under anoxic conditions it is released to the water column. Whether P precipitates and is permanently buried in the sediments or is recycled within the lake depends on several factors including lake morphometry, temperature regimes, and the dominant aquatic plant species (Genkai-Kato and Carpenter, 2005). In IBW, biotic uptake, abiotic adsorption, and physical dilution are all likely to contribute to observed postflood declines in SRP concentration. Primary production rates in the lakes can be high and swings in daily oxygen concentration large (Roach, 2005), suggesting that while biotic uptake is important, physical adsorption to

sediments may be temporary. Additionally, SRP in lake water is diluted as low-SRP canal water is diverted into the wash in the days following the flood. Our data do not permit assessment of the relative importance of these various mechanisms in IBW.

Ammonium concentration, like that of SRP, declined with days postflood, but unlike the findings of some previous studies (Correll et al., 1999),  $\text{NH}_4^+$  was not positively correlated with flood magnitude, but instead declined with or was uncorrelated with  $Q_{\text{max}}$ . This tendency of lakes to have lower  $\text{NH}_4^+$  concentrations following large floods may result from the physical dilution within the lakes. Detritus, including mineralizable N, accumulates in the watershed between floods and is often washed off the landscape in a flood's first flush (Welter et al., 2005). As a result, large floods likely have less mineralizable N per unit volume than smaller floods and thus large floods may not have as strong an effect on postflood  $\text{NH}_4^+$  concentrations as smaller floods.

In contrast to other Sonoran Desert streams where floods are an important source of  $\text{NO}_3^-$  (Grimm, 1992) floods in IBW did not increase  $\text{NO}_3^-$  concentration but if anything tended to reduce it, presumably through dilution, or had no effect. Dilution has been invoked as a mechanism to explain flood-driven declines in  $\text{NO}_3^-$  in other streams that have high  $\text{NO}_3^-$  loads. Working in southern Minnesota, Green et al. (2007) showed that storm flows diluted the high  $\text{NO}_3^-$  concentration in an agricultural stream. Flood magnitude did not remain a significant predictor in our regression models because it was positively correlated with loading rates in the upper-lateral wells and negatively correlated with loading rates in the lower-lateral wells (data not shown). That the two groups of wells had opposite relationships with flood magnitude more likely reflects an inverse relationship between when these two groups of wells were pumping (Fig. 2B), than any fundamental relationship between loading rates and flood size. Consequently, it is likely that the observed correlations between flood magnitude and loading rates were spurious and that a more extensive data set could more fully parse the effects of flood magnitude and  $\text{NO}_3^-$  loading on water chemistry in the lakes.

Even more unusual than the contrast between the effects of floods on IBW and more typical Sonoran Desert streams was the role management decisions played in driving nutrient concentrations. Multiple regression analysis indicated that much of the  $\text{NO}_3^-$  flowing through IBW was attributable to groundwater loading. This was despite the fact that data on groundwater pumping rates were only available as monthly totals. We believe that more variation could have been explained if data were available to fully model the proportion of groundwater, floodwater, and canal water in each lake on any given date. Even though our regression models were unable to precisely predict  $\text{NO}_3^-$  concentration, they do demonstrate that anthropogenically regulated groundwater additions were an important source of  $\text{NO}_3^-$  in the lakes of IBW. In short,  $\text{NO}_3^-$  concentration was largely determined by which spigots were turned.

The interaction of floods and management decisions in IBW generated important changes in the N/P of lake water. During periods when groundwater loading of  $\text{NO}_3^-$  was high,  $\text{NO}_3^-$  concentration and N/P were also high. Floods that occurred during periods of high loading typically failed to dilute  $\text{NO}_3^-$  concentration

