# The Urban-Rural Environment:

# Effects of Impervious Surface Land Cover on Lake Ecosystems

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# Abstract

The rate of urbanization of land has increased dramatically over the past decades and is expected to continue increasing as global populations continue to rise. Modifications of land associated with urbanization undoubtedly affect the adjacent and surrounding ecosystems, and urban ecosystem science has become an increasingly popular area of research to assess and quantify the ramifications of such drastic changes. The prevalence of impervious surfaces, one of the most defining characteristics of urban areas, has fundamentally altered the hydrology of urban ecosystems through decreased infiltration of surface water and rerouted hydrological flow paths. As a result, aquatic ecosystems positioned within urbanized areas have been significantly influenced by increases in stormwater runoff associated with efficient drainage networks. The altered hydrology within these urban systems has been shown to consistently negatively impact overall stream health. In contrast, urban lakes have been much less studied, yet have clearly been impacted by urbanization. Shallow lakes within the Twin Cities Metropolitan Area, Minnesota were assessed in 2007 for phytoplankton nutrient limitation and in 2007-2009 for nutrient biogeochemistry. Phytoplankton exhibited either multiple or co-nutrient limitation by nitrogen, phosphorus, and silica in 12 of the 17 lakes sampled in 2007. Strong negative relationships were observed across a gradient of impervious surface percentage within surrounding lake buffers for both TDN and DOC in 2007 and 2008. However, this gradient of imperviousness ranged from an agriculturally dominated landscape to a highly urbanized landscape. Therefore, lakes assessed in 2009 included reference sites dominated by forested land cover; these displayed similar concentrations of TDN and DOC as urban lakes. Chemical characterization of the DOC across these lakes nevertheless suggests DOC within urban lakes is dominated by autochthonous sources, while DOC in forested and agricultural lakes is dominated by allochthonous sources. These results suggest that urbanization, characterized by impervious surface land cover, and agricultural land use affect nutrient biogeochemistry and DOC character within lakes.

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# INTRODUCTION

Urban ecosystems have been experiencing significant expansion for the past 60 years and represent one of the most anthropogenically impacted ecosystems on the globe today.  As of 2005 approximately 49% of the global population resided in urban areas and predictions suggest this number could increase to nearly 70% by 2050 (United Nations Population Division 2009).  Demographic trends toward increased urbanization are even more impressive within developed nations.  For example, the current and projected percentages of the population residing within urban areas in Northern America are 81% in 2005 and 90% in 2050, respectively (United Nations Population Division 2009).  Given the high population density of urban areas and the associated unprecedented landscape scale modifications, impacts to the adjacent and surrounding ecological systems are certain and have become an increasingly important area of scientific research.

With such a large percentage of the population inhabiting these urban areas, drastic modifications to the landscape result in both indirect and direct effects on the associated ecosystems.  Modifications within the urban environment such as construction of buildings, roadways, and parking lots are observed by many on a daily basis.  These highly visible physical structures and modifications to the landscape have affected and are continuously affecting the surrounding ecosystems through indirect mechanisms such as noise and temperature pollution, increased concentrations of toxins and pollutants, and general loss of biodiversity (Rutherford et al. 1997, Davis et al. 2001, Ball et al. 1998, and Blair 1999).  In addition, these modifications have directly affected the natural terrestrial and aquatic ecosystems within the same space. For example, removal of natural tree stands, drainage of wetlands, and stream burial were common modifications to create a more uniform area suitable for development (Elmore and Kaushal 2008).

The drastic changes that occur within a natural environment during the preparation and expansion of urbanized areas are commonly observed along the urban fringe (Moore et al. 2003). The urban fringe can be defined as the perimeter of a highly urbanized area that experiences suburban expansion. As the population of cities increases, the establishment of distinct suburbs surrounding the urban core is a common phenomenon. Conversion of land into urban areas generally occurs at the fastest rate along these urban fringes for a number of reasons such as accessibility to the urban core for employment and other resources and the ability to escape the urban core and reside within a more suburban community. Encroachments of natural land and agricultural areas along the urban fringe are the most common land cover conversion at the urban fringe interface (Greene and Stager 2001). Therefore, ecosystems positioned along a transect across the urban fringe often span a gradient of land cover and land use patterns dominated by either natural or agricultural land in the outlying areas to intense urbanization within the urban core. The influences of these urban areas on the surrounding landscape and the negative impacts they have on the natural environment have fueled scientific inquiries to better understand the ecological ramifications of such changes.

### ***Urban Ecology***

Urban ecology has become an increasingly active area within ecosystem science in the past decades with much effort devoted to characterizing urban environments (Baker et al. 2001, Groffman et al. 2004, Pickett et al. 2008, Grimm et al. 2008, and Alberti et al. 2004). The evolution of urban ecology as a science has progressed from an originally descriptive approach, focused on species abundance and diversity, toward one which attempts to provide mechanistic explanations for the commonly observed patterns (Shochat et al. 2006). Beginning research studies focused on exploratory methodology to begin assessing urban ecosystems to provide some comparison with more natural systems. These research efforts quickly elucidated common patterns such as increased concentrations of toxins and pollutants as well as decreased biodiversity when compared with undisturbed ecosystems. Following the documentation of these somewhat expected patterns, the focus of urban ecology shifted to begin providing mechanistic explanations through primarily experimental studies (Shochat et al. 2006). For example, Helms et al. (2009) found hydrological and physicochemical conditions associated with impervious surface land cover decreased stream fish community diversity, richness, and biotic integrity. These findings began to provide a more mechanistic understanding of the effects of increased impervious surface land cover, such as increased hydrologic flashiness and water temperatures, on stream fish communities.

One result of the shift toward a more mechanistic understanding of urban ecology included close examination of existing models for biogeochemical cycles. These models were scrutinized for their applicability within urban environments because of their failure to incorporate human biogeochemical controls (Kaye et al. 2006). These controls are centered on the anthropogenic landscape-scale modifications imposed upon ecosystems as a result of urbanization such as, nutrient fluxes associated with high population densities, engineered hydrological systems to efficiently transport water off the landscape, and expansive areas of impervious surface land cover.

### ***Impervious Surface Land Cover***

The built environment of urban ecosystems is dominated by modifications that are heterogeneous at the landscape scale (Cadenasso et al. 2007). This heterogeneity has led to several different measures that may be used to describe the extent of urbanization within a given study area (McDonnell and Hahs 2008). Yet, one common characteristic across this heterogeneity in the urban environment is increased impervious surface land cover, which is defined as anthropogenically modified land cover that is impenetrable to water. Therefore, this consistent feature of urban ecosystems has resulted in many mechanistic studies focusing on impervious surface land cover, often the most dominant type of land cover within heavily urbanized ecosystems.

Impervious surface land cover is analyzed relatively efficiently using a combination of approaches including geographic information systems (GIS) and satellite imagery (Chabaeva et al. 2009). Many important relationships within urban ecology have identified impervious surface land cover as an important explanatory variable. For example, impervious surface land cover is highly correlated with many ecosystem properties in urban environments such as increased nutrient loading (Walsh et al. 2005), increased contaminant transport (Wei et al. 2010 and Wu et al. 1998), and decreased biodiversity within both terrestrial and aquatic systems (Rutherford et al. 1997 and Walsh et al. 2005).

Impervious surfaces most directly influence the hydrology within urban environments. As a result, urbanized areas dominated by impervious surface land cover have fundamental alterations to the hydrologic cycle that affect the connections between terrestrial and aquatic ecosystems (Lazaro 1990). Impervious surface land cover within watersheds directly results in increased runoff volumes, which must be dealt with in urbanized areas to minimize the effects of flooding. Efficient drainage networks are constructed to quickly flush water from the landscape and into streams, rivers, and lakes. These simplified flow paths, which interrupt the interactions among precipitation, groundwater, and surface water, significantly decrease the infiltration of surface flows into the terrestrial landscape. Brun and Band (2000) found a threshold of 20% impervious surface land cover results in significant changes to runoff ratios, which represent the proportion of precipitation that contributes to stormflow. Consequences associated with this phenomenon include decreased recharge of groundwater and increased channelization within streams as a result of increased flow volumes (Arnold and Gibbons 1996). Booth and Jackson (1997) provided evidence that levels of urbanization characterized by impervious surface land cover as low as 10% resulted in aquatic system degradation. Due to the disconnect between surface flow and the natural terrestrial environment such as plants, soils, and microbes, the previously existing natural methods of filtration and supply are disrupted. The subsequent transport of nutrients, pollutants, and toxins from the urban environment can be detrimental to overall water quality and the associated biotic communities.

### ***Water in the Urban Environment***

Maintaining acceptable water quality and quantity within urban aquatic ecosystems is critical from both a biological and economical standpoint. Deteriorated water bodies as a result of increased nutrient or pollutant loading often exhibit simplified biotic communities (Walsh et al. 2005). The transport of nutrients and pollutants from impervious surface land cover directly to aquatic ecosystems can be toxic to sensitive aquatic organisms. Consideration of an economical standpoint shows that relatively high and stable lake levels are important for influencing housing prices and a calculated recreational and aesthetic value (Lansford and Jones 1995). The resupply of ground water to maintain acceptable water table levels and thus lake levels can be interrupted by impervious surface land cover within a watershed (Erickson and Stefan 2009). In addition, efficient drainage networks can increase the variability in water levels by quickly aiding in the transport of large volumes of water to the receiving systems.

Acknowledgement of the water quality concerns associated with urbanization has resulted in the expansion of urban ecology to encompass aquatic systems, though much of the research to date has focused on urban streams. The “Urban Stream Syndrome” has been proposed as a framework for the consistent responses observed within urbanized stream ecosystems (Walsh et al. 2005). Some of the most commonly observed responses of streams to increased urbanization include an increase in the flashiness of the hydrograph, increased loading of nutrients and toxins, simplification of channel morphology, and decreased biotic diversity with increases in pollutant tolerant species. Altered ecosystem function has also been suggested as a symptom of stream urbanization (Meyer 2005). In addition, research influenced by the “Urban Stream Syndrome” has resulted in the proposal of a “Suburban Stream Syndrome”. This syndrome suggests similar detrimental responses within streams that experience low-density exurban expansion, with impervious surface land coverage as low as 4.7% (Cunningham et al. 2009). More specifically, concentrations of $NO_3$-N and $Cl^-$ were significantly increased relative to reference levels within the suburban streams studied (Cunningham et al. 2009). The establishment of these two stream syndromes provides an example of the attention urban streams have received within the broader context of urban ecology.

Lentic urban environments deserve equal attention because they provide invaluable resources for maintenance of biodiversity, provision of drinking water, and recreational activities. Quantifying the impacts of urbanization on lakes is a necessity for guiding management decisions. For example, Fraterrigo and Downing (2008) found that watershed transport capacity, the potential of a watershed to transport materials via overland flow, which is influenced by the hydrology, geology, soils and topography of a watershed, is an important variable when considering the influence of surrounding land use and land cover on lake chemistry. More specifically, in-lake processing and characteristics of the land directly surrounding the lake are more influential when watershed transport capacity is low. In contrast, lakes in watersheds with high transport capacity are more influenced by the land cover and land use throughout the watershed. Although these findings applied to agricultural watersheds, similar transport capacities can be envisioned within urbanized watersheds because of the increased drainage networks present in areas of high impervious surface land cover.

### ***Urban Aquatic Nutrient Biogeochemistry***

Previous work in urban streams has also focused on concentrations of carbon and nitrogen. Increased loading of nitrogen associated with surrounding urban land use was observed in Baltimore, MD streams (Shields et al. 2007). However, dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) loading from urban areas to streams have been hypothesized to lower in-stream concentrations of these nutrient constituents because of dilution attributed to efficient drainage networks removing water from the landscape prior to contact with terrestrial sources (Hook & Yeakley 2005). Nevertheless, previous studies have not provided support for this hypothesis (Hook & Yeakley 2005 and Aitkenhead-Peterson et al. 2009). Specifically, DOC and DON concentrations were analyzed in subtropical savanna biome stream watersheds of south-central Texas varying in urban and agricultural land use. Increased DOC concentrations were observed in high density and open area (i.e. parks and green space) urban land uses. Barnes and Raymond (2009) observed significant increases in dissolved inorganic carbon (DIC) export from urban and agricultural lands within temperate regions. More specifically, DIC export from urban watersheds was 7.8 times higher than forested watersheds and 2.0 times higher than agricultural watersheds. These increases were attributed to increased chemical weathering within the highly impacted ecosystems, increased $CO_2$ production from urban green spaces, and the contribution of organic matter from sewer lines and septic systems. However, examining the relationships between urban land use and dissolved carbon and nitrogen in lentic urban and suburban environments have received much less attention.

The prevalence of impervious surfaces within urbanized areas is potentially an important factor influencing nutrient inputs to lentic aquatic ecosystems. Due to the dramatically altered hydrologic cycle imposed upon aquatic systems in highly impervious watersheds, the resulting nutrient ratios may be significantly impacted. A negative relationship between both TDN and DOC and impervious surface land cover in surrounding lake buffers has been shown across an urban-rural gradient (Sterner Lab studies 2002-2003). It has been hypothesized that the mechanism responsible for these observations is a result of impervious surfaces disrupting the contact between surface run-off and the underlying soils and groundwater. Alterations to the nutrient biogeochemistry within these urbanized lakes may have implications on the biotic communities as well.

### ***Microbial Respiration and DOC Character***

Characterization of DOC has become an emerging field in ecosystem ecology because of advances in technology that allow efficient analysis of the highly diverse compounds comprising the DOC pool (Jaffe et al. 2008). The characterization allows more detailed descriptions of the relative contributions of DOC from autochthonous and allochthonous sources to aquatic systems, thereby providing a potential mechanistic explanation for differences observed within microbial community production rates (Sachse et al. 2005).

Bacterial production is reliant upon DOC as an energy source, and as a result, may be directly influenced by alterations to the DOC pool through urbanization. Sources of DOC have been shown to be important for rates of bacterial production because of the differences between autochthonous and allochthonous sources of DOC. Therefore, watershed characteristics that influence the mechanisms that drive the abundance of these two chemically disparate sources of DOC may also influence bacterial production.

### ***Phytoplankton Nutrient Limitation in the Urban Environment***

Generalized patterns of nutrient limitation have been proposed for marine and freshwater environments (Hecky and Kilham 1988). Specifically, nitrogen is predominantly described as the limiting nutrient in marine systems while phosphorus is most commonly termed the limiting nutrient in freshwater systems. However, recent research efforts have begun to question these broad generalizations and have suggested the previously established dichotomy may not be so clear (Elser et al. 1990, Maberly et al. 2002, Elser et al. 2007, and Sterner 2008).

Investigating how phytoplankton nutrient limitation may vary over a gradient of urbanization is novel. As watershed urbanization increases, the capacity for run-off to contact soils and groundwater becomes increasingly limited due to the increase in impervious surface land cover. Therefore, nutrients commonly obtained via contact with these sources (e.g. phosphorus and silica) may become severely depleted in run-off from highly impervious areas. These deficiencies may lead to patterns of phytoplankton nutrient limitation that are predictable within the urban environment.

Nutrient balances within aquatic ecosystems are fundamentally critical for their overall functioning. At the base of the food web, algal productivity is often nutrient limited and the quality of the algal food base from a grazer perspective is affected by the nutrient stoichiometry. Therefore, differential loading of particular nutrients associated with anthropogenically modified land uses and land covers may subsequently alter the stoichiometric ratios of nutrients available in the system. Identifying and understanding these differences will assist urban watershed districts, charged with managing the urban landscape, with maintaining a desired level of aquatic resource health.

