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EXECUTIVE SUMMARY

- The objective of this study was to provide data and guidance on determining the status of Beneficial Use Impairment #8 (Eutrophication or Undesirable Algae) and #13 (Degradation of Phytoplankton) for the Buffalo River Area of Concern (AOC). Specifically, the study: i) determined the trophic level of the AOC; ii) determined if microcystins (algal toxins) were present that may present a risk to fish, wildlife, or human health (as an indicator of undesirable algae); and iii) established the dominant phytoplankton taxa and examined community composition characteristics to determine if phytoplankton have been negatively impacted by human activity.
- Evaluation of the biological health of an AOC ecosystem is a complex issue and as a result, this study took a "weight of evidence" approach by applying several techniques to address objectives i) and iii), above.
- For the evaluation of trophic status (objective i), the following approaches were used: threshold levels of total phosphorus (TP), total nitrogen (TN) and chlorophyll a were determined through an extensive literature review; reference reach comparisons of TP and nitrate/nitrite; U.S. EPA ecoregion (percentile) analysis based on the New York State Department of Environmental Conservation RIBS (Rotating Intensive Basin Studies) data for TP and nitrate/nitrite.
- For the evaluation of phytoplankton community composition characteristics (objective iii), the following approaches were used: total phytoplankton abundance; species richness; Shannon-Weaver Index of Diversity; Centric:Pennate (C:P) ratio for diatoms; presence of indicator species; Trophic Diatom Index (TDI); and Pollution Tolerance Index (PTI).
- Routine manual sampling was done once a week for eight weeks at three sites on the Buffalo River, starting on 7/14/06 and ending on 8/31/06. The samples sites represented areas above the navigable channel (but downstream of Cazenovia Creek), the Ohio Street Bridge, and near the mouth of the Buffalo River (but upstream of the Buffalo Ship Canal). These routine samples were

analyzed for TP, nitrate/nitrite, ammonia, chlorophyll a, and total microcystin. Samples were collected biweekly (total of four sample dates) for phytoplankton population analysis (total count and taxa identification). Water quality (temperature, pH, conductivity, dissolved oxygen, turbidity, and fluorescence (chlorophyll a)) was monitored continuously at the Ohio Street Bridge using a YSI 6600 EDS datasonde.

- Based on a literature review, threshold levels of 42 µg/L TP and 8 µg/L chlorophyll a were chosen as a guideline for the Buffalo River. These levels generally could be considered as representing the division between a eutrophic and mesotrophic river, but it must be noted that threshold levels reported in the literature exhibit considerable variability. The mean level of TP and chlorophyll a from the Buffalo River samples were not significantly greater (α=0.05) than the selected threshold levels.
- Samples collected at two Cazenovia Creek headwater sites (west branch and east branch) were used to represent Reference Reach levels of TP and nitrate/nitrite. Recognizing that the Reference Reach sample set was small (n=2 for each site), the mean levels of TP and nitrate/nitrite from the Buffalo River sites were in the same range as the Reference Reach.
- The mean TP levels in the Buffalo River were greater than the 25th percentile of the medians of 16 rivers in the same ecoregion (RIBS data), while the mean nitrate/nitrite levels were less than the 25th percentile of the medians.
- A qualitative review of the literature showed that Buffalo River nutrient and chlorophyll a levels were similar to those reported for "low nutrient, high quality streams" (e.g. Minnesota Pollution Control Agency, 2003).
- The phytoplankton species richness in the Buffalo River was relatively high for this region, as was the Shannon-Weaver Index of Diversity. Generally, it is believed that lower species richness and Shannon-Weaver values will be observed with increasing trophic status.
- The C:P ratios for the four samples were highly variable and of little use for environmental interpretation in this study. Qualitatively, the assessment of indicator species showed taxa that represented eutrophic and poorer water

quality conditions were mixed with taxa that represented less nutrient-rich, mesotrophic conditions.