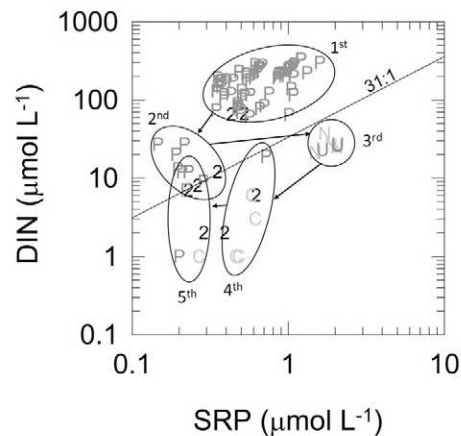


Fig. 4. Trajectory of nutrient bioassay results as lake chemistry moves through phase space defined by dissolved inorganic nitrogen ( $\text{DIN} = \text{NO}_3^- + \text{NH}_4^+$ ) and soluble reactive phosphorus (SRP) in outlet water of each lake. P indicates P limitation; N indicates N limitation; C indicates co-limitation; 2 indicates primary P limitation, secondary N limitation; and U indicates no nutrient limitation. The theoretical cutoff (atomic N/P = 31:1) is plotted for reference. See text for description of sequence from first to fifth circle.

enough to drive N/P below 31:1. In contrast, floods that occurred when groundwater loading rates were low often did cause N/P to dip below the 31:1 threshold. This mirrors findings of Correll et al. (1999) who found that storms drove down N/P in the Rhode River, a tidal tributary to the Chesapeake Bay, with ratios declining significantly with storm intensity. The largest storms drove N/P well below 16:1, causing Correll et al. to hypothesize that floods might produce temporary N limitation in the Bay.

Fluctuations in N/P observed along IBW's lake chain were affected by the path water followed before being diverted into the wash. Water that originated as groundwater was high in  $\text{NO}_3^-$ , low in SRP, and had a high N/P. Conversely, flood water, which entered IBW via overland flow, was comparatively low in  $\text{NO}_3^-$ , high in SRP, and had a low N/P. Water diverted into the Arizona Canal at its headgate had water chemistry that was intermediate between the two (G. Elliott, Salt River Project, personal communication, 2005). Thus, when a subsurface flowpath dominated lake chemistry, N/P was high. Conversely, when overland flows dominated, N/P was low. This is analogous to the results of Green et al. (2007) who demonstrated that the ratio of  $\text{NO}_3^-/\text{TP}$  was high during baseflow when the proportion of groundwater in the stream was high and declined when water contributed via overland flowpaths dominated. This pattern may result when a basin drains agricultural fields (Green et al., 2007) or bears the legacies of past agricultural use (this study), and thus groundwater  $\text{NO}_3^-$  concentrations are high enough to overwhelm retention mechanisms like denitrification that limit the flux of  $\text{NO}_3^-$  to the stream.

## Nutrient Limitation

Our experiments demonstrated that nutrient limitation of phytoplankton varied depending on the N/P of water flowing through the lakes of IBW. As predicted, when SRP concentration was  $>1 \mu\text{mol L}^{-1}$  and  $\text{N/P} < 31:1$ , phytoplankton growth was either N limited or not limited by N or P. At all other times, growth was initially P limited or co-limited by N and P. Although conditions

producing N limitation were met only briefly during 2003 (Fig. 4), the year bioassays were conducted, the frequency with which N/P dropped below 31:1 in 2002 (Fig. 2C) suggests that shifts in nutrient limitation may be a relatively common phenomenon. In fact, a survey of the N/P of runoff from 2002 storm events in several urban catchments of the CAP ecosystem revealed that nearly half were below the Redfield ratio of 16:1 (Grimm et al., 2004).

This is one of the few studies that links anthropogenic influences on stream water chemistry to aquatic ecosystem structure and function. Other researchers have examined how changes in N/P of human-influenced water bodies altered phytoplankton dynamics and nutrient limitation (Hlaili et al., 2006). However, the present study is the first to demonstrate that the effects of management decisions about how a large-scale municipal irrigation system is operated cascade through aquatic ecosystems of the urban environment, altering patterns of nutrient limitation and, in all likelihood, community dynamics. We hypothesize that changes in the composition of IBW's phytoplankton community are produced by shifts in nutrient limitation. Other researchers have demonstrated that changes in nutrient availability can produce large shifts in community composition of other aquatic ecosystems (Stelzer and Lamberti, 2001). For example, numerous researchers have demonstrated that N limitation can promote blooms of N-fixing cyanobacteria in lakes (Smith, 1983), lagoons (Hlaili et al., 2006), and streams including Sycamore Creek (Grimm and Petrone, 1997).