### *Nutrient Biogeochemistry and Biotic Responses Across an Urban-Rural Gradient*

Shallow lakes spanning a gradient of urbanization within the Twin Cities Metropolitan Area (TCMA), as measured by impervious surface land cover, were sampled to assess the effects of impervious surface land cover on nutrient biogeochemistry, DOC character, phytoplankton nutrient limitation, and microbial respiration. However, urban-rural gradients often represent a trade-off between impervious surface land cover associated with the urban areas and intensive row crop agriculture associated with the rural areas. This project incorporates lakes with relatively pristine, urbanized, and agriculturally dominated watersheds to compare the effects of urbanization and agricultural practices on shallow lakes. The existing limited research on nutrient balances in lentic urban environments will benefit from a better understanding of the effects of increasing impervious surface land cover. In addition, knowledge regarding the effects of impervious surface land cover on phytoplankton nutrient limitation provides critical information for addressing the management of urban eutrophication (Dodds and Priscu 1990).

## MATERIALS & METHODS

### *Site Selection & Sampling*

Lakes sampled in this study represent a subset of the 100 lakes sampled by Sterner Lab studies (2002-2003). Briefly, 100 stratified random points were placed throughout the seven county Twin Cities Metropolitan Area and permanent water bodies nearest to each point were identified using a combination of geographic information systems (GIS) and ground identification. The resulting habitats consisted of ponds and lakes spanning a wide range of dominant land cover classes identified using GIS within concentric circles surrounding each lake. These neighborhood radii were calculated based on lake radius, assuming the lake was circular, and consisted of three sizes - r1, r2, and r3, which represented 1x, 2x, and 3x the radius of the lake. This study used the largest neighborhood radii, r3, for identification of surrounding land cover types, unless otherwise noted. The % ISLC is defined as the percent of "weighted" impervious surface and represents the average percent of impervious surface land cover within the r3 buffer, which provides a more refined measure of impervious surface land cover. ISLC was calculated using the following equation:

$$\mathrm{ISLC} = \frac{\sum_{0}^{100} \%\ \textit{imperviousness x pixels}}{\textit{total pixel number of the lake buffer}} \qquad (1)$$

The 100 - lake study system consisted of lakes spanning a wide range in size and depth because of the randomly placed points. The goal of this project was to assess the effects of impervious surface land cover on lake ecosystems. However, lake size and depth have strong influences on lake ecosystem characteristics and are likely highly confounding variables when attempting to assess the effect of impervious surface land cover. Therefore to select a subset for the present study, the database was filtered to identify lakes with public access that were of similar size (>1 ha and ≤70 ha) and depth (≤20m). This filtering resulted in 17 possible sites, which were each sampled a single time during the summer of 2007 (Table 1). In 2008, the number of sites (n=6) was decreased further to accommodate an increase in sampling frequency of each lake to assess potential temporal effects. Sampling locations consisted of four lakes in 2007 and an additional two lakes from the 100 – lake study system, all of which were within approximately 45 kilometers of one another in an attempt to control variability associated with large spatial scales (Table 2). In 2009 (n=8), the addition of two reference sites dominated by forested land cover within the neighborhood radii was necessary to assess the differing effects associated with urban, agricultural, and natural land use. The two additional forested sites were within the same geographic area described above (Table 3).

The sampling period of 2007 spanned 70 Julian days and each of the 17 lakes was sampled a single time. This protocol raised the issue of whether a single sampling adequately gives a representative value. Therefore, lakes sampled during 2008 and 2009 were sampled multiple times during the respective seasons, and for each individual sampling date the complete set of lakes was sampled. This combination of sampling regimes balances sampling a greater diversity of lakes with limited frequency and sampling a subset of lakes with higher frequency to assess temporal effects.

At each sampling event a composite water sample was collected from three pelagic sites within each lake taken from 0.5m below the surface. Temperature, dissolved oxygen (DO), conductivity, and pH were measured using a Hydrolab MS5 (Hach Company) deployed to a depth of 0.5m. Water was collected using a Van Dorn sampler and transferred to acid washed (10% HCl) 1L polycarbonate sample bottles. Water samples were stored on ice in a cooler until arrival at the lab (< 8 hours) when all samples were processed.

### ***Water Quality Analyses***

Whole lake water was filtered through 80 µm mesh to remove large zooplankton and particulates, and samples were frozen to assess total phosphorus (TP). Total nitrogen (TN) was determined by the sum of total dissolved nitrogen (TDN), and particulate organic nitrogen (PON). In addition, whole lake water was filtered through 0.4 µm Whatman polycarbonate filters into 125 ml polycarbonate sample bottles and frozen for subsequent analysis of dissolved organic carbon (DOC), TDN, and total dissolved phosphorus (TDP). DOC and TDN were analyzed using an automated Shimadzu TOC-Vcsh Total Organic Carbon Analyzer (Shimadzu Scientific Instruments), and TDP was analyzed using the potassium persulfate oxidation benchtop method (Wetzel and Likens 2000).

To assess particulate carbon, nitrogen, and phosphorus, pre-combusted Whatman GF/F filters were rinsed with 50 ml of 1% HCl and 50 ml of nanopure water and were produced for each sample by filtering whole lake water. Two filters were produced for both the particulate carbon/nitrogen sample and particulate phosphorus (PP) sample.

Particulate carbon and nitrogen were analyzed using the combustion method with a Perkin Elmer 2400 CHN Elemental Analyzer (PerkinElmer, Inc.).

Chlorophyll *a* samples were prepared in triplicate for each lake by filtering whole water through Whatman GF/F filters. Concentrations of chlorophyll *a* were determined by a 90% acetone extraction and subsequent analysis on a Turner Designs 10-AU fluorometer (Welschmeyer 1994).

### *DOC Characterization*

Lake water was filtered through Whatman 0.2µm polycarbonate filters into pre-combusted amber glass vials and stored at 4°C until analysis (<4 months). Spectrophotometric absorption of samples was performed using a scan from 200-600 nm on a Varian Cary 50 Bio UV-Visible Spectrophotometer (Varian, Inc.). Specific ultra-violet absorbance at 254 nm ($SUVA_{254}$), normalized for DOC concentration, was used as a technique to estimate the content of aromatic carbon within the samples (Weishaar et al. 2003). Excitation emission matrices (EEMs) were collected using a Fluoromax-3 Horiba Jobin Yvon Fluorometer (Horiba Scientific) every 10 nm using an excitation range of 250-400 nm and an emission range of 350-550 nm every 2nm. An established parallel factor analysis (PARAFAC) model was used to model the EEMs in MATLAB (Cory and McKnight 2005). This particular model identified 13 components, seven of which are quinine-like, two are amino acid-like, and four are unknown. The validity of using the established PARAFAC model was assessed by comparing the maximum intensity of the measured EEMs with the maximum intensity in the residual EEMs, which represents the differences between the measured and modeled EEMs. A maximum intensity in the residual EEM that is <10% of the maximum intensity in the modeled EEM represents correct modeling by the PARAFAC model used (Fellman et al. 2009).

### *Algal Bioassays*

Each of the 17 lakes sampled during the summer of 2007 was tested for algal nutrient limitation. Dilution nutrient enrichment bioassays were performed in 250 ml polycarbonate Erlenmeyer flasks by mixing 20 ml of whole lake water with 180 ml of lake water filtered through a 127 mm Whatman extra thick pre-filter and a 142 mm 0.2 µm Whatman polycarbonate filter (Paerl and Bowles 1987 and Sterner and Grover 1998). All water for each lake was collected at a depth of 0.5 m and represents a composite sample of three sites within each lake. Erlenmeyer flasks were acid washed in 10% HCl for 24 hours prior to each experiment. Algal nutrient enrichment bioassays were incubated for 90 hours at 22°C with a light intensity of 200 $\mu Em^{-2}s^{-1}$on a 15:9 light:dark cycle similar to the average day length to mimic ambient light conditions during the sampling period. During the incubation period, flasks were hand swirled three times daily to limit algal sedimentation. Nitrogen, phosphorus, and silica nutrient enrichments were performed in triplicate using a full factorial design giving a total of 27 flasks with the inclusion of undiluted and diluted controls. A 25 $\mu mol\ L^{-1}$ spike of $NH_4NO_3$, a 3 $\mu mol\ L^{-1}$ spike of $NaH_2PO_4 \bullet H_2O$, and a 25 $\mu mol\ L^{-1}$ spike of $Na_2SiO_3 \bullet 5H_2O$ were added in 1 ml volumes to respective samples. The concentration of each spike represents the increase in concentration of the respective nutrient in each bioassay treatment.

Algal growth was assessed by filtering the contents of each flask onto a Whatman GF/F filter, which was analyzed for chlorophyll *a*. Algal growth rate was calculated using the following equation:

$$\text{Algal growth rate} = \frac{\ln(\text{chl } a_{\text{final}} / \text{chl } a_{\text{initial}})}{\text{incubation duration in days}} \qquad (2)$$

The three replicates of each bioassay treatment were averaged to represent the algal growth rate achieved in each treatment. Nutrient limitation within each lake was determined with multi-way ANOVA using Statistica 9.1 (StatSoft, Inc.).

### ***Microbial Respiration Bioassays***

Microbial respiration bioassays were performed in pre-combusted glass amber vials using 1.0µm filtered lake water collected on August 8th and August 25th, 2009. All water for each lake was collected at a depth of 0.5 m and represents a composite sample of three sites within each lake. Microbial respiration bioassays were conducted in triplicate for each treatment and incubated for 48 hours at 26ºC. Microbial respiration was determined by assessing the change in oxygen concentration across three treatments per lake. An initial control was killed using 60µL of $HgCl_2$ prior to incubation to control for changes in oxygen throughout the incubation period. The remaining two treatments were a control and the carbon enrichment treatment, which were both incubated prior to addition of the mercuric chloride. Carbon enrichment was performed by adding $C_6H_{12}O_6$ in 500µM spikes via a volume of 50µL (Vrede 2005). Oxygen concentrations were assessed in all treatments using membrane-inlet mass spectrometry (MIMS) (Tortell 2005).

# RESULTS

## *Lake and Land Cover Characteristics*

This project focuses on the weighted percentage of impervious surface land cover (%ISLC) in the surrounding buffer of interest. Lakes spanned a wide range of %ISLC (0.05 - 80.11) in 2007, (0.62 - 60.61) in 2008, and (0.41 - 60.61) in 2009. However, each buffer was also characterized using a more detailed land cover classification scheme (Table 4). Inclusion of these land covers in the analysis broadened the potential list of land covers that may influence the lake ecosystems under investigation. Table 5 displays correlations among %ISLC and level 1 land cover predictor variables for lakes sampled in 2007, 2008, and 2009. The number of significant correlations is greater in 2007 (8) when 17 lakes were sampled than in 2008 and 2009 (3) when six and eight lakes were sampled, respectively. The greater diversity of sites sampled in 2007 likely provides a better representation of the landscape-scale land cover characteristics within the seven-county TCMA.

Most notable were the significant positive correlations between %ISLC and the urban land cover class across all three years, which was to be expected because the urban land cover class was defined by areas with different thresholds of %ISLC. Yet, %ISLC was selected as the primary predictor variable in this study because it represents a more refined measure of impervious surface land cover based on an individual pixel basis. The removal and addition of sites across years resulted in some inconsistent significant relationships between land cover variables across years. Table 5 highlights not only the correlations among land cover variables, but also the negative impacts urbanization has on natural land cover variables such as forests, open water, and wetlands. In addition, the negative correlation between %ISLC and agriculture highlights the phenomenon of urbanization displacing agricultural land along the urban fringe (Greene and Stager 2001).

Lakes sampled in 2007 spanned a limited size (1.22ha to 65.56ha) and maximum depth (0.9m to 20.0m) gradient and spanned the seven-county TCMA. However, all sites sampled in 2008 and 2009 were small shallow lakes (<25ha and <5m maximum depth) that were within approximately 45 kilometers of one another, which aided in minimizing variation in lake size and differences associated with geography that have previously been shown to affect lake ecosystems (Tessier and Woodruff 2002 and Sobek et al. 2007). The prevalence of small lakes across the globe has recently been highlighted and understanding the functioning of these small, yet abundant water bodies is important (Downing et al. 2006). Therefore, this study attempted to assess broader scale effects associated with impervious surface land cover percentage by sampling a greater diversity of lakes, as well as a more refined analysis of a focused geographic region with increased emphasis on capturing temporal effects.

### ***Nutrients***

#### *Sample Year 2007*

DOC and TDN concentrations were both significantly negatively related to %ISLC and percentage of urban land cover from the level 1 land cover predictors, and all relationships were best fit by nonlinear functions, as determined by $R^2$ (Figures 1 and 2). The nonlinearity of these relationships was driven by the rapid decrease in concentrations of both DOC and TDN at %ISLC and percentage of urban land cover values less than 20%, and the relatively constant DOC and TDN concentrations at higher %ISLC and percentage of urban land cover.

In contrast, PP concentration was significantly positively related to %ISLC and significantly negatively related to percentage of open water land cover from the level 1 land cover predictors (Figure 3). Sterner Lab studies (2002-2003) found a positive relationship between particulate phosphorus and %ISLC only at the smallest buffer size (r1). Although the largest buffer size (r3) has been used consistently throughout this project, a test of the particulate phosphorus relationship with %ISLC using the r1 buffer was performed to assess the validity of the findings by the Sterner Lab. Figure 4 displays the very slight improvement in the $R^2$ and $p$ values achieved when using the %ISLC in the 1r buffer as the independent variable as found by the Sterner Lab, which displays the resiliency of this relationship across years. However, the significant positive relationship between particulate phosphorus and %ISLC was only found in 2007 regardless of the buffer size used for the %ISLC.

*Sample Year 2008*

Data from 2008 represent averages of the five sampling dates (four sampling dates for lake 2-25), and therefore figures have error bars representing ± one standard deviation. Site N-24 was an outlier with respect to nutrient concentrations and was removed from all analyses in 2008 and 2009 (Tables 2 and 3). The close proximity to a wastewater plant and compost site as well as the high populations of carp observed during sampling efforts justified the exclusion of this site due to the strong effects benthivorous fish can have on regime shifts within shallow lakes (Zimmer et al. 2009).

There was no significant relationship between DOC and %ISLC in 2008, yet a similar negative trend was observed as in 2007 (Figure 5A). However, percentage of wetland cover was the best land cover predictor of DOC and can best be explained by previous research displaying the high loading of DOC from wetland land covers (Detenbeck et al. 1993, Xenopoulos et al. 2003, and Sobek et al. 2007) (Figure 5B). Unlike the relationship found in 2007, TDN concentration was not significantly related to %ISLC (Figure 6A). The best level 1 land cover predictor was percentage of agriculture, but the relationship was weak and insignificant (Figure 6B). TDN from lake N-39 sampled during 2008 had an uncharacteristically high standard deviation driven by a single sample collected on Julian day 191, but the cause of such a reading was unknown.

### *Sample Year 2009*

Data from 2009 represent averages of the four sampling dates, and therefore figures have error bars representing ± one standard deviation. The addition of two forested sites in 2009 (sites F-01 and F-04) was to distinguish between the potentially different effects associated with anthropogenic landscape modifications due to urbanization and agricultural land conversion. Therefore, these sites are excluded from the linear regressions, unless otherwise noted.