- The TDI values can range between 1 (clean water) and 5 (nutrient rich and/or organic polluted water). The TDI values for the Buffalo River were in the 3.0-4.8 range. By comparison, the TDI values at two sites on Eighteenmile Creek, NY were in the 4.4-4.5 range, while a eutrophic river in England, impacted by a sewage treatment plant, had a TDI value of 4.63.
- For this study, the tolerance values for individual species in the PTI ranged between 1 and 5. An important difference between the PTI and TDI is that the tolerance rating of the PTI is *inverse* to the to pollution sensitivity rating of the TDI; for the PTI a number near 1 indicates most tolerant taxa, while a number near 5 indicates a predominance of sensitive taxa. The PTI values for the Buffalo River ranged between 2.9 and 3.6.
- Total microcystin was detected in all Buffalo River samples, but at levels well below the WHO guideline. *Microcystis spp.* algae were not observed in the water samples, but low levels of other microcystin-producing algae (e.g. *Planktothrix agardhii, Anabaena flos-aquae*) were observed.
- The fluorescence measurements from the YSI 6600 EDS datasonde were similar to the laboratory measurements of chlorophyll a. Based on the YSI measurements, the weekly average chlorophyll a (calculated from 15 minute time step measurements) ranged between 1.69 and 7.55 µg/L. The total abundance counts (cells/mL) from the algal enumerations were relatively low and this was consistent with the low chlorophyll a levels.
- Dissolved oxygen levels in the middle section of the Buffalo River frequently were less than state guidelines for this class of river, a finding which is consistent with previous studies. Low dissolved oxygen levels primarily are impacted by the hydraulics of the Buffalo River.
- Turbidity can be high in the Buffalo River during storm events (in some cases exceeding 1,000 NTU), but during dry weather in 2006 turbidity at the Ohio Street Bridge site was in the range of 27 NTU. Dry weather turbidity levels in the range of 10-24 NTU were observed in the summers of 2003 and 2004. It

appears unlikely that the turbidity levels are high enough to suppress algal abundance, given the nutrient levels in the river, but this should be investigated in more detail.

- In conclusion, the weight of evidence suggests that the Buffalo River AOC does not have a eutrophication problem at this time, but nutrient levels are sufficiently high that implementation of watershed BMPs and water quality monitoring should be continued. Based on the microcystin analysis as an indicator, the AOC also does not have a problem with undesirable algae. It is suggested that BUI #8 can be delisted.
- The weight of evidence is a little less clear for BUI #13. Reference criteria and endpoints have not been established specifically for the Great Lakes, although this is a SOLEC objective. Many studies that have assessed plankton population structure in a lotic environment focused on periphyton rather than phytoplankton. There is a need for further research on standardized population structure indices and their environmental interpretation. The phytoplankton population structure appears to reflect the suburban/urban environment. There appears to be some anthropogenic impact as reflected by the TDI and PTI and presence of certain indicator species, but these impacts do not seem to indicate extreme stress. It is suggested that BUI #13 can be delisted, but periodic monitoring of the phytoplankton population should be undertaken.

1. INTRODUCTION

1.1. Project Objectives

Following a thorough review of Beneficial Use Impairments (BUIs) for the Buffalo River Area of Concern (AOC), it was concluded that there were not enough data to determine the current status of BUI #8 (Eutrophication or Undesirable Algae) or BUI #13 (Degradation of Phytoplankton)(Buffalo Niagara Riverkeeper, 2005). One immediate goal of the Buffalo River Remedial Advisory Committee is to gather information related to BUIs #8 and #13 and determine if these individual impairments can be de-listed.

To help address the de-listing issue for BUIs #8 and #13, the objectives of this study are: 1) determine the trophic level of the AOC; 2) determine if microcystins (algal toxins) are present that may present a risk to fish, wildlife, or human health (as an indicator of undesirable algae); and 3) establish the dominant phytoplankton taxa in the Buffalo River AOC and use community composition characteristics to determine whether phytoplankton have been negatively impacted by human activity. The issue of de-listing BUIs #8 and #13 is complicated by the fact that de-listing criteria and/or restoration targets have not been established for these BUIs in the Buffalo River AOC. As a secondary objective of this study, evaluation criteria are identified that could be used in establishing the de-listing goals for BUIs #8 and #13.

1.2. Background to the Problem

Measures to control phosphorus discharges to the Great Lakes first were implemented in the 1970's in an effort to maintain algal biomass below that of a nuisance condition and these efforts appear to have reduced phosphorus concentrations and chlorophyll (a measure of algal biomass) in the intervening years (Makarewicz and Betram, 1991; Charlton et al., 1999). Unfortunately, in the past five years, *Cladophora* growth has re-emerged as a management problem in parts of the Great Lakes and this suggests that the lakes may still be in a condition of transition (Bootsma et al., 2005). Despite advances in phosphorus management Bertram and Stadler-Salt (2000) noted that tributary monitoring still was insufficient to accurately evaluate phosphorus loadings and

the Buffalo River is no exception to this conclusion. Furthermore, while it is generally accepted that phytoplankton composition changes with nutrient fluxes because individual taxa have different requirements and that there may be some indicator species that can mark the trophic level of a water body, the *State of the Lakes – 2005 Report* states "No assessment of 'ecosystem health' is currently possible on the basis of phytoplankton community data since reference criteria and endpoints have yet to be developed." In general, toxic algae blooms have been occurring more frequently throughout the world (Hallegraeff, 1993). Brittain et al. (2000) and Murphy et al. (2003) found microcystin toxins in samples from various locations in Lake Erie and Hamilton Harbor. In fact, Hamilton Harbor was posted in 2001 to warn people of the risks of contact and not to eat the fish due to concerns about microcystin levels. So, what are the issues?