Our bioassays suggest that temporal changes in nutrient limitation, an important indicator of ecosystem function, result from the interaction of management decisions and active hydrology. Although laboratory bioassays are an accepted approach to showing temporal and spatial variation in nutrient limitation in lakes (Elser et al., 1990; Maberly et al., 2002), we recognize that they do have some limitations. Perhaps most importantly for this experiment, they are unable to account for other potentially limiting factors, specifically light. Light can limit actual rates of photosynthesis in lakes even when bioassays indicate nutrient limitation. In highly productive lakes like those of IBW where daily oxygen swings of  $>1000 \mu\text{mol L}^{-1}$  (Roach, 2005) are common, in situ self-shading may limit phytoplankton growth before nutrient concentrations. Nevertheless, with proper statistical replication, bioassays can provide useful information about spatial and temporal variability in limiting factors (Elser et al., 1990), and we remain confident that our bioassays accurately reflect the changes in processes governing phytoplankton growth in IBW.

Because bioassays are conducted on grab samples they provide an estimate of the nutrient status of a lake at a specific point in time. This is critical when shifts in water chemistry are abrupt, as is the case when a turn of a spigot or a flash flood can alter relative nutrient availability. This temporal variability may explain why previous research in IBW failed to demonstrate such dynamic responses (Goettl, 2001). In this previous experiment nutrient-diffusing substrates, which provide a time-integrated measure of relative nutrient concentration over several weeks, indicated P limitation in the summer when groundwater contributions are high, and no limitation during the rest of the year (Goettl, 2001). The periods of N limitation

in both 2002 and 2003 were likely brief. However, during periods of reduced groundwater withdrawals or extensive flooding, N limitation may become more common. Conversely, any decrease in flooding or accelerated groundwater withdrawal, such as might accompany further population growth or drought (both anticipated for the Southwest) would likely push the system toward more frequent and severe P limitation.

## Synthesis

If Williamson et al. (2008) are correct and lakes are indeed sentinels of environmental change than what do the lakes of IBW tell us? Our research demonstrates that a key aspect of ecosystem status, nutrient limitation of primary producer growth, is not only controlled by natural variation in hydrology and weather but also by decisions about how to move water through an extensively engineered hydrologic system. The ramifications of choices about which water sources are used to meet system-wide demand—choices that are made with little regard for N/P ratios and potential nutrient limitation—were manifest in IBW's lakes.

Our results argue for careful evaluation of the consequences of redistributing water and relying on groundwater to supplement surface flows. Because groundwater residence times can be very long, the legacies of previous management practices (e.g., fertilizer use) may persist in groundwater for decades and produce ecological surprises when water is returned to the surface. Explicit consideration of these legacies creates an additional challenge for water managers attempting to ensure a stable supply of potable water while maintaining ecosystem function. This issue is likely to arise more frequently as agricultural lands are converted to urban uses (del Mar López et al., 2001). In some respects this reliance on groundwater makes the CAP ecosystem unusual. Many cities do not augment their surface streams and lakes with groundwater. However, point source discharges with water chemistry that is radically different from the receiving water are common. Wastewater treatment plants, for example, are well-known sources of N and P that affect nutrient processing in streams (Martí et al., 2004). Perhaps even more important are the unintended consequences of diverting water from one basin to another in response to spatially segregated demand. Arid and semiarid cities around the globe are facing issues of water scarcity (Iglesias et al., 2007). Water markets are now used in Chile to help apportion surface flows between various sectors (Heame, 2007), while cities throughout the western United States increasingly rely on trans-basin diversions to meet their needs (Libecap, 2005; Roach et al., 2008). Because trans-basin diversions often supplement flows in one river with water diverted from another catchment, they have the potential to change the spatial and temporal availability of water and nutrients, altering ecosystem processes in the recipient water bodies. As our research demonstrates, choices about where to draw water may alter ecosystem function in ways previously not considered. Careful examination of the effects of mixing surface water with supplemental flows from novel sources, be they groundwater aquifers or stream water from outside the basin, is clearly warranted. This is especially true for the artificial water bodies that increasingly populate many urban landscapes.