DOC concentrations were not significantly negatively related to %ISLC, yet a general negative trend existed, similar to 2008 (Figure 7A). The best level 1 land cover predictor DOC concentration was percentage of urban land cover, which is consistent with the results from 2007. DOC concentrations were significantly negatively related to percentage of urban land cover (Figure 7B). In contrast, there was no significant relationship found for TDN with either %ISLC or the best level 1 land cover predictor, which was percentage of urban land cover (Figure 8). The forested sites (gray triangles) in Figure 7 clearly fall outside of the fitted relationships found for DOC concentration because of their deviation from the best fit line. This is also the case for Figure 8, although it is less apparent because of the absence of significant linear relationships.

### *All Sample Years*

Relationships between nutrient ratios (TN:TP, TOC:TN, TOC:TP, PN:PP, PC:PN, PC:PP, TDN:TDP, DOC:TDN, and DOC:TDP) and %ISLC were analyzed across all years, but no significant relationships were observed. Compiling all samples from 2007, 2008, and 2009 showed the highly significant nonlinear negative relationships between %ISLC and both concentrations of DOC and TDN (Figure 9). Regardless of the year sampled, %ISLC appears to be a strong predictor of both DOC and TDN within the shallow lakes sampled for this study. Again, the nonlinear trend is driven by the rapid decrease in DOC and TDN concentration up to approximately 20 %ISLC and the subsequent relatively constant DOC and TDN concentration as %ISLC increases to the maximum values observed in this study.

## ***DOC Characterization***

$SUVA_{254}$ was calculated in 2008 and 2009 to aid in characterizing the DOC. Although no statistically significant relationships were found between %ISLC and $SUVA_{254}$, a highly suggestive negative trend was observed in both 2008 and 2009

(Figures 10 and 11). Figure 12 includes the forested sites from 2009 in the linear regression to show their general fit to the linear model.

The fluorescence index (FI) is another measurement used to assess whether DOC may be of autochthonous or allochthonous origin (McKnight et al. 2001). However, no clear relationship existed between %ISLC and the FI regardless of inclusion of the forested sites (Figures 13 and 14).

Figure 15 displays the significant linear relationships as identified by $p < 0.05$ between %ISLC and the percentage of each PARAFAC component present in the sample. Component 1 and component 10 were both unknown, yet they were significantly negatively related to %ISLC (Figure 15A and 15D). Components 8 and 12 are suggested as being linked to microbial matter rather than higher plant material (i.e. terrestrial sources), and both of these components were significantly positively related to %ISLC (Figure 15C and 15E). However, component 2 is also suggested as being linked to microbial organic matter and it was negatively related to %ISLC (Figure 15B).

### ***Algal Nutrient Limitation***

Multiple-limitation by N, P, and Si or co-limitation by N and P were the most common classifications of nutrient limitation and were observed in 12 of 17 lakes, while nitrogen limitation occurred in four lakes, and no nutrient limitation was identified in one lake. There was no discernible trend between %ISLC and the observed limiting nutrient for phytoplankton growth within lakes sampled in 2007 (Figure 16 and Table 6). In addition, the dominance of co-limitation by nitrogen and phosphorus and high variability of TN:TP ratios for a particular nutrient limitation status suggests there was no relationship between nutrient limitation and TN:TP ratios within the lakes studied.

There was no relationship between the growth rate of the algal community in the control treatments versus %ISLC (Figure 17). Although a consistent trend in nutrient limitation was not seen across the gradient of impervious surface land cover, algal growth rate increases following nutrient amendment significantly decreased with the percentage of impervious surface land cover (Figure 18). More specifically, algal communities from sites with low impervious surface land cover exhibited larger increases in growth rate upon nutrient amendment versus sites with high impervious surface land cover.

### ***Microbial Respiration Bioassays***

There was a strong non-linear negative relationship with the difference in oxygen consumption between the control and carbon addition treatments and %ISLC (Figure 19). A strong decrease in the amount of oxygen consumed during the 48-hour incubation period appears to occur up to a level of approximately 15% ISLC. The non-linear negative relationship observed in the microbial respiration bioassays is similar to the non-linear negative relationship observed between DOC concentration and %ISLC. The decrease in oxygen consumption was consistent across both sampling dates for which data are available, but given the limited data (two sampling dates in 2008) relationships should be interpreted cautiously.

## DISCUSSION

### ***Impervious Surface Land Cover and Nutrient Biogeochemistry***

#### *Effects on Individual Nutrient Constituents*

Concentrations of DOC and TDN displayed non-linear, negative relationships with %ISLC and were consistent across the three consecutive years in this study as well as with data collected in 2000 (Sterner Lab studies 2002-2003). The proposed mechanism to explain this relationship within lakes in the TCMA centers on the effect of impervious surfaces and their expansive coverage within urbanized areas. DOC and TDN can be transported to aquatic ecosystems via surface and sub-surface flows following interaction between runoff and the terrestrial landscape. However, within urban environments the connections between surface runoff and terrestrial soils are disconnected because of the presence of impervious surface land cover. Runoff that once contacted the abiotic and biotic natural terrestrial environment via surface flows or infiltration and subsequent sub-surface flows is diverted directly to the receiving waters through efficient drainage networks. Therefore, lakes within urban environments prior to development presumably received inputs of DOC and TDN from the terrestrial landscape through surface and sub-surface flows and their developed counterparts are now disconnected from that source.

The negative non-linear relationship observed between TDN concentrations and %ISLC, is consistent with patterns of $NO_3$-N observed in small streams in Maryland (Kaushal et al. 2008). Catchments with greater than 60% agricultural land use had the highest $NO_3$-N concentrations, and catchments with greater than 60% urban land use had the lowest $NO_3$-N concentrations. However, catchments dominated by forested land cover were intermediate with respect to $NO_3$-N. The intermediate concentration of TDN within forested catchments was not observed in the lakes studied here, but the small number of sites limits the establishment of a substantial conclusion. Nevertheless, lakes dominated by agricultural and urban land use appear to follow similar patterns with respect to TDN concentrations as small streams from Montgomery County, Maryland.

The significant positive relationship between PP and %ISLC was only observed in 2007, but this result is consistent with data collected on a larger set of lakes in 2000 (Sterner Lab studes 2002-2003). In addition, a strong negative relationship was seen between PP and the percent of open water within the surrounding neighborhood radii. One potential explanation for this relationship is the settling of particles that may occur within open water bodies surrounding the lake under investigation thereby removing PP from the water before it is able to ultimately reach the lake in question (Maynard et al. 2009). However, upstream connectivity to open water habitats was not assessed.

Compiling all years of DOC and TDN data highlights the strong non-linear negative relationship that was consistent across the lakes sampled in this study. Therefore, the urban to rural gradient has strong effects on the dissolved nutrient constituents of carbon and nitrogen. In addition, the urban to rural gradient affects concentrations of PP in an opposite manner. These patterns suggest impervious surface land cover affects nutrient constituents differently potentially leading to a distinct urban lake stoichiometric signature, which may influence phytoplankton nutrient limitation.

### *Phytoplankton Nutrient Limitation*

Co-limitation by N and P or multiple-limitation by N, P, and Si were the most common patterns of phytoplankton nutrient limitation observed in this study. The original hypothesis that potentially limiting nutrients commonly transported to lakes via surface flows or groundwater inputs, such as phosphorus and silica, were diminished within urban lakes because of the disconnect between water and the terrestrial soils was not supported. Yet, the results of this study are supported by an increasing body of literature pointing toward co-limitation and multiple nutrient limitation of phytoplankton in freshwater systems (Elser et al. 1990, Maberly et al. 2002, Dzialowski et al. 2005, Elser et al. 2007, and Sterner 2008). Although there is a scale disconnect between bottle bioassay experiments and ecosystem scale management decisions, these results provide a starting point for urban lake management. The multiple and co-nutrient limitation most commonly observed suggest multiple nutrients should be actively managed to minimize nuisance phytoplankton blooms that commonly degrade urban water quality.

Although a distinct pattern of nutrient limitation was not observed across the urban-rural gradient, relationships regarding phytoplankton growth rate responses to nutrient enrichments were observed. The negative relationship between the maximal phytoplankton growth rate increase in response to nutrient enrichment and %ISLC may be indicative of functional differences in the phytoplankton communities across the urban-rural gradient. More specifically, the absence of a relationship between phytoplankton growth rate in the control bioassays and %ISLC provides support that the phytoplankton communities were growing at similar rates across the urban-rural gradient prior to nutrient amendment. This also suggests that the source water is not inhibiting phytoplankton growth via high concentrations of pollutants or toxins. One possible explanation for the negative relationship between phytoplankton maximal growth rate increase in response to nutrient enrichment and %ISLC is a shift in size structure of the phytoplankton community, though the phytoplankton community was not characterized in this study. For example, phytoplankton communities in lakes with low %ISLC may be comprised of smaller species, which would result in a lower surface area to volume ratio and potentially higher maximal growth rates. Another possible explanation for this relationship is that phytoplankton communities in lakes with low %ISLC may be more diverse, which could also potentially result in a more efficient use of the nutrient amendment. Although the exact cause of this pattern is unknown, the absence of a relationship between the control treatment and %ISLC suggests that the cause may lie within the phytoplankton community characteristics. Therefore, the potential implications of this pattern may be that lakes with low %ISLC have an increased ability to respond to nutrient pulses or enrichments.

### ***Impervious Surface Land Cover and Organic Carbon***

#### *DOC Concentration Across an Urban Gradient*

Factors influencing DOC concentrations within lakes at a broad scale have been assessed. More specifically, analysis of a database of 7,514 lakes spanning six continents displayed negative relationships between DOC concentrations and altitude, mean annual runoff, and precipitation (Sobek et al. 2007). In contrast, conductivity, soil carbon density, and soil C:N displayed positive relationships with DOC concentrations. These global patterns highlight the many different controls on DOC within lakes. However, this study suggests that within a confined geographic area, land cover within surrounding neighborhood radii can influence both DOC concentration and character.

The high negative correlation between %ISLC and agricultural land use across years raised the question of whether the DOC decrease is driven by an increase in urbanization or a decrease in agricultural land (Table 5A, B, and C). To address this, two additional reference sites dominated by forested land cover in the neighborhood radii were included in 2009. Figure 7 displays the DOC concentration of these lakes is similar to the sites with high %ISLC, yet much less than the sites with low %ISLC, which are dominated by agricultural land use in the neighborhood radii. Therefore, the negative relationship between DOC and %ISLC may be driven more by the effects of agricultural land providing high levels of DOC rather than urban areas diminishing DOC. Izbicki et al. 2007 observed higher concentrations of DOC within a tributary stream draining agricultural land than from an urban drain and river. These results are in support of previous work where high loadings of DOC from agricultural systems to streams were observed (Warrner et al. 2009 and Royer and David 2005).

### *DOC Character Across an Urban Gradient*

Decreased concentrations of DOC are not the only difference observed with increased %ISLC. The chemical characterization of the DOC pool changes as well. Measures of aromaticity and allochthonous versus autochthonous sources of the DOC pool provide support for strong differences in DOC chemical character within lakes across the urban-rural gradient in this study.

$SUVA_{254}$ serves as a proxy of the percentage of aromatic carbon present in the DOC pool. The negative relationships between $SUVA_{254}$ and %ISLC suggest DOC in lakes surrounded by impervious surfaces tends to be less aromatic and of lower molecular weight and therefore more representative of an autochthonous origin (Weishaar et al. 2003). This pattern is consistent with the prediction that contributions of DOC from the terrestrial landscape are diminished through urbanization because of the disconnect between surface flows and groundwater flows by increases in %ISLC. Aromaticity of the dissolved carbon pool has implications for the bacterial community that uses it as a source of fuel. Specifically, DOC with a high percentage of aromatic carbon is generally less labile and therefore does not serve as a readily available fuel source for the bacterial community (Lennon and Cottingham 2005).

The FI provides a measure that can be used to assess the dominance of the DOC pool by either terrestrial or microbial sources. The low variability and intermediate values of the fluorescence index suggests a combination of autochthonous and allochthonous sources to the DOC pool. This measure was developed using end members from the DOC spectrum (McKnight et al. 2001). Specifically, Antarctic DOC was used as the microbial reference and large river DOC was used as the terrestrial reference. Therefore, it is reasonable that this particular measure did not clearly differentiate the less dramatic differences in DOC source material present in the lakes of this study. This is further supported by FI values from 54 aqueous samples from 11 geographic regions that displayed a limited range of FI values when compared with those observed by McKnight et al. (2001) (Macalady and Walton-Day 2009). The intermediate FI values observed in this study from structurally similar shallow lakes highlight the contribution of both terrestrial and microbial sources of DOC across the urban-rural gradient. This pattern is not surprising given that none of the DOC pools within the lakes sampled were expected to be dominated by a sole source of DOC.

PARAFAC components provide another line of evidence suggesting urban lake DOC pools are dominated more by autochthonous sources of DOC rather than allochthonous sources. Two of the three known components supported the prediction that urban lake DOC is more autochthonous as inferred by their positive relationships with %ISLC. One of the components, component 2, did not display the expected positive relationship with %ISLC, yet other results within this study have suggested microbial sources of DOC should increase within urban lakes. The small number of sites restricted the ability to develop a novel PARAFAC model, but the existing model used still identified several strong relationships. Future research could focus on identifying the chemical structure of both the unknown components as well as providing a more detailed description of the chemical structures. In addition, a larger-scale urban lake study could develop a novel PARAFAC model that would presumably better identify unique components across the urban-rural gradient.

Given the consistencies between the SUVA and PARAFAC data these results provide strong evidence that the DOC pool within urban environments differs significantly from less urban habitats. More specifically, the hypothesized decrease in terrestrial sources of carbon to lakes within urban landscapes is consistent with the decreases in aromaticity and presence of organic matter derived from allochthonous sources.

### *Discrepancy Between DOC Concentration and Character*

The similarity in total DOC concentration between the forested and highly urbanized lakes is somewhat surprising when considering the hypothesized mechanism causing the observed differences in DOC character (i.e. autochthonous and allochthonous source material). Impervious surface land cover associated with urbanization is hypothesized to decrease the import of terrestrial organic matter to aquatic systems because overland flow is restricted from contact with terrestrial soils. Therefore, in the forested lakes one may predict that the absence of impervious surface land cover would allow organic matter of terrestrial origin to enter the lake. The $SUVA_{254}$ and EEMs data support this prediction, in that DOC from the forested lakes exhibits significantly higher $SUVA_{254}$ values and the presence of terrestrially derived fluorophores in the EEMs.

In contrast, urbanized lakes with a prevalence of surrounding ISLC are expected to have inflow that has decreased or completely detached contact with terrestrial vegetation and soils. Therefore, assuming similar in-lake processes regarding DOC cycling, it may be expected that urbanized lakes would have decreased DOC concentrations because of the removal of the terrestrial source. However, this pattern was not observed. One possible explanation could be either decreased in situ production of DOC in forested lakes or increased in situ DOC production in urbanized lakes. Algal biomass is an indicator of in situ production and could possibly compensate for the missing terrestrial source of DOC in the urbanized lakes, but chlorophyll *a* values were not significantly different across the ISLC gradient.

Another possible explanation could be differences in the rates of processing DOC between the forested and urbanized lakes. Increased processing of DOC in the forested sites, or decreased processing of DOC in the urbanized sites could potentially explain the similarity in overall DOC concentration. This explanation is not well supported by the differences in DOC character across the ISLC gradient. Specifically, DOC from agricultural and forested lakes has increased $SUVA_{254}$ values and fluorophores indicative of terrestrial derived organic matter, which both suggest the organic matter present in these lakes should be less favorable to the microbial communities. In addition, DOC from urbanized lakes exhibits the exact opposite pattern, and would therefore be expected to be more susceptible to microbial degradation.