1.2.1. Nutrients and Eutrophication

Eutrophication is the "aging process" of a waterbody, whereby biochemical processes work together with geomorphic processes to "close out" the waterbody. Eutrophication may be characterized as a sequence of events starting with nutrient enrichment, and proceeding to the growth and die-off of phytoplankton, the accumulation of detritus, the growth of bacteria, the depletion of dissolved oxygen, and finally, the dislocation of higher aquatic organisms (Marsh, 1991; Wright, 2005; Chiras and Reganold, 2005). Eutrophication is a naturally-occurring process that can be accelerated by human activity, in which case it may be termed *cultural eutrophication.* In essence, various human activities increase the rate of nutrient input to a waterbody such that the eutrophication rate may be up to three orders of magnitude faster than under natural conditions (Chiras and Reganold, 2005). The trophic status of lakes frequently is classified as either *oligotrophic* (low nutrient levels, clear water, food chain based on bottom dwelling green plants, low total biomass per unit volume of water, typical of pristine glacial lakes in northern Minnesota, Wisconsin, Michigan), *mesotrophic* (moderate nutrient, dissolved oxygen, clarity, total biomass; fish such as northern pike and walleye may be plentiful in northern lakes; lakes suitable for swimming, boating and

fishing), or *eutrophic* (nutrient rich, turbid, with high plankton biomass). Clearly, greatest concern occurs when a waterbody becomes eutrophic.

The U.S. EPA (2000a) noted that nutrient enrichment "frequently ranks as one of the top causes of water resource impairment". In 40 percent of rivers and 51 percent of lakes surveyed by the U.S. EPA and reported impaired, nutrients were listed as the primary cause of impairment. The macronutrients, phosphorus (P) and nitrogen (N), typically are the nutrients identified as having the largest role in the eutrophication process. The relative impacts and characteristics of the cycle related to each nutrient is well-reviewed elsewhere (e.g. U.S. EPA, 2000a; Wetzel, 2001; Walker et al., 2006). Most research examining the relationship between N and P and levels of algae has focused on lake systems (e.g. Vollenwieder and Kerekes, 1982). Research on the nutrient and trophic status of *lotic* (flowing water) systems is much sparser and tends to focus on *periphyton* (or benthic algae and other organisms that grow on stable surfaces such as rock, woody debris, and vascular plants) growth in wadable rivers rather than *phytoplankton* (photosynthesizing organisms suspended in the water column) in larger rivers (Dodds and Welch, 2000; Minnesota Pollution Control Agency, 2003; Dodds, 2006). In cases where threshold N and P levels have been identified for water quality guidelines, Walker et al., 2006 note that the reported thresholds vary by an order of magnitude. In part, this variability is related to the complex factors that affect phytoplankton biomass, in addition to nutrient levels. These factors include water velocity (e.g. dislodgement and entrainment of periphyton), solar radiation levels, water column turbidity, temperature, consumption by zooplankton, and benthic suspension feeders (e.g. clams).

Furthermore, it is frequently assumed that P is the limiting factor in lotic systems because it occurs in the least amount relative to the needs of plants. However, more recent evidence suggests this is not always the case (Dodds and Welch, 2000; Dodds, 2006) and it also is important to consider N because the blue-green algae (or cyanobacteria) like *Microcystis spp.* do not fix significant amounts of nitrogen and are stimulated by dissolved inoraganic nitrogen availability. Production of the microcystin toxin also may be correlated with nitrogen availability (Sivonen, 1990).

Ultimately, it is the biomass production and level of biomass at which a nuisance or other negative impacts occur (e.g. dissolved oxygen depletion, pH alterations, shifting distribution of higher-order organisms) that is of greatest interest and as such, some government agencies and researchers have developed guidelines for periphyton and phytoplankton levels (e.g. Vollenweider and Kerekes, 1982; Dodds and Welch, 2000; U.S. EPA, 2000a; Walker et al., 2006). In some cases, the guidance levels of biomass production are developed in consideration of total phosphorus (TP) and total nitrogen (TN) levels, as a dose-response type approach. Frequently, the guidance levels are expressed in terms of chlorophyll a (the predominant green pigment used in photosynthesis), rather than actual phytoplankton biomass since it is easier to measure and generally there is a strong correlation between chlorophyll a and biomass (Voros and Padisak, 1991; Walker et al., 2006).

1.2.2. Alternative Approaches to Evaluating Trophic Status of a River

In addition to developing nutrient criteria from thresholds established in the literature, the U.S. EPA (2000a) suggests two other approaches to identifying nutrient and algal criteria: the reference reach approach; and a predictive relationship approach to select nutrient concentrations that will result in appropriate levels of algal biomass. The latter approach could involve the use of biocriteria in the form of multimetric indices, as discussed in Section 1.2.3.