## Supplemental Information Available

Supplemental material available online at <http://jeq.sciijournals.org> contains one table reporting qualitative results of the 104 bioassays conducted in 2003 and the nutrient water chemistry of the lake associated with each bioassay.

## Acknowledgments

We thank Marcia Kyle, John Schampel, and Jim Elser for assistance with the bioassays; Gregg Elliott, Dennis Shirley, the Salt River Project and Errol L. Montgomery and Associates, Inc. for providing data on groundwater pumping rates, well chemistry, and the configuration of the lateral irrigation canals; Cathy Cochert, Tom Colella, Nicole Garber, Tamara Harms, Libby Larson, Derek Stauffer, Rich Sheibley, Phil Tarrant, and Harriet Van Vleck for help in the lab and in the field; Satish Gupta and several anonymous reviewers for their comments which improved the manuscript. This research was supported by the National Science Foundation, grants DEB-DEB-9714833 & DEB-0423704 (Central Arizona-Phoenix LTER to NBG) and DGE-9987612 (IGERT in Urban Ecology for support of WJR).

## References

- Baker, L.A., Y. Xu, L. Lauver, D. Hope, and J. Edmonds. 2001. Nitrogen balance for the Central Arizona-Phoenix (CAP) ecosystem. *Ecosystems* 4:582–602.
- Bernhardt, E.S., L.E. Band, C.J. Walsh, and P.E. Berke. 2008. Understanding, managing, and minimizing urban impacts on surface water nitrogen loading. *Ann. N. Y. Acad. Sci.* 1134:61–96.
- Carpenter, S.R., N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Appl.* 8:559–568.
- Correll, D.L., T.E. Jordan, and D.E. Weller. 1999. Transport of nitrogen and phosphorus from Rhode River watersheds during storm events. *Water Resour. Res.* 35:2513–2521.
- del Mar López, T., T. Aide, and J. Thomlinson. 2001. Urban expansion and the loss of prime agricultural lands in Puerto Rico. *Ambio* 30:49–54.
- Downing, J.A., and E. McCauley. 1992. The nitrogen:phosphorus relationship in lakes. *Limnol. Oceanogr.* 37:936–945.
- Elser, J.J., M.E.S. Bracken, E.E. Cleland, D.S. Gruner, W.S. Harpole, H. Hillebrand, J.T. Ngai, E.W. Seabloom, J.B. Shurlin, and J.E. Smith. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecol. Lett.* 10:1135–1142.
- Elser, J.J., E.R. Marzolf, and C.R. Goldman. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: A review and critique of experimental enrichments. *Can. J. Fish. Aquat. Sci.* 47:1468–1477.
- Foley, J.A., R. DeFries, G.P. Asner, C. Barford, G. Bonan, S.R. Carpenter, E.S. Chapin, M.T. Coe, G.C. Daily, H.K. Gibbs, J.H. Helkowski, T. Holloway, E.A. Howard, C.J. Kucharik, C. Monfreda, J.A. Patz, I.C. Prentice, N. Ramankutty, and P.K. Snyder. 2005. Global consequence of land use. *Science (Washington, DC)* 309:570–574.
- Genkai-Kato, M., and S.R. Carpenter. 2005. Eutrophication due to phosphorus recycling in relation to Lake Morphometry, temperature, and macrophytes. *Ecology* 86:210–219.
- Goettl, A.M. 2001. Nutrient limitation in Indian Bend Wash: An urban stream in the Sonoran Desert. Masters thesis. Arizona State Univ., Tempe.
- Green, M.B., J.L. Nieber, G. Johnson, J. Manger, and B. Schaefer. 2007. Flow path influence on N:P ratio in two headwater streams: A paired watershed study. *J. Geophys. Res.-Biogeosciences* 112:GO30105, doi:10.1029/2007JG000403.
- Grimm, N.B. 1992. Biogeochemistry of nitrogen in Sonoran Desert streams. *Limnol. Aquat. Biol.* Southwest 2:139–188.
- Grimm, N.B., R. Arrowsmith, C. Eisinger, J. Heffernan, D.B. Lewis, A. MacLeod, L. Preshad, W.J. Roach, T. Rychener, and R.W. Sheibley. 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. p. 129–146. *In* G. Asner and R. Houghton (ed.) *Ecosystems and land use change*. Vol. 153. American Geophysical Union, Washington, DC.
- Grimm, N.B., and S.G. Fisher. 1986. Nitrogen limitation in a Sonoran Desert stream. *J. N. Am. Benthol. Soc.* 5:2–15.