Ultraviolet light has a strong influence on the degradation of DOC (Häder et al. 1998). Therefore, differences in the light environment between forested and urbanized lakes could help explain the discrepancy in DOC concentration. The presumed decrease in DOC within forested sites when taking into consideration the inputs from the terrestrial environment, suggests increased DOC degradation via breakdown by ultraviolet light. Given the undisturbed surrounding habitat of forested lakes, it is hard to imagine there is a significant decrease in tree cover within these sites that would potentially allow increased ultraviolet light penetration. In addition, the character of the DOC within forested sites is suggestive of a more terrestrially dominated source, which would also inhibit penetration of ultraviolet light because of the associated increase in aromaticity. Therefore, this hypothesis does not appear to adequately explain the observed patterns.

Contributions of DOC from different types of land cover could also account for the discrepancy in DOC concentration. Wetlands are known to act as strong contributors of DOC to surrounding aquatic ecosystems (Xenopoulos et al. 2003 and Sobek et al.

2007). Additionally, for this hypothesis to be true, some type of land cover within the urbanized landscape would need to contribute significantly higher rates of DOC additions to the lakes to account for the presumed missing terrestrial source on account of increased impervious surfaces.

Finally, differences in the microbial community structure could contribute to either increased processing in forested lakes or decreased processing in urbanized lakes. For example, microbial diversity could be an important factor influencing DOC processing. There are large bodies of evidence that point toward increased efficiency and production in communities with increased diversity (Cardinale et al. 2009 and Tilman et al. 2006). Perhaps pollutants or toxins have led to biotic simplification of the microbial community within urbanized lakes that has decreased DOC processing ability. Biotic simplification is a well documented phenomenon across multiple trophic levels in both terrestrial and aquatic urban ecosystems as a result of increased urbanization and agricultural land use (Walsh et al. 2005 and Ekroos et al. 2010). However, differences between the microbial communities were not characterized and could prove to be the mechanism behind the discrepancy between DOC concentration and character with respect to the surrounding land use.

### *Effect on Microbial Respiration*

The non-linear negative relationship between the increase in oxygen consumption of the microbial community following glucose enrichment and %ISLC is suggestive of differences in respiration abilities between microbial communities across the urban-rural gradient. Farjalla et al. (2009) suggested bacterial production and respiration increased when both leachates from aquatic macrophytes and naturally humic refractory dissolved organic matter (DOM) were provided. The diversity of carbon sources available to the bacterial community was important. Concentrations of DOC within the lakes studied were generally greater than 5mg/L, which has previously been suggested as a transition point between net autotrophy and net heterotrophy (Jansson et al. 2000 and Prairie et al. 2002). Therefore, perhaps the greater supply of both allochthonous and autochthonous sources of carbon within forested and agricultural sites may contribute to the observed trend of increased microbial respiration within these systems. In contrast, urbanized systems which receive fewer sources of allochthonous carbon because of the decreased connectivity with terrestrial sources of carbon may limit the ability of the microbial community to respond maximally to pulses of carbon.

This non-linear negative relationship is also driven by strong decreases in oxygen consumption up to an ISLC of about 20%, a number previously suggested as a threshold of %ISLC after which negative effects of urbanization are often observed (Brun and Band 2000). Potential implications of this relationship are decreased processing of DOC by the bacterial communities within urbanized lake ecosystems, which can have strong effects on the functioning of the lake ecosystem as a whole (Lennon and Cottingham 2008).

### ***Conclusion***

Consistent patterns of nutrient concentrations, DOC character, and biotic responses of the phytoplankton and microbial communities to increased impervious surface land cover were observed across years. These results provide novel contributions to the understanding of lentic urban systems. While urban streams have received much of the attention with respect to urban aquatic research, urban lakes provide similar ecological, aesthetic, and recreational opportunities and therefore should receive equal amounts of attention within urban ecosystem research. This study provides strong evidence for some of the effects associated with paving over the landscape, and emphasizes the effects of urbanization on the surrounding lake ecosystems even at relatively low intensities (20%).

Table 1. Summary of general lake characteristics sampled during the summer of 2007. Lake ID: Lake Identification; JSD: Julian Sampling Date; ISLC: Impervious Surface Land Cover; Temp: Temperature; DO: Dissolved Oxygen; TN: Total Nitrogen; TP: Total Phosphorus; Chl *a*: Chlorophyll *a*.

| Lake ID | Latitude | Longitude | JSD | Area (ha) | Max Depth (m) | ISLC (%) | Temp ( °C ) | DO (% Sat) | Conductivity (mS/m) | TN (mg/L) | TP (µg/L) | Chl *a* (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-46 | 44°41'14.17"N | 93°25'5.32"W | 156 | 5.43 | 3.0 | 14.29 | 18.97 | 100.5 | 0.22 | 0.69 | 109.52 | 3.77 |
| N-21 | 44°40'28.03"N | 93°32'38.05"W | 156 | 12.52 | 5.0 | 0.62 | 21.94 | 105.5 | 0.36 | 1.47 | 187.34 | 17.91 |
| 1-27 | 45° 2'25.96"N | 93°19'19.99"W | 157 | 7.28 | 11.0 | 61.25 | 20.94 | 163.5 | 0.49 | 0.90 | 94.42 | 56.18 |
| 1-25 | 45° 3'43.87"N | 93°15'15.57"W | 157 | 5.92 | 3.0 | 69.93 | 20.53 | 91.4 | 0.60 | 1.16 | 117.35 | 31.66 |
| N-25 | 45°20'14.24"N | 93° 2'31.21"W | 162 | 26.65 | 0.9 | 0.05 | 24.90 | 108.2 | 0.20 | 1.20 | 93.83 | 5.81 |
| 1-13 | 44°54'51.16"N | 93° 4'17.69"W | 162 | 3.19 | 1.8 | 74.15 | 25.64 | 105.7 | 0.30 | 0.97 | 70.95 | 2.93 |
| 1-20 | 44°54'16.83"N | 93° 8'59.73"W | 163 | 19.42 | 6.0 | 28.51 | 25.83 | 146.3 | 0.77 | 0.69 | 38.90 | 10.99 |
| 1-12 | 44°54'0.58"N | 93° 9'34.21"W | 163 | 1.22 | 9.0 | 2.57 | 26.74 | 133.5 | 0.71 | 0.98 | 44.74 | 10.19 |
| N-39 | 44°39'47.13"N | 93°37'52.14"W | 172 | 6.88 | 2.0 | 49.67 | 24.48 | 138.7 | 0.51 | 0.63 | 30.39 | 6.04 |
| N-48 | 44°33'53.54"N | 93°42'18.87"W | 172 | 7.68 | 1.3 | 2.43 | 23.96 | 104.0 | 0.46 | 1.32 | 54.40 | 8.59 |
| 2-05 | 44°47'44.51"N | 93° 5'45.96"W | 173 | 2.09 | 2.0 | 10.89 | 23.25 | 82.4 | 0.11 | 1.29 | 83.36 | 51.36 |
| 1-24 | 44°51'24.11"N | 93°15'44.88"W | 173 | 2.75 | 6.0 | 80.11 | 23.84 | 70.5 | 0.75 | 0.60 | 54.32 | 1.76 |
| 2-20 | 44°48'23.88"N | 93°32'2.41"W | 190 | 1.95 | 2.5 | 13.54 | 24.82 | 65.0 | 0.55 | 1.31 | 114.22 | 15.58 |
| 2-14 | 44°50'15.63"N | 93°38'31.65"W | 190 | 65.56 | 20.0 | 11.74 | 27.58 | 101.0 | 0.36 | 0.96 | 29.31 | 8.34 |
| 1-07 | 44°58'10.08"N | 93°17'5.26"W | 191 | 2.01 | 5.1 | 63.39 | 27.05 | 121.8 | 1.51 | 1.40 | 110.86 | 53.60 |
| 1-15 | 44°57'15.19"N | 93°18'19.93"W | 191 | 44.11 | 9.0 | 57.92 | 26.94 | 132.4 | 0.58 | 1.25 | 76.72 | 59.92 |
| N-26 | 45°18'41.87"N | 93°14'14.55"W | 226 | 2.27 | 2.1 | 51.24 | 23.02 | 104.1 | 0.56 | 1.24 | 136.63 | 113.92 |

Table 2. Summary of general lake characteristics sampled during the summer of 2008. Values are averages of all sampling dates and ± one standard deviation is presented in parentheses. Lake ID: Lake Identification; JSD: Julian Sampling Date; ISLC: Impervious Surface Land Cover; Temp: Temperature; TN: Total Nitrogen; TP: Total Phosphorus; Chl *a*: Chlorophyll *a*.

| Lake ID | Latitude | Longitude | JSD | Area (ha) | Max Depth (m) | ISLC (%) | Temp ( °C ) | pH | TN (mg/L) | TP (μg/L) | Chl a (μg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| N-21 | 44°40'28.03"N | 93°32'38.05"W | 170, 191, 205, 218, 233 | 12.52 | 5.0 | 0.62 | 25.63 (1.75) | 9.90 (0.08) | 2.02 (0.40) | 171.21 (87.18) | 13.01 (9.20) |
| N-24 | 44°46'15.63"N | 93°47'45.45"W | 170, 191, 205, 218, 233 | 23.47 | 1.0 | 16.90 | 23.93 (1.50) | 8.76 (0.33) | 7.10 (4.11) | 317.45 (110.18) | 189.46 (119.84) |
| N-39 | 44°39'47.13"N | 93°37'52.14"W | 170, 191, 205, 218, 233 | 6.88 | 2.0 | 49.67 | 25.17 (1.80) | 8.64 (0.23) | 1.58 (1.26) | 48.28 (16.37) | 16.73 (6.02) |
| N-46 | 44°41'14.17"N | 93°25'5.32"W | 170, 191, 205, 218, 233 | 5.43 | 3.0 | 14.29 | 25.67 (1.40) | 9.67 (0.54) | 0.87 (0.12) | 41.46 (12.63) | 12.70 (9.42) |
| N-48 | 44°33'53.54"N | 93°42'18.87"W | 170, 191, 205, 218, 233 | 7.68 | 1.3 | 2.43 | 24.30 (2.57) | 8.41 (0.15) | 1.70 (0.20) | 78.04 (26.12) | 30.60 (16.74) |
| 2-25 | 44°44'27.73"N | 93°15'58.14"W | 191, 205, 218, 233 | 3.64 | 5.0 | 60.61 | 26.95 (0.92) | 10.21 (0.19) | 1.06 (0.12) | 46.00 (10.17) | 41.95 (21.57) |

Table 3. Summary of general lake characteristics sampled during the summer of 2009. Values are averages of all sampling dates and ± one standard deviation is presented in parentheses. Lake ID: Lake Identification; JSD: Julian Sampling Date; ISLC: Impervious Surface Land Cover; Temp: Temperature; TN: Total Nitrogen; TP: Total Phosphorus; Chl *a*: Chlorophyll *a*.

| Lake ID | Latitude | Longitude | JSD | Area (ha) | Max Depth (m) | ISLC (%) | Temp ( °C ) | Conductivity (mS/m) | pH | TN (mg/L) | TP (µg/L) | Chl a (µg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-21 | 44°40'28.03"N | 93°32'38.05"W | 99, 113, 127, 141 | 12.52 | 5.0 | 0.62 | 14.34 (5.35) | 0.43 (0.03) | 8.88 (0.42) | 1.68 (0.09) | 54.76 (31.97) | 12.15 (10.92) |
| N-24 | 44°46'15.63"N | 93°47'45.45"W | 99, 113, 127, 141 | 23.47 | 1.0 | 16.90 | 13.43 (5.44) | 0.79 (0.03) | 8.55 (0.37) | 3.71 (1.44) | 177.6 (75.16) | 64.71 (40.39) |
| N-39 | 44°39'47.13"N | 93°37'52.14"W | 99, 113, 127, 141 | 6.88 | 2.0 | 49.67 | 14.50 (5.27) | 0.69 (0.04) | 8.84 (0.17) | 0.66 (0.12) | 28.26 (6.72) | 5.76 (4.64) |
| N-46 | 44°41'14.17"N | 93°25'5.32"W | 99, 113, 127, 141 | 5.43 | 3.0 | 14.29 | 14.31 (5.22) | 0.27 (0.01) | 9.02 (0.31) | 0.78 (0.12) | 38.01 (7.33) | 10.44 (5.09) |
| N-48 | 44°33'53.54"N | 93°42'18.87"W | 99, 113, 127, 141 | 7.68 | 1.3 | 2.43 | 12.78 (5.42) | 0.49 (0.05) | 8.20 (0.15) | 1.61 (0.44) | 41.71 (6.07) | 14.74 (11.49) |
| 2-25 | 44°44'27.73"N | 93°15'58.14"W | 99, 113, 127, 141 | 3.64 | 5.0 | 60.61 | 13.96 (5.11) | 0.67 (0.02) | 8.45 (0.91) | 0.75 (0.10) | 30.77 (12.99) | 12.79 (6.44) |
| F-01 | 44°43'19.18"N | 93°20'40.47"W | 99, 113, 127, 141 | 2.93 | 0.5 | 1.76 | 16.01 (4.83) | 0.17 (0.02) | 7.31 (0.29) | 0.89 (0.20) | 21.77 (12.77) | 3.78 (2.63) |
| F-04 | 44°42'19.72"N | 93°19'29.37"W | 99, 113, 127, 141 | 4.80 | 1.7 | 0.41 | 15.96 (5.00) | 0.16 (0.01) | 7.90 (0.08) | 0.65 (0.06) | 20.14 (5.90) | 5.95 (1.26) |

Table 4. Land cover classifications, abbreviations, and definitions.

| **Level 1** | **Level 2** | **Definition** |
|---|---|---|
| Urban/Developed (URB) | High Intensity Urban | > 50% solid impervious surfaces of human-made materials |
| | Low Intensity Urban | ≤ 50% solid impervious surfaces of human-made materials |
| | Transportation/ Asphalt/Concrete | Major roads |
| Agriculture (AGR) | Herbaceous/Field Crops | Including row crops, forage crops, and small grains |
| Forest (FOR) | Coniferous | Evergreen forest land |
| | Broad-leaved Deciduous | Deciduous forest land |
| Open Water (OPW) | Open water | Permanent open water, lakes, reservoirs, streams, bays, and estuaries |
| Wetland (WTL) | Emergent Wet Meadow | Wet meadow, poor fen, rich fen, cattail marsh, and mixed emergent marsh |
| | Lowland Shrub | Temporarily flooded shrubland, alder swamp, wet meadow shrub subtype, and willow swamp |
| | Forested Wetland | Forested wetland |

Table 5. Pearson product moment correlations for percentage of impervious surface land cover and level 1 land cover types surrounding sampling sites in A) 2007, B) 2008, and C) 2009 (bold entries are significant at the α = 0.05 level). Refer to Table 4 for definitions of land cover abbreviations.