Reference reaches are relatively undisturbed stream segments that can serve as examples of the natural biological integrity of a region. The U.S. EPA (2000a) suggests three approaches to using reference reaches in establishing water quality criteria:

i. Characterize reference reaches for each stream class within a region using best professional judgment and use these reference conditions to develop criteria.
ii. Identify the 75^{th} percentile of the frequency distribution of *reference* streams for a class of streams and use this percentile to develop criteria.
iii. Calculate the 5^{th} to 25^{th} percentile of the frequency distribution of the general population of a class of streams and use the selected percentile to develop criteria.

For approaches (ii) and (iii), the U.S. EPA generally suggests the use of the "ecoregion" concept to identify reference streams. At the highest classification level, the U.S. has been divided into 14 nutrient ecoregions based on landscape-level geographic features including climate, topography, regional geology and soils, biogeography, and broad land use patterns. All of these factors may account, by different degrees, for variations in water quality and aquatic biota assemblages and therefore it makes some intuitive sense to select reference streams within a common ecoregion (Commission for Environmental Cooperation, 1997; U.S. EPA, 2000a). Approach (ii) above, may be used if it is known that the *reference* streams selected for the frequency analysis truly are minimally impacted by anthropogenic activities. Approach (iii) would be used in regions where the number of minimally impacted water bodies is small. In this case, the lower percentile accounts for the effect of including impacted streams in the frequency analysis. A similar approach to evaluating trophic status has been investigated in Canada (Gartner Lee Limited, 2006). Figure 1.1 shows both the 25th and 75th percentile options and illustrates the presumption that these two alternative methods should approach a common reference condition along a continuum of data points. In this example, the 75th percentile of the reference stream data distribution produces a total phosphorus reference condition of 20 µg/L while the 25th percentile produces a value of 25 µg/L.

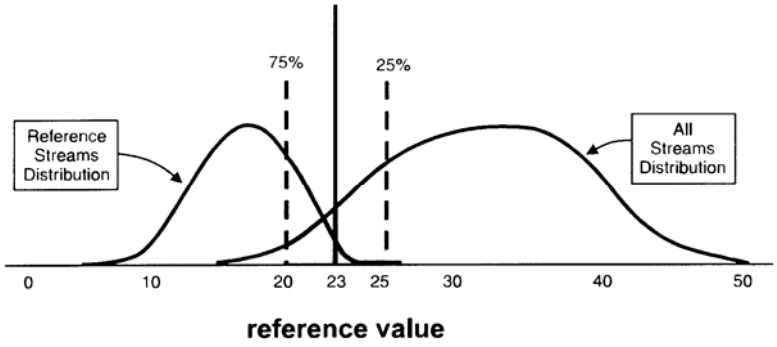


Figure 1.1 Selecting reference values for total phosphorus concentration (µg/L) using percentiles from reference streams (75% approach) and general stream population (25% approach) (from U.S. EPA, 2000a).

1.2.3. Phytoplankton Population Dynamics and Water Quality

It is generally accepted that phytoplankton composition changes with nutrient flux and in response to pollutant levels in a waterbody because of different nutrient needs, sensitivities to contaminants and "ecostrategies" to inhabit different types of water bodies (Mur et al., 1999; U.S. EPA, 2000a). Early work on the population dynamic-water quality interaction focused on the identification of pollution tolerant indicator species (Palmer, 1969; 1977; Glooschenko and Alvis, 1973; Lowe, 1974; van Landingham, 1982; Olive and Karn, 1980; Moraitou-Apostolopoulou and Ignatiades, 1980; Pfiester et al., 1980; Kromer Baker and Baker, 1981; Makarewicz and Bertram, 1991; Villena and Romo, 2003). More recently, attention has focused on using combinations of indices (including species richness, Shannon-Weaver Index of Diversity, Trophic Diatom Index, Biological Diatom Index, and Specific Polluosensitivity Index), together with Rapid Bioassessment Protocols and multivariate statistical analysis (e.g. Principal Component Analysis) to identify water quality impacts on phytoplankton population distributions (e.g. del Giorgio et al., 1991; Barbour et al., 1999; Ponader and Charles, 2003; Mercado, 2003; Environment Canada, 2004; Wang et al., 2005).