- Grimm, N.B., and K.C. Petrone. 1997. Nitrogen fixation in a desert stream ecosystem. *Biogeochemistry* 37:33–61.
- Grimm, N.B., S.H. Faeth, N.E. Golubiewski, C.R. Redman, J. Wu, X. Bai, and J.M. Briggs. 2008. Global change and the ecology of cities. *Science (Washington, DC)* 319:756–760.
- Groffman, P.M., A.M. Dorsey, and P.M. Mayer. 2005. N processing within geomorphic structures in urban streams. *J. N. Am. Benthol. Soc.* 24:613–625.
- Groffman, P.M., N.L. Law, K.T. Belt, L.E. Band, and G.T. Fisher. 2004. Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems* 7:391–403.
- Hearne, R.R. 2007. Water markets as a mechanism for intersectoral water transfers: The Elqui Basin in Chile. *Paddy Water Environ.* 5:223–227.
- Hlaili, A.S., M.-A. Chikhaiui, B. El Grami, and H.H. Mabrouk. 2006. Effects of N and P supply on phytoplankton in Bizerte Lagoon (western Mediterranean). *J. Exp. Mar. Biol. Ecol.* 333:79–96.
- Hope, D., A.H. Chan, N.W. Naegeli, and N.B. Grimm. 2004. Nutrients on asphalt parking surfaces in an arid urban environment. *Water Air Soil Pollut. Focus* 4:371–390.
- Howarth, R., B.G.D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N.F. Caraco, T. Jordan, F. Brerendse, J.R. Freney, V. Kudeyarov, P. Murdoch, and Z.L. Zhu. 1996. Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. *Biogeochemistry* 35:75–139.
- Iglesias, A., L. Garrote, F. Flores, and M. Moneo. 2007. Challenges to manage the risk of water scarcity and climate change in the Mediterranean. *Water Resour. Manage.* 21:775–788.
- Kaye, J., P.M. Groffman, N.B. Grimm, L.A. Baker, and R.V. Pouyat. 2006. A distinct urban biogeochemistry? *Trends Ecol. Evol.* 21:192–199.
- King, K.W., J.C. Balogh, K.L. Hughes, and R.D. Harmel. 2007. Nutrient load generated by storm event runoff from a golf course watershed. *J. Environ. Qual.* 36:1021–1030.
- Libecap, G.D. 2005. Chinatown: Owens Valley and western water reallocation—Getting the record straight and what it means for water markets. *Tex. Law Rev.* 83:2055–2089.
- Lovett, G., M. Traynor, R.V. Pouyat, M.M. Carreiro, W.X. Zhu, and J.W. Baxter. 2000. Atmospheric deposition to oak forests along an urban-rural gradient. *Environ. Sci. Technol.* 34:4294–4300.
- Maberly, S.C., L. King, M.M. Dent, R.I. Jones, and G. Gibson. 2002. Nutrient limitation of phytoplankton and periphyton growth in upland lakes. *Freshwater Biol.* 47:2136–2152.
- Martí, E., J. Autmatell, L. Godé, M. Poch, and F. Sabater. 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. *J. Environ. Qual.* 33:285–293.
- Matson, P.A., W.J. Parton, A.G. Power, and M.J. Swift. 1997. Agricultural intensification and ecosystem properties. *Science (Washington, DC)* 277:504–509.
- Meyer, J.L., and G.E. Likens. 1979. Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology* 60:1255–1269.
- Mulholland, P.J., J.D. Newbold, J.W. Elwood, L.A. Ferren, and J.R. Webster. 1985. Phosphorus spiraling in a woodland stream: Seasonal variations. *Ecology* 66:1012–1023.
- North Indian Bend Wash Participating Companies. 2002. Annual site monitoring report, North Indian Bend Wash Superfund Site, Scottsdale, Arizona. Prepared for USEPA Region IX by Errol L. Montgomery & Assoc., Tucson, AZ.
- North Indian Bend Wash Participating Companies. 2003. Annual site monitoring report, North Indian Bend Wash superfund site, Scottsdale, Arizona. Prepared for USEPA Region IX by Errol L. Montgomery & Assoc., Tucson, AZ.
- Paul, M.J., and J.L. Meyer. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32:333–365.
- Pickett, S.T.A., J. Burch, S.E. Dalton, T.W. Foresman, J.M. Grove, and R. Rowntree. 1997. A conceptual framework for the study of human ecosystems in urban areas. *Urban Ecosyst.* 1:185–199.
- Roach, W.J. 2005. How anthropogenic modifications influence the cycling of nitrogen in Indian Bend Wash, an urban desert stream. Ph.D. diss.