A.

| | **ISLC** | **URB** | **AGR** | **FOR** | **OPW** | **WTL** |
|---|---|---|---|---|---|---|
| **ISLC** | 1.000 | **0.981** | **-0.485** | **-0.492** | **-0.587** | **-0.618** |
| **URB** | | 1.000 | -0.452 | -0.456 | **-0.596** | **-0.698** |
| **AGR** | | | 1.000 | -0.229 | -0.012 | 0.001 |
| **FOR** | | | | 1.000 | **0.552** | 0.080 |
| **OPW** | | | | | 1.000 | 0.231 |
| **WTL** | | | | | | 1.000 |

B.

| | **ISLC** | **URB** | **AGR** | **FOR** | **OPW** | **WTL** |
|---|---|---|---|---|---|---|
| **ISLC** | 1.000 | **0.982** | -0.721 | 0.158 | -0.485 | -0.754 |
| **URB** | | 1.000 | -0.690 | 0.164 | -0.550 | **-0.816** |
| **AGR** | | | 1.000 | -0.731 | -0.224 | 0.166 |
| **FOR** | | | | 1.000 | 0.625 | 0.252 |
| **OPW** | | | | | 1.000 | **0.899** |
| **WTL** | | | | | | 1.000 |

C.

| | **ISLC** | **URB** | **AGR** | **FOR** | **OPW** | **WTL** |
|---|---|---|---|---|---|---|
| **ISLC** | 1.000 | **0.985** | -0.410 | -0.409 | -0.257 | **-0.789** |
| **URB** | | 1.000 | -0.370 | -0.429 | -0.305 | **-0.832** |
| **AGR** | | | 1.000 | -0.532 | -0.067 | -0.137 |
| **FOR** | | | | 1.000 | -0.144 | 0.642 |
| **OPW** | | | | | 1.000 | 0.346 |
| **WTL** | | | | | | 1.000 |

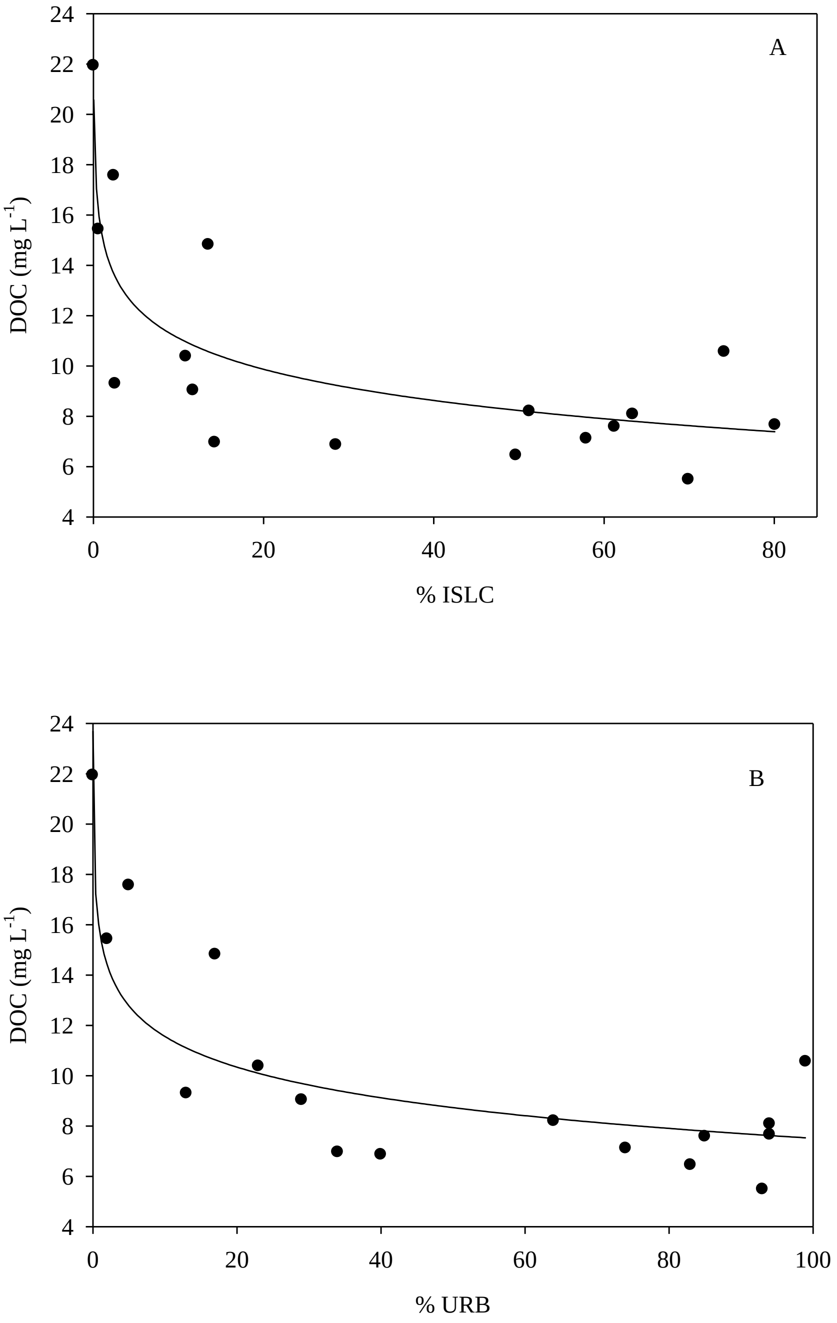

Figure 1. Relationships between DOC and percentage of impervious surface land cover (% ISLC) and the best level 1 land cover predictor in 2007. (A) %ISLC (y = -1.911 × ln(x) + 15.242; $R^2 = 0.66$; df = 16; $p < 0.0001$) and (B) urban (URB) (y = -1.757 × ln(x) + 15.603; $R^2 = 0.66$; df = 16; $p < 0.0001$).

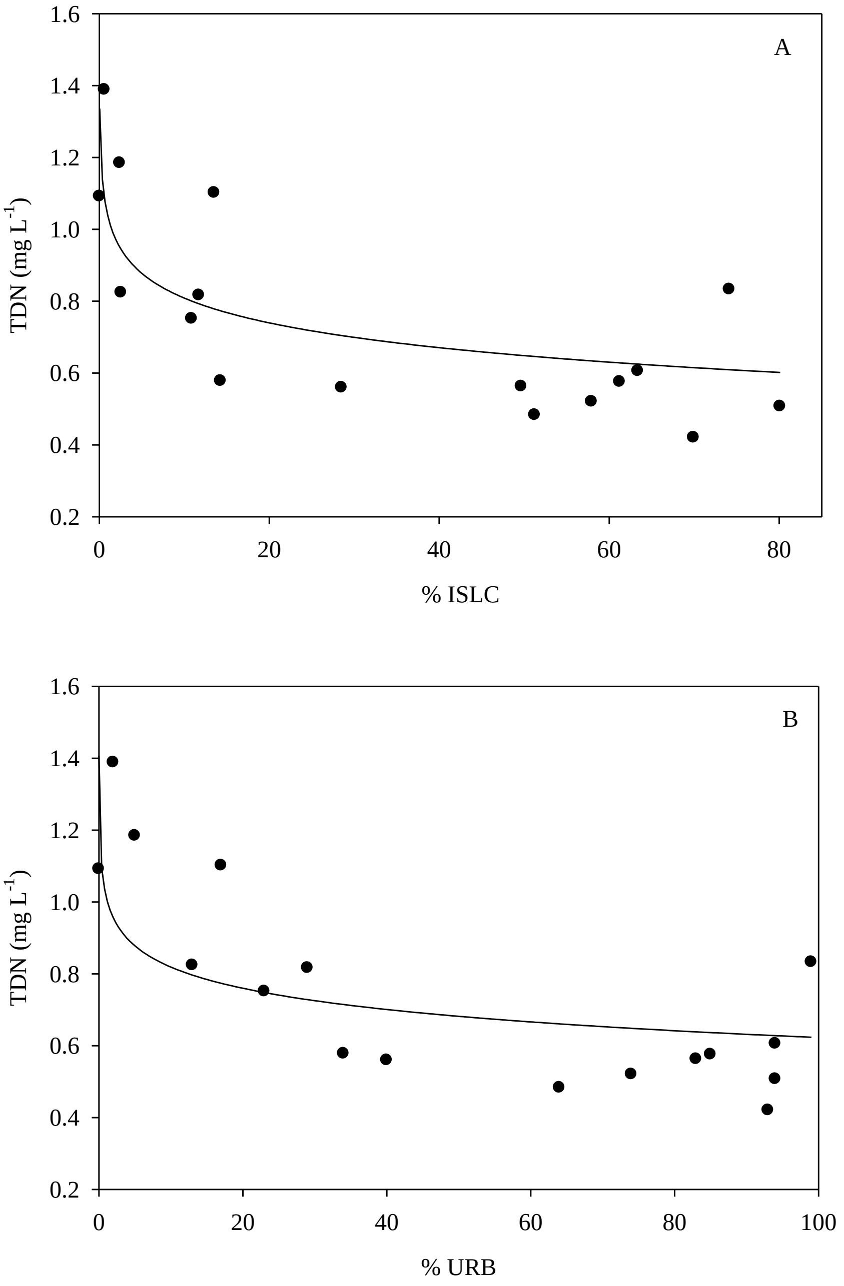

Figure 2. Relationships between TDN and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor in 2007. (A) %ISLC ($y = -0.108 \times \ln(x) + 1.0387$; $R^2 = 0.59$; df = 16; $p = 0.0003$) and (B) urban (URB) ($y = -0.085 \times x + 1.015$; $R^2 = 0.45$; df = 16; $p = 0.0032$).

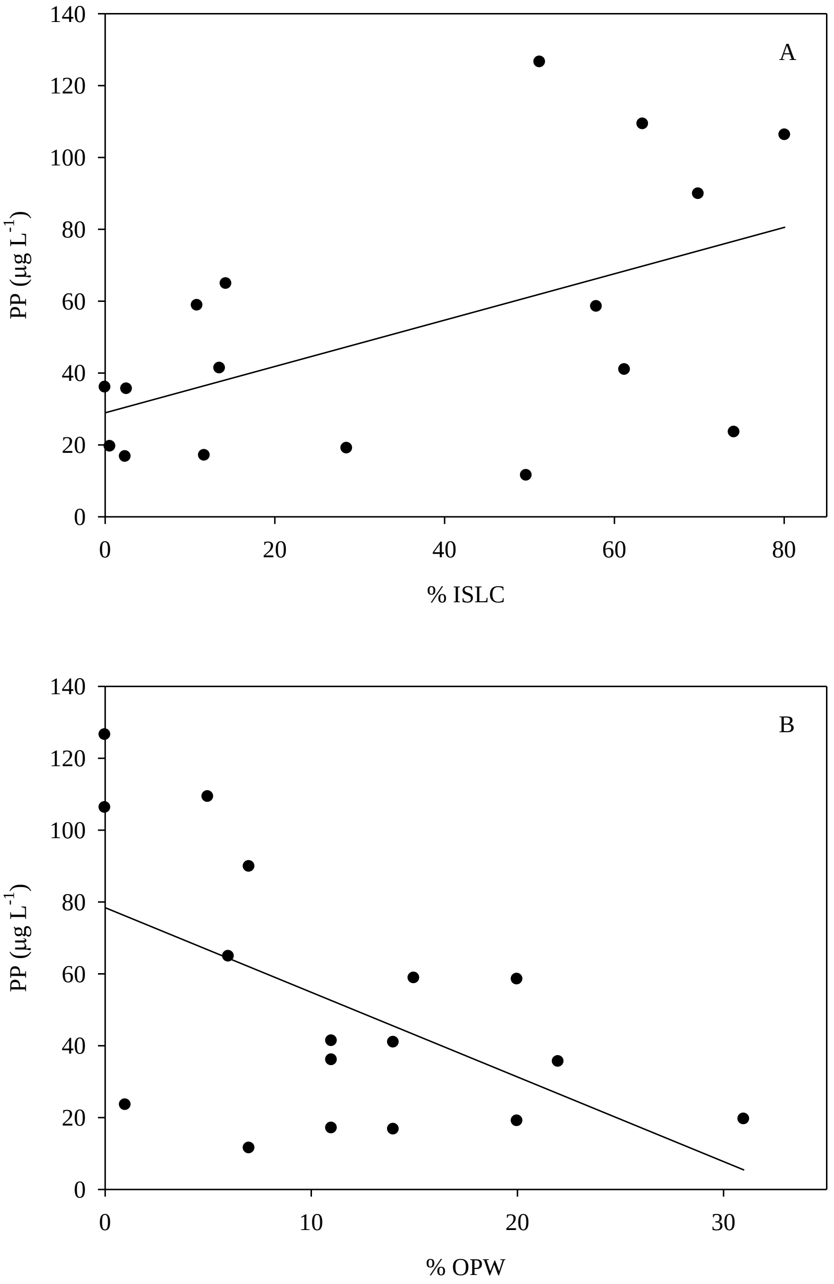

Figure 3. Relationships between PP and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor in 2007. (A) %ISLC (y = 0.6448 × x + 28.919; $R^2 = 0.27$; df = 16; $p = 0.0322$) and (B) open water (OPW) (y = -2.355 × x + 78.4; $R^2 = 0.30$; df = 16; $p = 0.0231$).

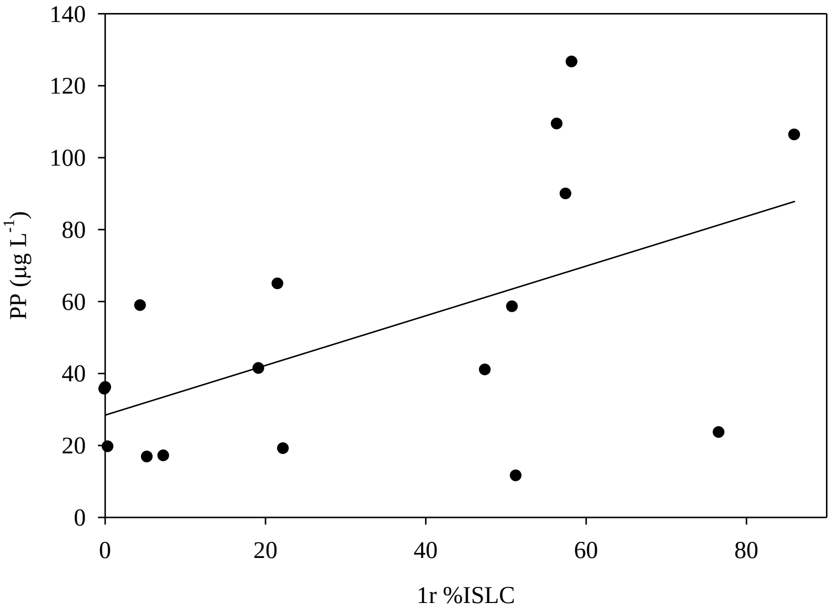

Figure 4. Positive relationship between particulate phosphorus (PP) and percentage of impervious surface land cover in the r1 buffer (1r % ISLC) in 2007 (y = 0.6903 × x + 28.426; $R^2 = 0.30$; df = 16; $p = 0.0236$).