Over the past decade there has been increased interest, work, and acceptance of biological monitoring as a means of assessing the health of a water system, particularly as embodied by Rapid Bioassessment Protocols (e.g. Barbour et al., 1999; Blocksom and Winters, 2006). A number of indices have been developed to assess the data collected through biological monitoring. Some indices, such as the Pollution Tolerance Index for Diatoms, tend to focus on specific links between algal population changes and water chemistry, while others consider the relative abundance of algal species and their preferences for specific habitat conditions (including physical conditions) (Barbour et al., 1999; Fore and Grafe, 2002). The common element to these indices is that they synthesize extensive data and information into single values that facilitates interpretation as well as communication to the general public (see also House, 1990). Furthermore, the indices reflect biological response to environmental stresses at the site, which potentially provides more useful information for management decisions than a simple comparison to

water quality guidelines. Increasingly, it is common to use combinations of indices to assess biological integrity (Fore and Grafe, 2002; Greer et al., 2002; Bate et al., 2004).

1.2.4. Harmful Algae Blooms

Harmful algae blooms (HABs) are a global phenomenon observed in both freshwater and marine environments. In the past, most media attention and research focused on "Red Tide", associated with blooms of *Karenia brevis* in the marine environment. In addition to killing fish, brevetoxins produced by *K. brevis* can become concentrated in the tissues of shellfish that feed on the algae. People who eat these shellfish may suffer from neurotoxic shellfish poisoning, a food poisoning that can cause severe gastrointestinal and neurologic symptoms, such as tingling fingers or toes (http://www.cdc.gov/hab/redtide/about.htm).

In freshwater systems, certain cyanobacteria can produce neurotoxins and hepatotoxins. Effects of the toxins range from diarrhea, vomiting and flu-like symptoms in humans swimming in the water, to human and animal mortality. In the various reported incidents of poisoning in humans and livestock caused by cyanobacteria or their toxins, *Microcystis spp.* is the most frequently cited organism (Kuiper-Goodman et al., 1999). *Microcystis spp.* (and less commonly, other algae species such as *Planktothrix agardhii* and *Anabaena flos-aquae*) can produce a family of toxins, generally known as microcystins (Carmichael and Bent, 1981; Kuiper-Goodman et al., 1999; Laub et al., 2002) of which Microcystin-LR, is highly toxic. Microcystin is a hepatotoxin and Ndebele and Magadza (2006) suggested that the 300% rise in gastrointestinal infections and 400% increase in liver cancer in Harare, Zimbabwe between 1991 and 2001 may be related to the elevated levels of microcystin in the city's drinking water reservoir. Microcystin-LR levels in the reservoir ranged between 18 and 22.5 µg/L; the WHO advisory level for Microcystin-LR is 1 µg/L. Moreno et al. (2005) reported total microcystin concencentrations of up to 6.40 µg/L from a river in Spain, of which Microcystin-LR and –RR were the main components.

1.2.5. The Great Lakes Situation

In 1992 the State of the Lakes Ecosystem Conferences (SOLECs) were initiated by the U.S. and Canadian governments with the objectives of assessing the state of the Great Lakes ecosystem based on accepted indicators; strengthening decision-making and management; informing local decision makers of Great Lakes environmental issues; and providing a forum for communication and networking amongst all stakeholders (Shear et al., 2003). These meetings are held biannually, with a summary report issued after each meeting. By 1998, the SOLEC meetings began to identify ecosystem health indicators, their units of measure, and their reference criteria or endpoints. This identification process involved input from over 150 people, including citizens and a core working group and expert panel. Initially, the group identified over 800 potential indicators, a number which was ultimately reduced to 82 through review and discussion. In 2002, reports were prepared for 43 of the indicators that had available data. The remaining indicators were not evaluated because the required data had not been collected, but over time it is expected that the full suite of indicators will be assessed; it also is possible new indicators will be added (Shear et al., 2005).

SOLEC identified two indicators pertinent to this study. Indicator #109 is *Phytoplankton Populations* and Indicator #111 is *Phosphorus Concentrations and Loadings*. As noted above, the *State of the Lakes – 2005 Report* concluded "No assessment of 'ecosystem health' is currently possible on the basis of phytoplankton community data since reference criteria and endpoints have yet to be developed" (Environment Canada and U.S. EPA, 2005). Although the SOLEC 2005 report noted that a detailed record of phytoplankton biomass and community structure has been generated for the Great Lakes, there are problems with study comparability and concerns that the "unusual" conditions of the lakes are such that responses of individual phytoplankton species to their chemical environment may be fundamentally different from other lakes. It was recommended that "there is an urgent need for the development of an objective, quantifiable index specific to the Great Lakes to permit the use of phytoplankton data in the assessment of ecosystem health". It may be that one or more of the index approaches noted in Section 1.2.3 is appropriate.