- (Publ. no. 3194962). Arizona State Univ., Tempe.
- Roach, W.J., J.H. Heffernan, N.B. Grimm, R. Arrowsmith, C. Eisinger, and T. Rychner. 2008. Unintended consequences of urbanization for aquatic ecosystems: A case study from the Arizona desert. *Bioscience* 58:715–727.
- Smith, V.H. 1983. Low nitrogen to phosphorus ratios favor dominance by blue-green algae in lake phytoplankton. *Science* (Washington, DC) 221:669–671.
- Sommer, U. 1989. Nutrient status and nutrient competition of phytoplankton in a shallow, hypertrophic lake. *Limnol. Oceanogr.* 34:1162–1173.
- Spalding, R.F., and M.E. Exner. 1993. Occurrence of nitrate in groundwater—A review. *J. Environ. Qual.* 22:392–402.
- SYSTAT Software, Inc. 2002. SYSTAT, Version 10. Systat Software, Inc., Richmond, CA.
- Stelzer, R.S., and G.A. Lamberti. 2001. Effects of N:P ratio and total nutrient concentration on stream periphyton community structure, biomass, and elemental composition. *Limnol. Oceanogr.* 46:356–367.
- Walsh, C.J., A.H. Roy, J.W. Feminella, P.D. Cottingham, P.M. Groffman, and R.P. Morgan, II. 2005. The urban stream syndrome: Current knowledge and the search for a cure. *J. N. Am. Benthol. Soc.* 24:706–723.
- Welter, J.W., S.G. Fisher, and N.B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. *Biogeochemistry* 76:421–440.
- Williams, M., C. Hopkinson, E. Rastetter, and J. Vallino. 2004. N budgets and aquatic uptake in the Ipswich River basin, northern Massachusetts. *Water Resour. Res.* 40:W11201.
- Williamson, C.E., W.K. Dodds, T.K. Kratz, and M.A. Palmer. 2008. Lakes and streams as sentinels of environmental change in terrestrial and atmospheric processes. *Front. Ecol. Environ.* 6:247–254.
- Wollheim, W.M., B.A. Pellerin, C.J. Vörösmarty, and C.S. Hopkinson. 2005. N retention in urbanizing headwater catchments. *Ecosystems* 8:871–884.
- Xu, Y., L. Baker, and P. Johnson. 2007. Effect of land use change on temporal trends in groundwater nitrate concentrations in and around Phoenix, Arizona. *Ground Water* 27:49–56.