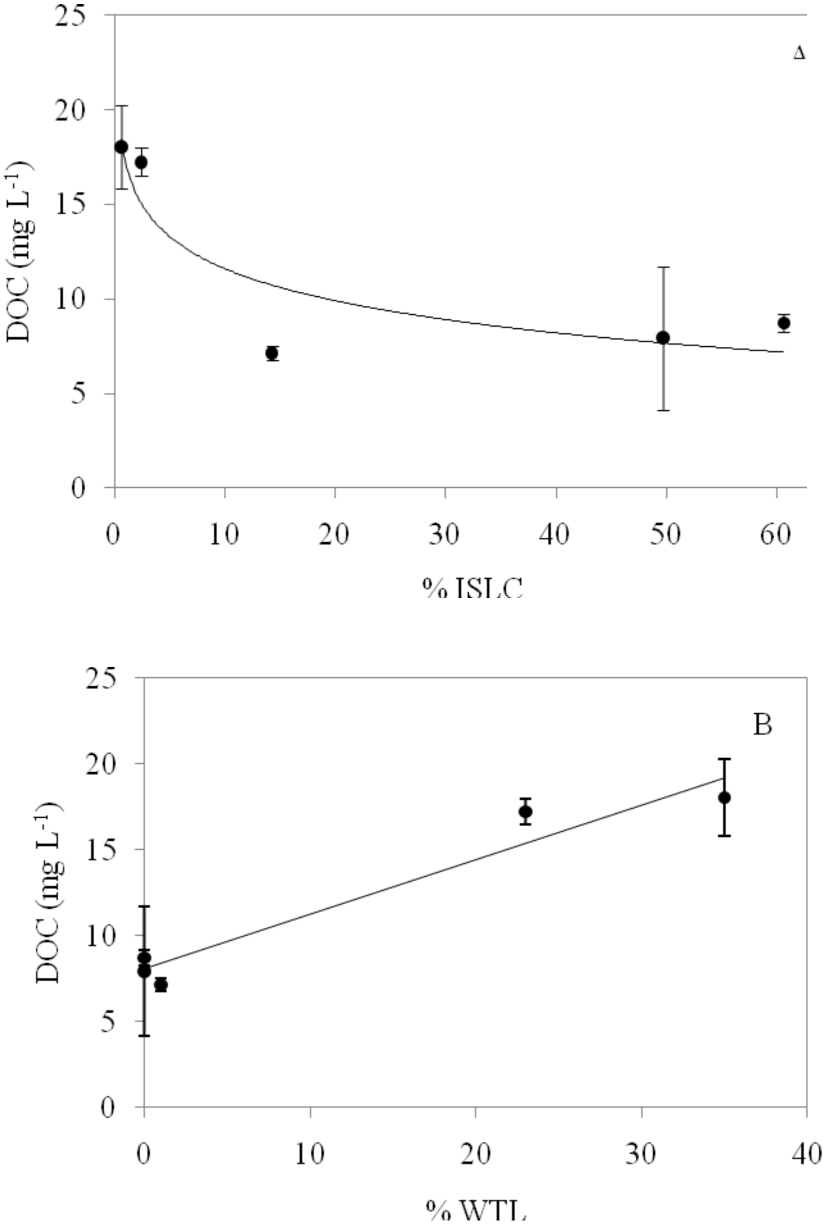

Figure 5. Relationships between DOC and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor ± one standard deviation in 2008. (A) %ISLC ($y = -2.456\ln(x) + 17.26$; $R^2 = 0.8241$; df = 4; $p < 0.05$) and (B) wetland (WTL) ($y = 0.3189 \times x + 8.0566$; $R^2 = 0.94$; df = 4; $p < 0.05$).

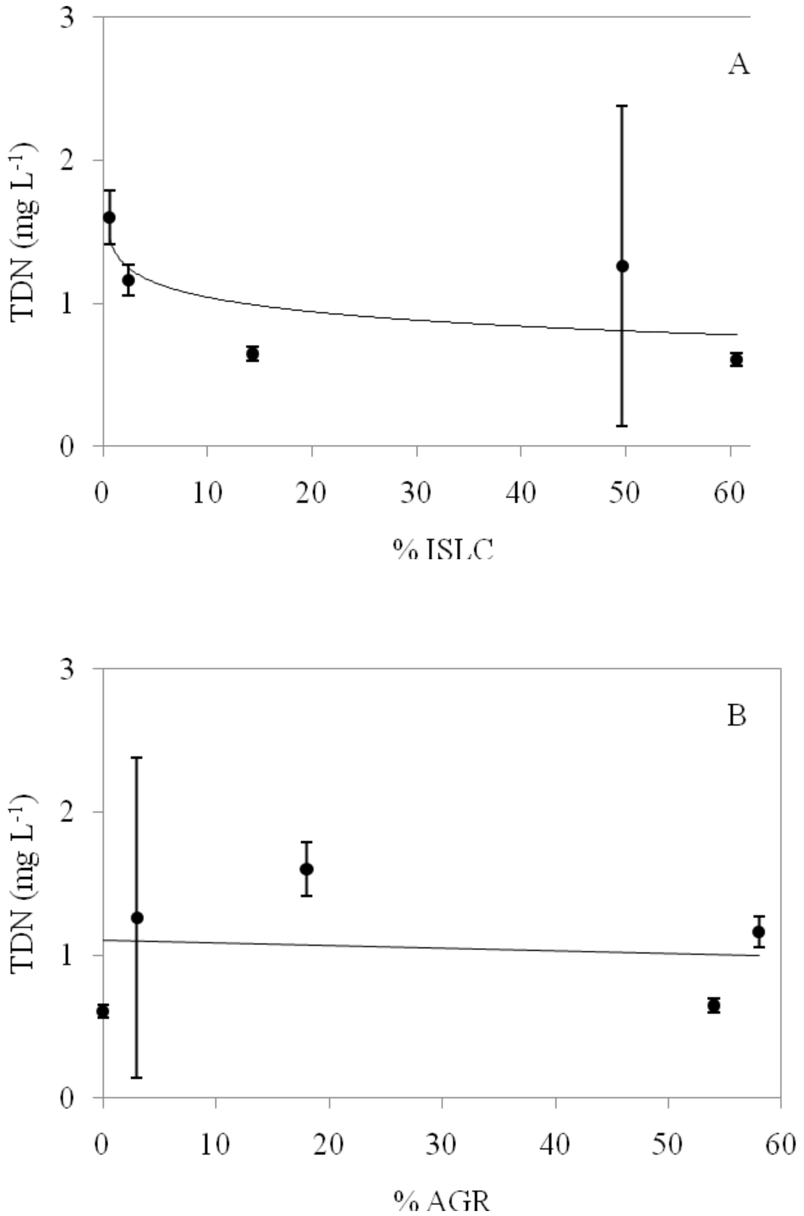

Figure 6. Relationships between TDN and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor ± one standard deviation in 2008. (A) %ISLC ($y = -0.146\ln(x) + 1.3803$; $R^2 = 0.47$; df = 4; $p > 0.05$) and (B) agriculture (AGR) ($y = -0.0018 \times x + 1.1028$; $R^2 = 0.01$; df = 4; $p > 0.05$).

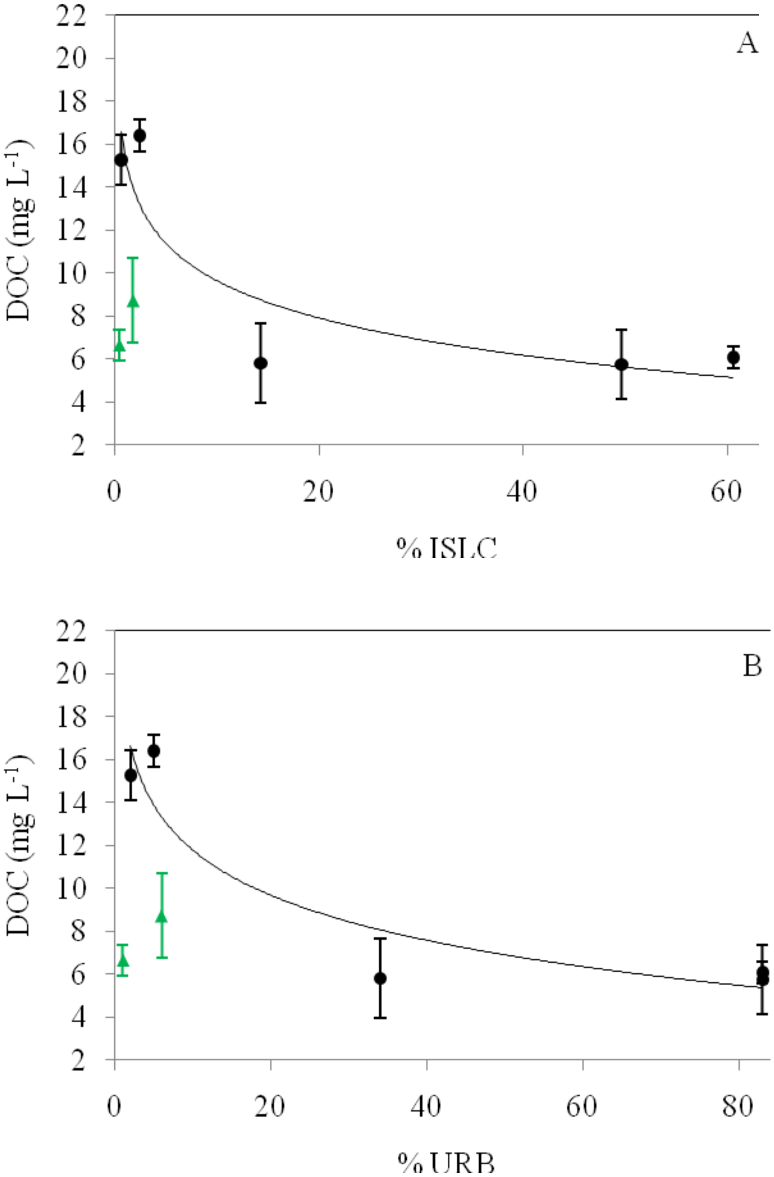

Figure 7. Relationships between DOC and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor ± one standard deviation excluding reference sites (green triangles) in 2009. (A) %ISLC (y = -2.505ln(x) + 15.416; $R^2 = 0.82$; df = 4; $p < 0.05$) and (B) urban (URB) (y = -3.027ln(x) + 18.746; $R^2 = 0.88$; df = 4; $p < 0.05$).

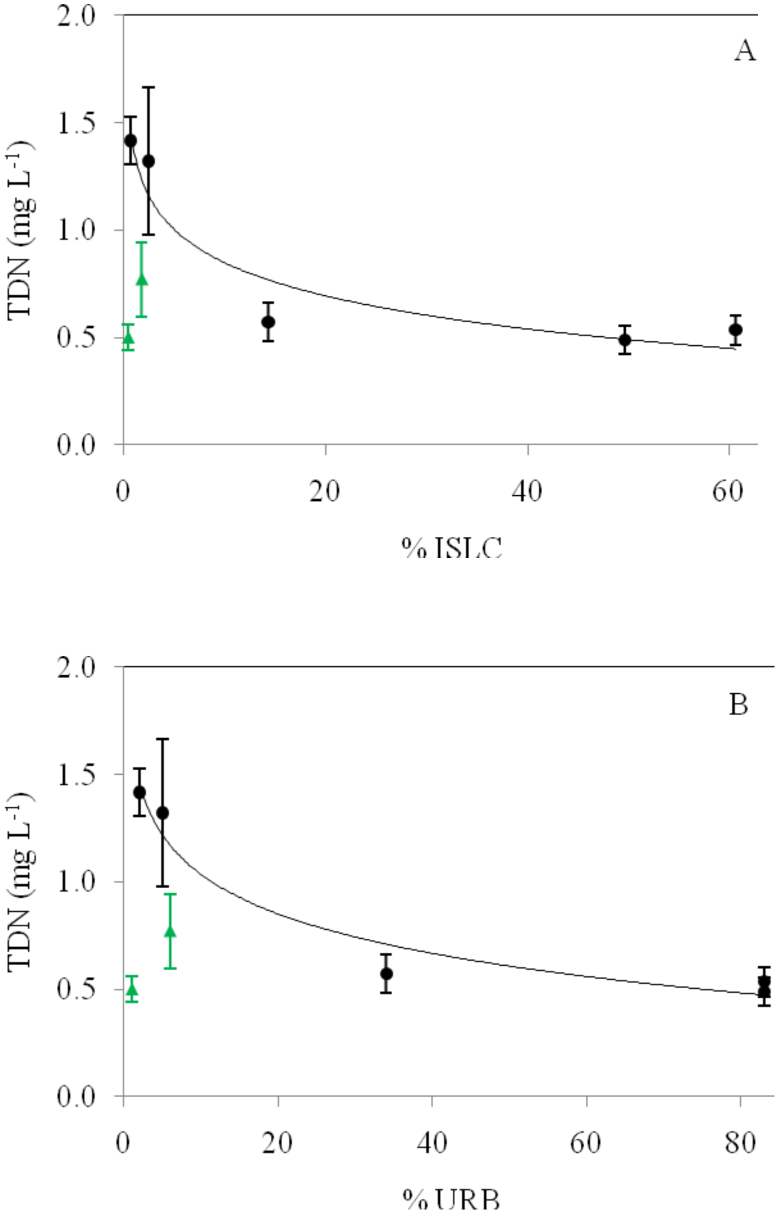

Figure 8. Relationships between TDN and percentage of impervious surface land cover (% ISLC) and the best level 1land cover predictor ± one standard deviation excluding reference sites (gray triangles) in 2009. (A) %ISLC (y = -0.223ln(x) + 1.3602; $R^2 = 0.91$; df = 4; $p < 0.05$) and (B) urban (URB) (y = -0.265ln(x) + 1.6457; $R^2 = 0.96$; df = 4; $p < 0.05$).

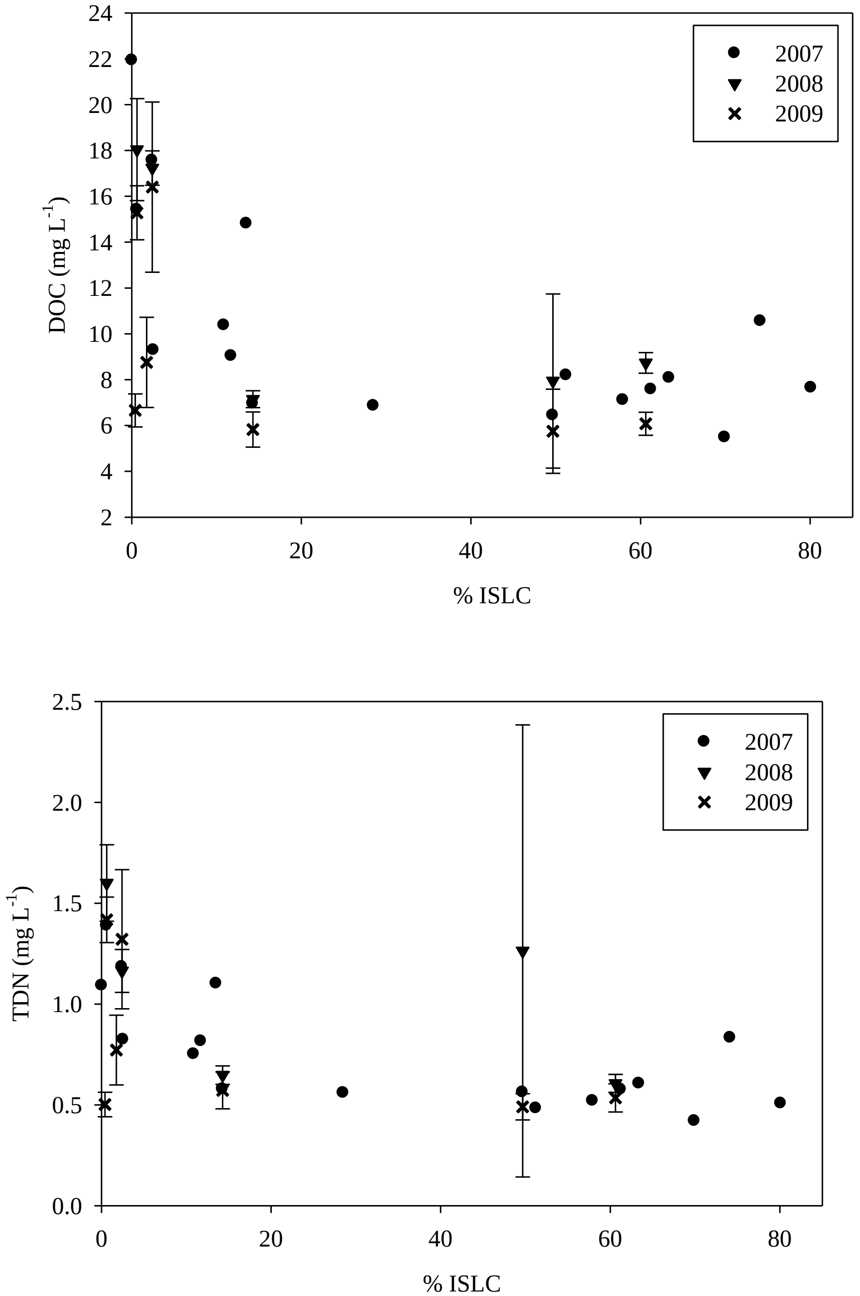

Figure 9. Compiled data from 2007, 2008, and 2009 and relationships between dissolved nutrients and percentage of impervious surface land cover (% ISLC) excluding reference sites. (A) Dissolved organic carbon (DOC) ($y = -2.205 \times \ln(x) + 16.523$; $R^2 = 0.52$; df = 69; $p < 0.0001$) and (B) total dissolved nitrogen (TDN) ($y = -0.117 \times \ln(x) + 1.4714$; $R^2 = 0.22$; df = 69; $p < 0.0001$).