The goals for phosphorus control are to maintain an oligotrophic state in Lakes Superior, Huron, and Michigan; to maintain algal biomass below that of a nuisance condition in Lakes Erie and Ontario; and to eliminate algal nuisance growth in bays and in other areas where they occur (Environment Canada and U.S. EPA, 2005). To meet these goals, total phosphorus guidelines are: Lake Superor – 5 µg/L; Lake Huron – 5 µg/L; Lake Michigan – 7 µg/L; Lake Erie (western basin) – 15 µg/L; Lake Erie (central basin) – 10 µg/L; Lake Erie (eastern basin) – 10 µg/L; Lake Ontario – 10 µg/L. Charlton et al. (1999) showed that summer total phosphorus levels declined in Lake Erie between the early 1970's and 1995, in response to phosphorus control measures (and in some way, by zebra mussel invasion), but levels increased between 1995 and 1999 in the eastern and central basins. The 1997 data reported by Charlton et al. (1999) indicated that the central and eastern basins of Lake Erie were meeting the 10 µg/L guideline, but the 15 µg/L guideline for the western basin was not being met. Makarewicz and Bertram (1991) concluded that the western basin of Lake Erie shifted from eutrophic to mesotrophic conditions between 1970 and 1985 and the eastern basin shifted from mesotrophic to oligotrophic during the same time. More recent data reported by Environment Canada and U.S. EPA (2005) shows that the western basin continues to not meet the 15 µg/L guideline. Generally, Lakes Superior, Huron, Michigan, and Ontario are meeting their open water guidelines (Environment Canada and U.S. EPA, 2005) although Makarewicz et al. (2006) reported that total phosphorus in Lake Ontario nearshore and embayment areas of New York State (41% of sample sites) did not meet the guideline in 2004. Charlton et al. (1999) also noted that nitrate/nitrite levels in Lake Erie have increased, while chlorophyll a levels have declined.

Although as noted above, *Cladophora* growth has re-emerged as a management problem in parts of the Great Lakes (Bootsma et al., 2005), it was decided to focus on algae with a potential health impact in this study, as the indicator for BUI #8. Brittain et al. (2000) first reported the presence of microcystins in Lake Erie and subsequently Murphy et al. (2003) detected microcystins at Presque Isle, PA and Wendt Beach (Erie County, NY) as well as in Hamilton Harbor, ON. Levels of total microcystin were low at Presque Isle and Wendt Beach (maximum level of 26 samples was 0.407 µg/L at Presque Isle), while in Hamilton Harbor the maximum level reached 238.8 µg/L. As a result,

Hamilton Harbor was posted in 2001, warning people of the risks of contact and not to eat the fish. Boyer (2006) reported microcystin levels between 14 and 20 µg/L in western Lake Erie, generally related to the Maumee River region, while lower levels were reported from the Sandusky Harbor (0.5-0.7 µg/L) and Long Point Bay (0.25 µg/L) on the Canadian side of the lake. Microcystin levels for an area near the south shore of Lake Ontario exhibited low levels of microcystin (0.003-0.008 µg/L) in recent sampling (Makarewicz et al., 2006).

1.3. The Buffalo River Watershed

The Buffalo River drains an area of 1,155 km^2 (447 mi^2) and Cayuga, Buffalo, and Cazenovia creeks are the three major tributaries within the watershed (Figure 1.2). The Buffalo River watershed occupies two physiographic regions. The northern and western portion of the watershed is within the Erie-Ontario Lake Plain Province, while the southern part of the watershed is within the Alleghany Plateau Province. The Erie-Ontario Province formerly was a glacial lake bed and therefore has limited relief. The watershed consists primarily of 21 different soil series, but the majority of soils texturally are a silt loam (U.S. Department of Agriculture, 1986). The slopes of these soil units range between nearly level and 0.50, while the drainage classification ranges from very poorly drained to excessively drained (U.S. Department of Agriculture, 1986).

The climate of the Buffalo area is classified under the Koppen system as humid continental with a mild summer (Dfb) (Gabler et al., 1997). Annual total precipitation at the Buffalo Airport averages 98 cm (38.6 in), with February being the driest month (5.9 cm (2.32 in) of precipitation) and August being the wettest month (10.6 cm (4.17 in) of precipitation). The lowest monthly mean flow recorded at U.S. Geological Survey (USGS) gauge stations on each of the tributaries (Figure 1.2) typically occurs in July and August when evapotranspiration is highest (Cayuga Cr. - 0.70 m^3s^{-1} (24.6 cfs); Buffalo Cr. - 1.30 m^3s^{-1} (45.8 cfs); and Cazenovia Cr. - 1.35 $m^3 s^{-1}$ (47.8 cfs)). Highest monthly mean flow on the three tributaries typically occurs in March (Cayuga Cr. – 9.68 m^3s^{-1} (342 cfs); Buffalo Cr. – 14.0 m^3s^{-1} (495 cfs); and Cazenovia Cr. – 15.6 m^3s^{-1} (551 cfs)) as the result of snowmelt and spring rainfall.