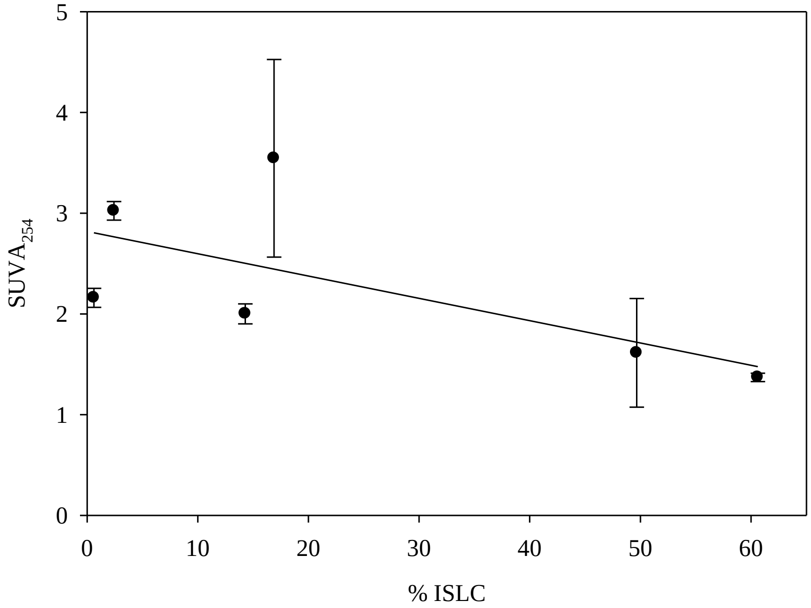

Figure 10. Relationship between SUVA$_{254}$ and percentage of impervious surface land cover (% ISLC) ± one standard deviation in 2008 ($y = 0.0222 \times x + 2.8184$; $R^2 = 0.44$; df = 5; $p = 0.1506$).

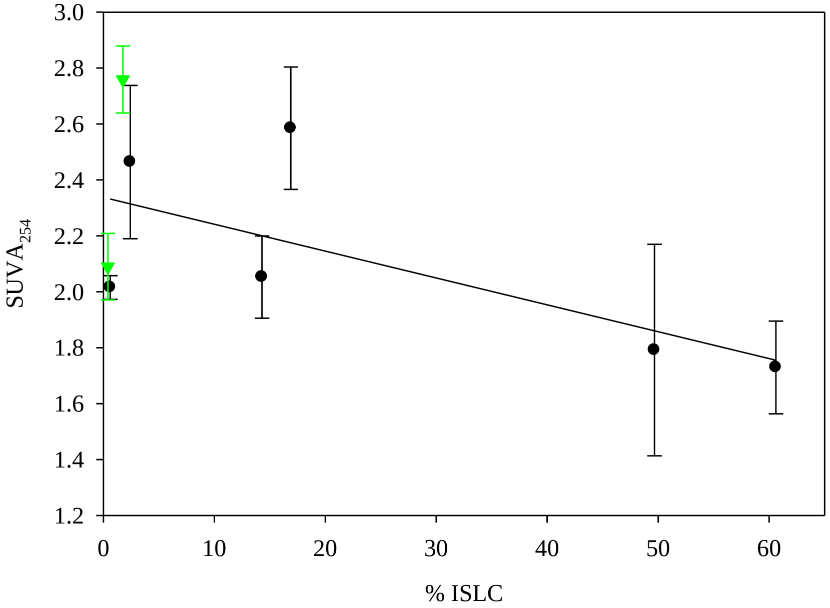

Figure 11. Relationship between $SUVA_{254}$ and percentage of impervious surface land cover (% ISLC) ± one standard deviation excluding reference sites (green triangles) in 2009 (y = -0.0096 × x + 2.3377; $R^2 = 0.48$; df = 5; $p = 0.1247$).

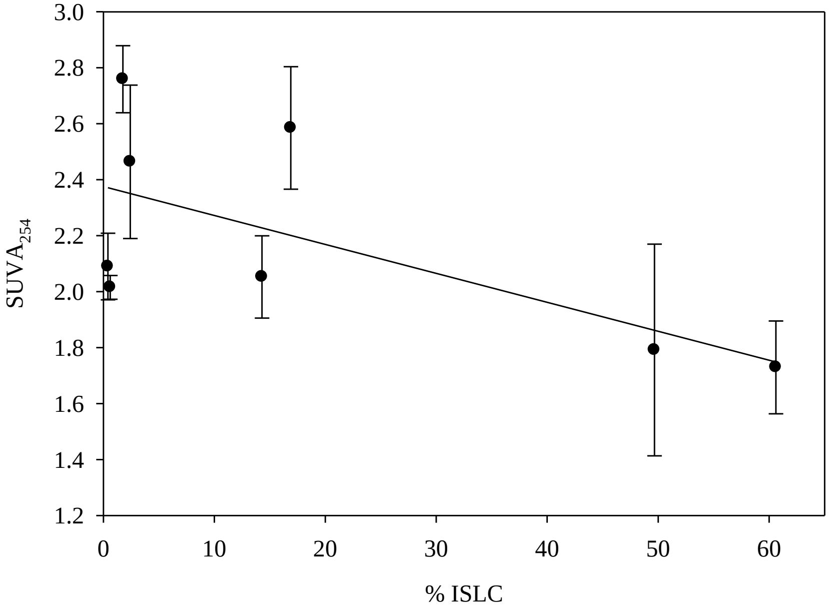

Figure 12. Relationship between $SUVA_{254}$ and percentage of impervious surface land cover (% ISLC) ± one standard deviation in 2009 (y = -0.0103 × x + 2.3754; $R^2 = 0.43$; df = 7; $p = 0.0763$).

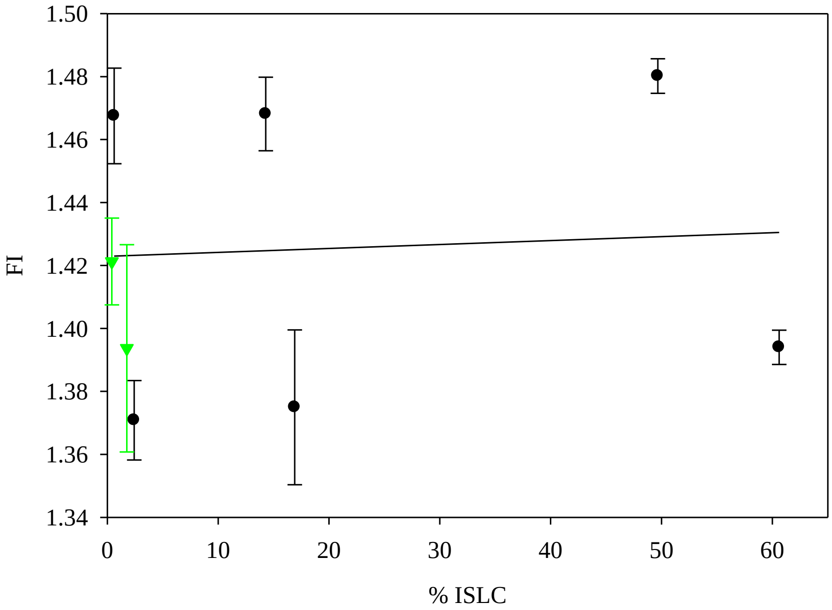

Figure 13. Relationship between fluorescence index (FI) and percentage of impervious surface land cover (% ISLC) ± one standard deviation excluding reference sites (green triangles) in 2009 (y = 0.0001 × x + 1.4229; $R^2$ = 0.001; df = 5; $p$ = 0.9514).

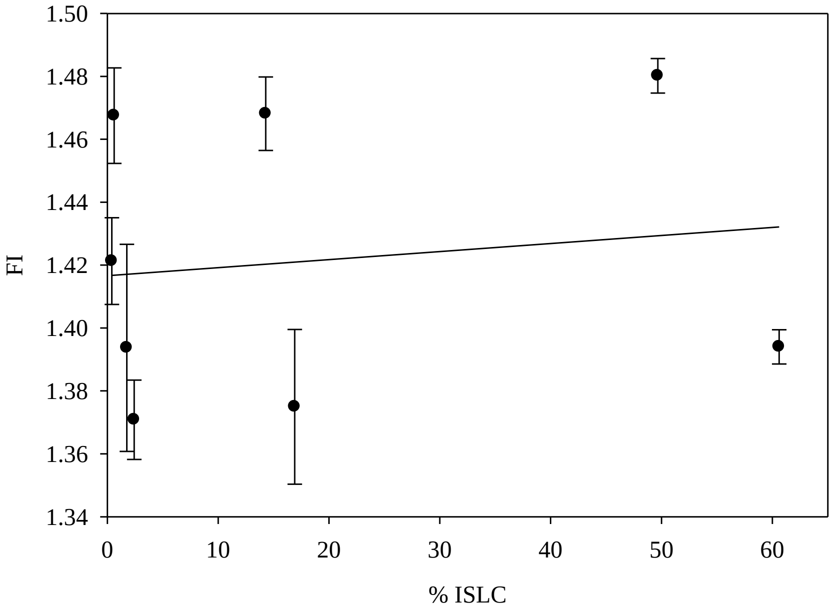

Figure 14. Relationship between fluorescence index (FI) and percentage of impervious surface land cover (% ISLC) ± one standard deviation in 2009 (y = 0.0003 × x + 1.4166; $R^2$ = 0.01; df = 7; $p$ = 0.7883).

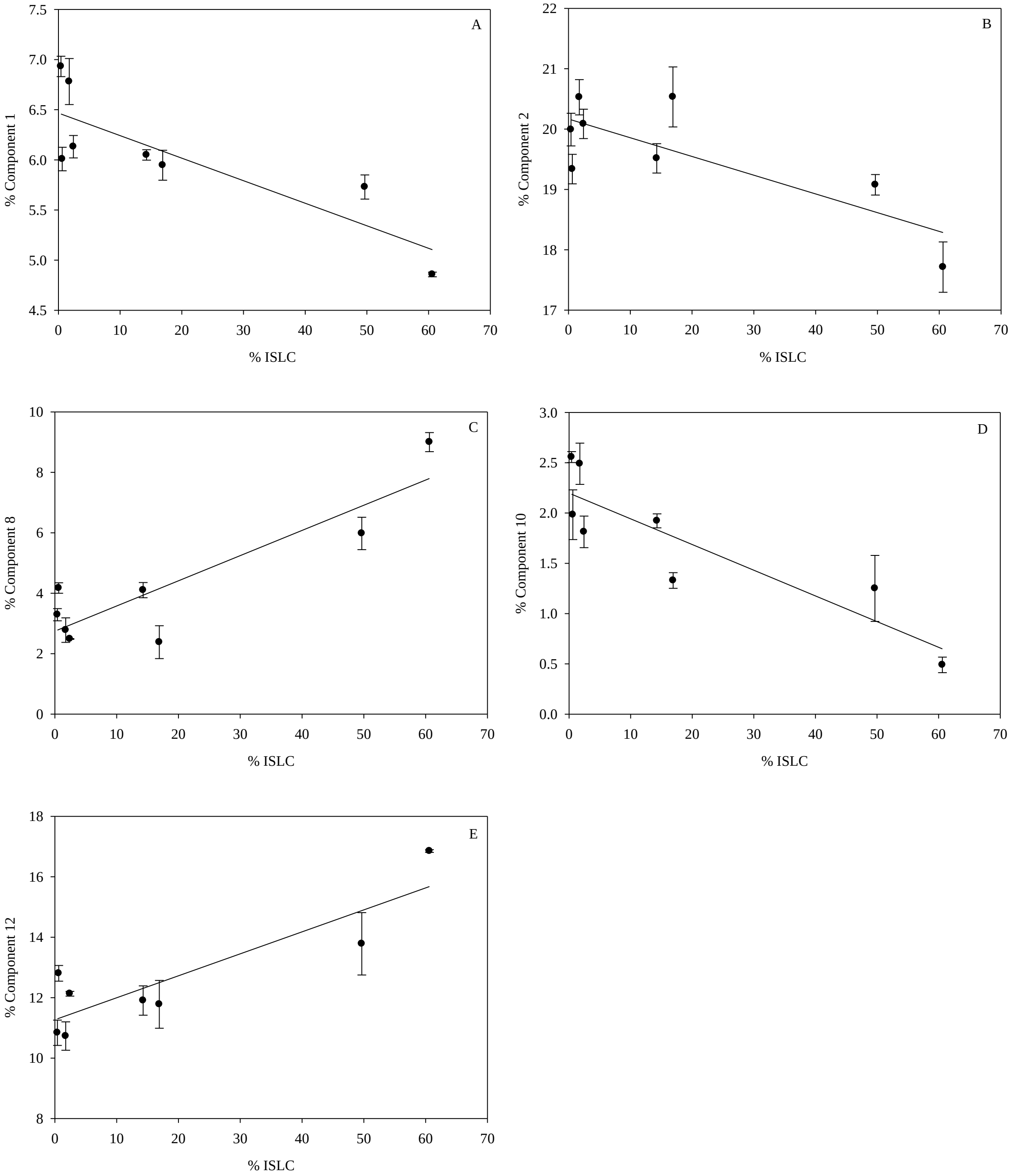

Figure 15. Significant relationships between percentage of PARAFAC components and percentage of impervious surface land cover (% ISLC) ± one standard deviation. (A) Component 1 (y = -0.0225 × x + 6.4663; $R^2 = 0.70$; df = 7; $p = 0.0097$), (B) Component 2 (y = -0.031 × x + 20.166; $R^2 = 0.63$; df = 7; $p = 0.0185$), (C) Component 8 (y = 0.0834 × x + 2.7444; $R^2 = 0.78$; df = 7; $p = 0.0037$), (D) Component 10 (y = -0.0255 × x + 2.1972; $R^2 = 0.78$; df = 7; $p = 0.0036$), and (E) Component 12 (y = 0.0727 × x + 11.268; $R^2 = 0.76$; df = 7; $p = 0.0048$).

Figure 16. Average growth rate per day (± one standard deviation) for nutrient enrichment bioassays. CD: Control Diluted; N: nitrogen; P: phosphorus; Si: silica; NP: nitrogen and phosphorus; NSi: silica and nitrogen; PSi: silica and phosphorus; NPSi: nitrogen, phosphorus, and silica and the corresponding *p*-value of the highest order interaction as determined through multi-way ANOVA.

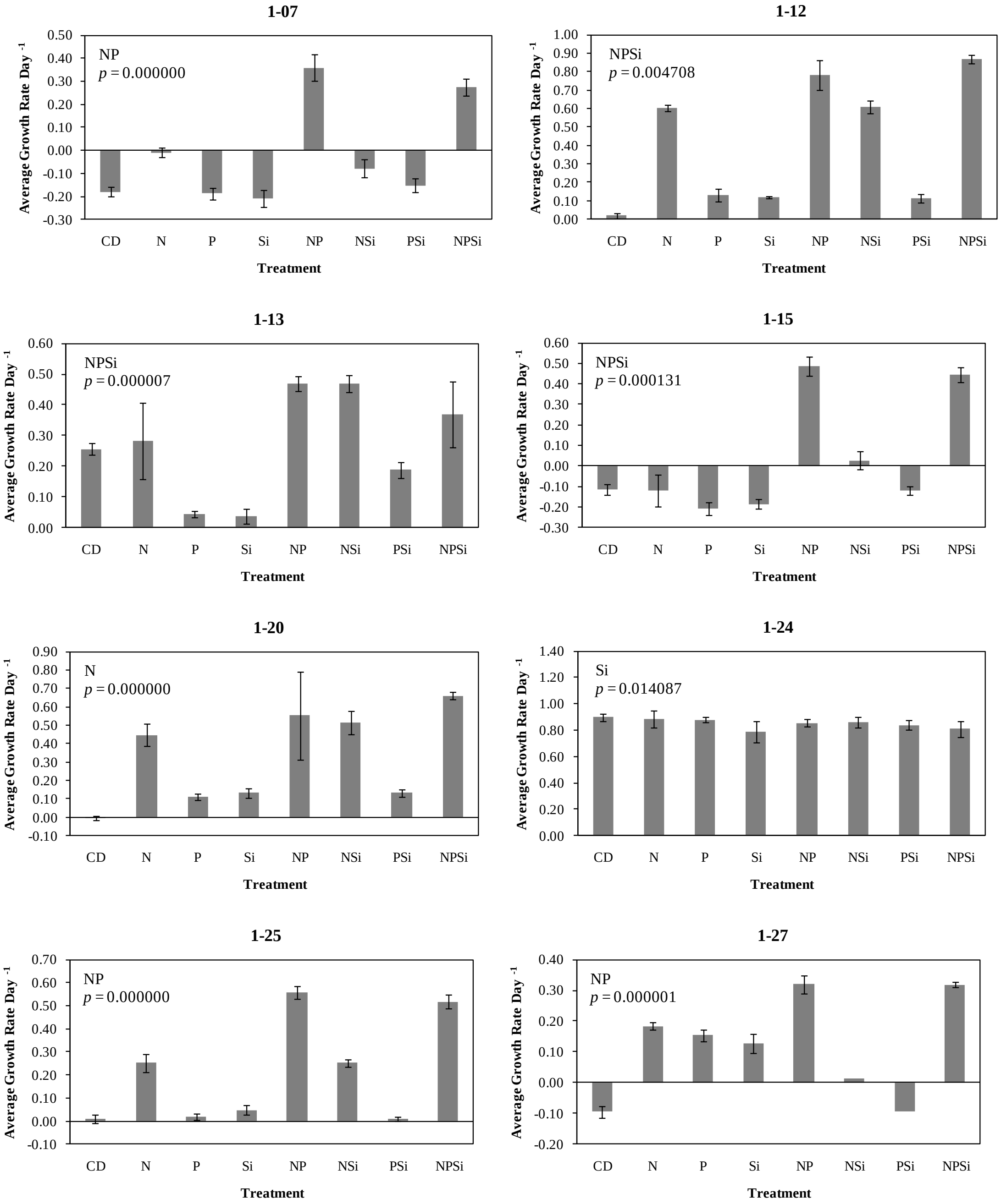

Figure 16 (continued).

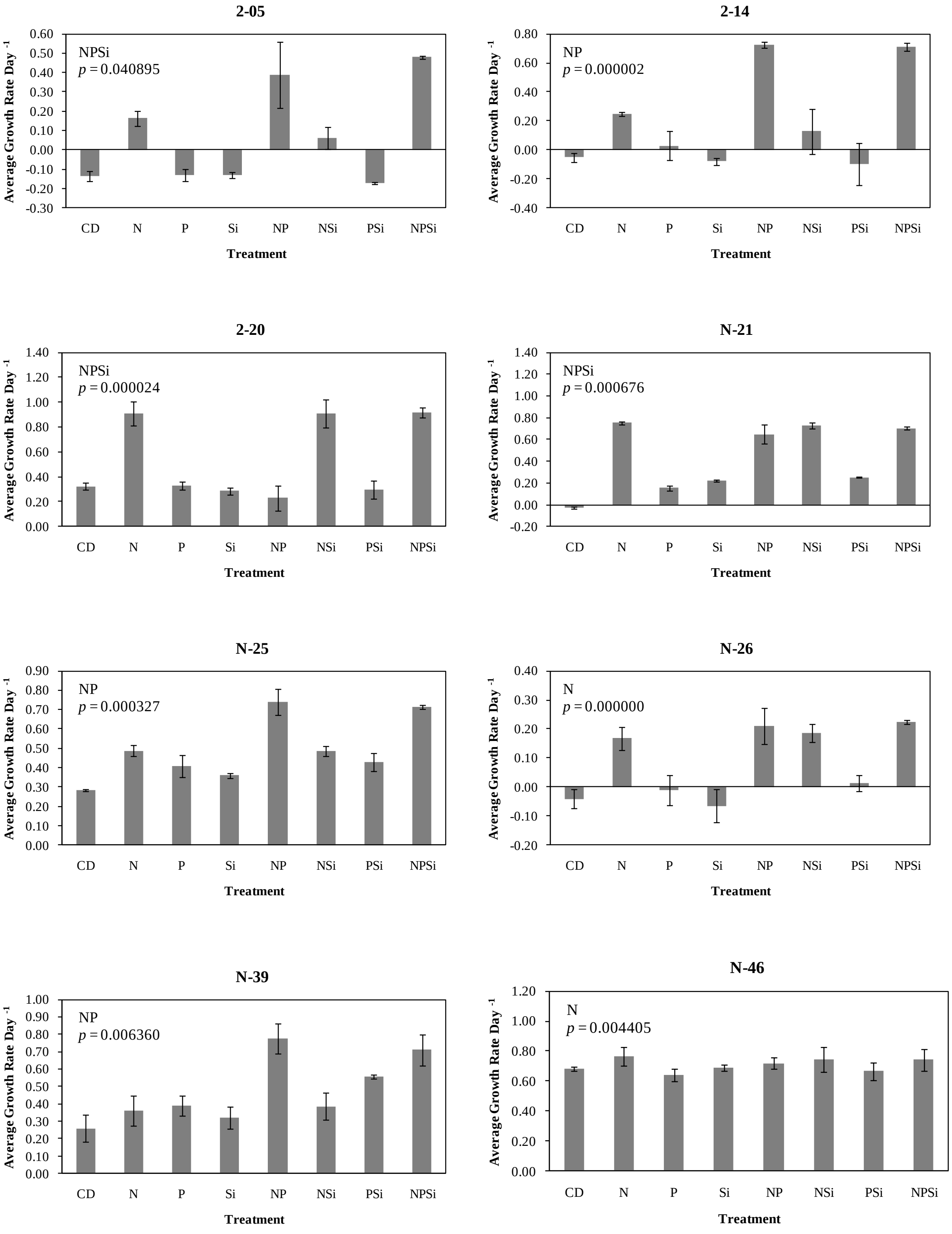

Figure 16 (continued).

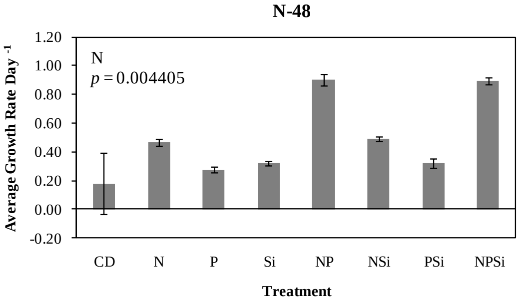

Table 6. Assigned nutrient limitation for each of the 17 lakes sampled during the summer of 2007 and corresponding percentage of impervious surface land cover.

| Lake | %ISLC | Nutrient Limitation |
|---|---|---|
| N25 | 0.05 | N/P Limitation |
| N21 | 0.62 | N/P/Si Limitation |
| N48 | 2.43 | N Limitation |
| 112 | 2.57 | N/P/Si Limitation |
| 205 | 10.89 | N/P/Si Limitation |
| 214 | 11.74 | N/P Limitation |
| 220 | 13.54 | N/P/Si Limitation |
| N46 | 14.29 | N Limitation |
| 120 | 28.51 | N Limitation |
| N39 | 49.67 | N/P Limitation |
| N26 | 51.24 | N Limitation |
| 115 | 57.92 | N/P/Si Limitation |
| 127 | 61.25 | N/P Limitation |
| 107 | 63.39 | N/P Limitation |
| 125 | 69.93 | N/P Limitation |
| 113 | 74.15 | N/P/Si Limitation |
| 124 | 80.11 | None |

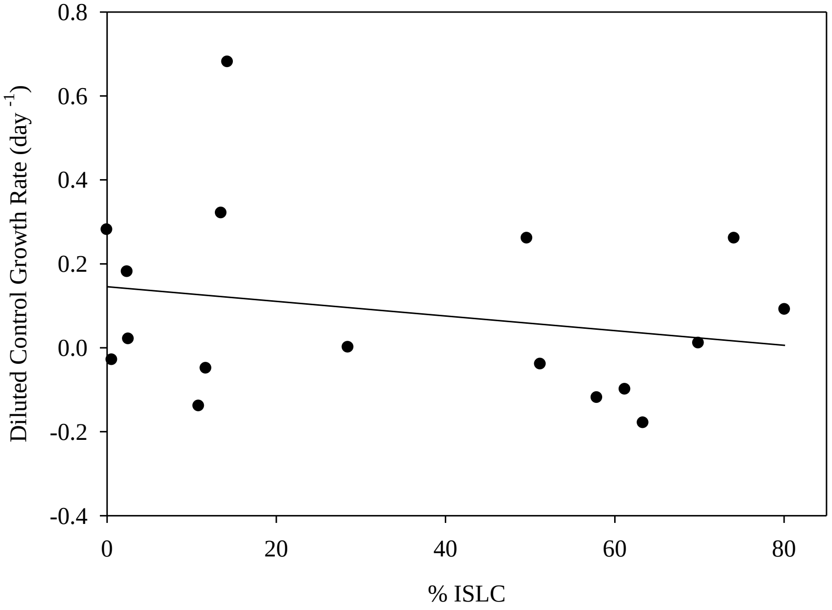

Figure 17. No significant relationship between diluted control growth rate and percentage of impervious surface land cover (%ISLC) (y = -0.0017 × x + 0.1455; $R^2$ = 0.0542; df = 16; $p$ = 0.3686).

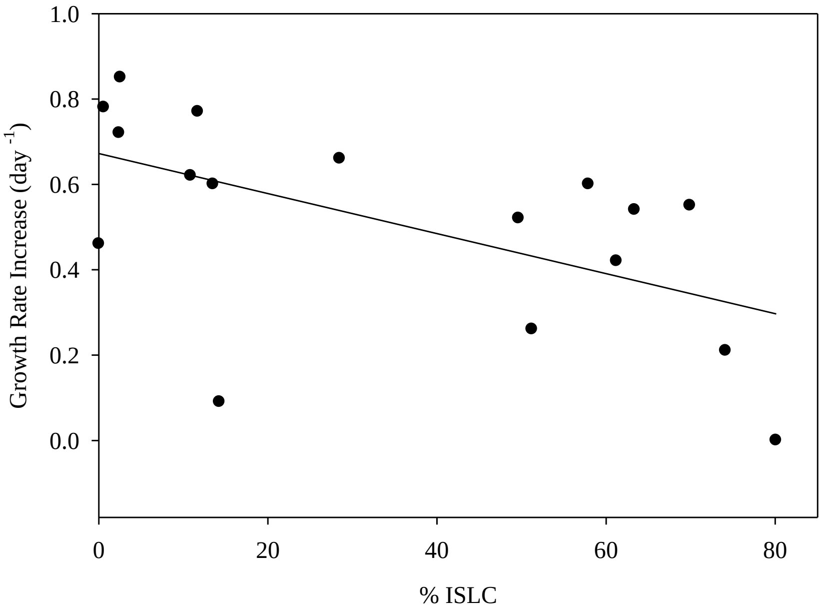

Figure 18. Negative relationship between phytoplankton growth rate increase achieved in nutrient enrichment bioassays and percentage of impervious surface land cover (%ISLC) ($y = -0.0047 \times x + 0.6723$; $R^2 = 0.32$; df = 16; $p = 0.0179$).

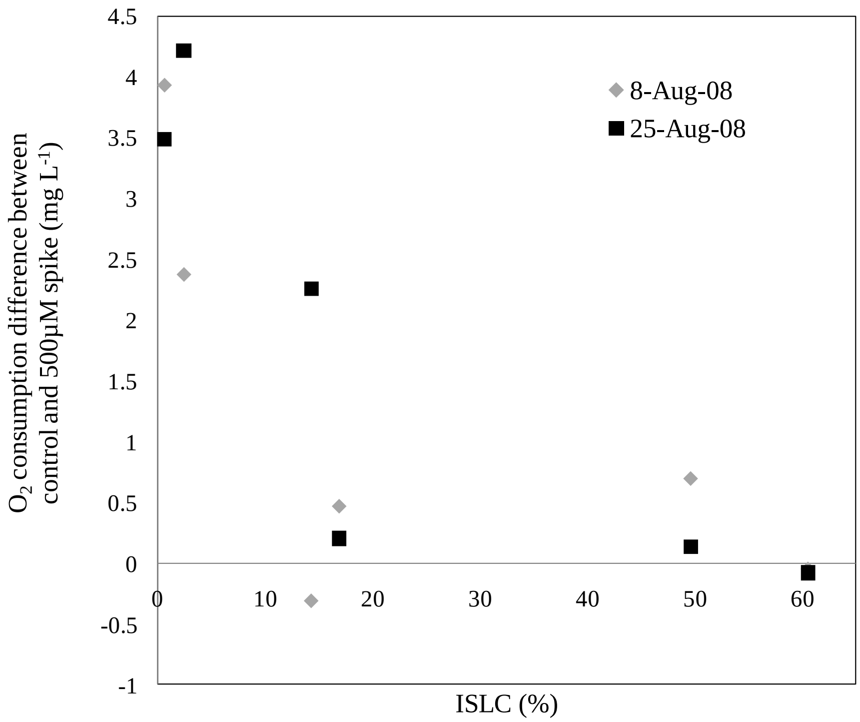

Figure 19. Oxygen consumption difference between treatments receiving no glucose spike and those receiving a 500µM glucose spike on two dates from August 2008.

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