Land use within the watershed varies. Much of the upper portion of the watershed is characterized by woods and farmland, but prior to joining the Buffalo River the creeks also pass through several small communities and receive industrial, commercial, residential, and municipal discharges (Irvine and Pettibone, 1996). The lower Buffalo River historically has been highly urbanized and industrialized (Sauer, 1979; Rossi, 1995) and this appears to be the principal reason why only the lower 9.6 km (6 mi) of the river was designated an AOC by the International Joint Commission. The change in the industrial composition of the AOC between 1929 and 1990 was documented and mapped by Irvine et al. (2003).

Much of the Buffalo River AOC is designated as a navigable channel and is maintained at a minimum depth of 7m (22 ft) by the Buffalo District USACE. This dredged reach is wider and deeper than the tributaries, but the bed slope is shallower. As a result of the changes in the hydraulic geometry, flow velocities within most of the AOC typically are less than those of the tributaries, producing local shoaling areas as sediment deposits. The Buffalo River Improvement Corporation (BRIC) was created in 1967 to supply industries along the Buffalo River with water for cooling and processing purposes. The water is pumped from Lake Erie and ultimately augments flows in the Buffalo River. The design operation of the BRIC system is 2.18 $m^3 s^{-1}$ (77 cfs) and during its early years of operation often contributed 90% of the total river flow in the drier summer months (Sauer, 1979). This flow augmentation helped to improve the water quality of the river at the time. As industry has declined along the river, so too has the BRIC pumping rate. Pumping rates in the early part of this decade averaged 0.66 $m^3 s^{-1}$ (23 cfs).

1.3.1. Previous Algae Studies, Buffalo River Watershed

Only two algae studies have been done for the Buffalo River watershed since the initiation of the Remedial Action Plan process. Martin (1991) examined diatom taxa characteristics for samples collected from the beds of two sites on the east branch of Cazenovia Creek and two sites on tributaries. Population composition was similar for the two sites on Cazenovia Creek, while the populations from the tributaries were dissimilar to each other and to the Cazenovia Creek sites. Martin (1991) concluded that the sites

were indicative of an unpolluted environment because the populations generally exhibited a few species (2-3) with a relatively high abundance (10-20% of the population) and several species (9-20) with moderate abundance (1-10% of the population). Species richness at the sites averaged between 32 and 57.

Shero (1995) sampled periphyton from the Buffalo Harbor breakwall and at four sites along the Buffalo River AOC and concluded that the population reflected moderately high nutrients, but did not characterize a significantly degraded environment. Some common species were observed in both the Martin (1991) and Shero (1995) studies. *Cladaphora* was observed in increasing abundance at the Buffalo Harbor and lower Buffalo River sites through the summer of 1992, but was not observed at the three upper river sites.

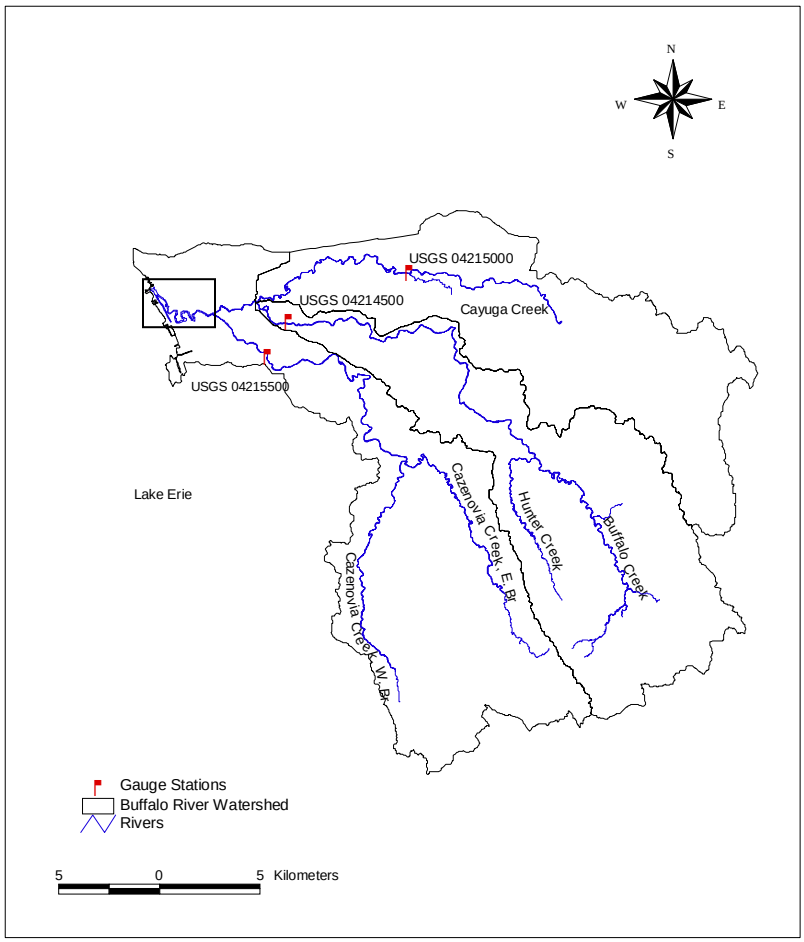


Figure 1.2 Buffalo River Watershed and USGS gauging stations. The AOC is enclosed by the black box.

2. METHODS

2.1. Manual Water Quality Sampling

Routine manual sampling was done once a week for eight weeks at three sites, starting on 7/14/06 and ending on 8/31/06. Sample site locations are shown in Figure 2.1 and photos of the individual locations are shown in Figures 2.2-2.4. The upstream-most site (Site 1) was located just upstream of the dredged, navigable channel and downstream of the mouth of Cazenovia Creek (WGS 84, 677215 m E; 4747563 m N). The middle site (Site 2) represented a mid-point location of the Area of Concern, at Ohio Street Bridge (WGS 84, 674236 m E; 4747724 m N). This site location has been used by numerous past studies (e.g. Irvine et al., 2005a, b). It also is a New York State Department of Environmental Conservation (NYSDEC) RIBS (Rotating Intensive Basin Sampling) program site, and as such facilitates data comparisons. The downstream site (Site 3) was located near the mouth of the Buffalo River, but upstream of the Buffalo Ship Canal (WGS 84, 673332 m E; 4749034 m N). With the exception of the 7/20/06 date, sampling was done in the morning, between 9:30 and 11:30. The sampling on 7/20/06 was done in the early afternoon, between 14:00 and 15:25. A field duplicate sample was collected at Site 2 on 8/31/06.

Water samples were collected from a 14-foot Boston Whaler at a 1.5 m depth using a Van Doren sampler. To avoid cross-contamination, the first cast of the Van Doren at each site was discarded, while the second cast was used to fill the sample bottles. Samples at Sites 1 and 3 were collected at mid-channel locations, while samples at Site 2 were collected approximately 6 ft (1.83 m) out from the bank.

Samples were collected for total phosphorus, nitrate/nitrite, ammonia, chlorophyll a, and total microcystin analysis. A total of 3 L of water was placed in amber glass bottles for the chlorophyll a and total microcystin analysis. Separate plastic sample bottles were used for total phosphorus, ammonia and nitrate/nitrite (total of 16 oz or 473 mL) and these samples were preserved in the field with H_2SO_4 to a pH of <2. All samples were kept on ice from collection time until delivery to the analytical laboratories.

Samples also were collected on 7/20/06, 8/2/06, 8/16/06, and 8/31/06 at Site 2 for phytoplankton population analysis (total count and taxa identification). A 100 mL sample was collected on each date and preserved in the field with 3 mL of 25% glutaraldehyde. The samples were kept on ice until couriered to the laboratory for analysis.

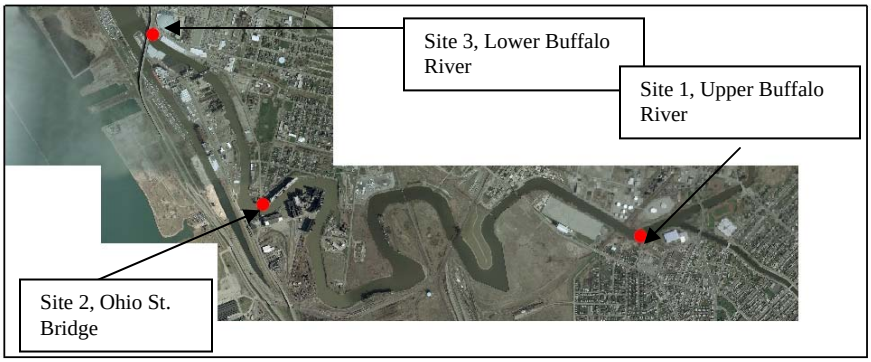


Figure 2.1 Sample site locations.

2.2. Continuous Water Quality Monitoring

A YSI 6600 EDS datasonde was installed at Site 2 (Ohio St. Bridge) to record temperature, pH, conductivity, dissolved oxygen, turbidity, and fluorescence (chlorophyll a) at 15 minute time steps between 7/7/06 and 8/31/06. The YSI datasonde was contained within a capped PVC tube (Figure 2.5). The lower section of the PVC tube had holes drilled through it to allow the water to move freely past the YSI sensors. The PVC tube protected the YSI from damage due to floating storm debris in the river and the locked cap provided a level of security from tampering. The YSI datasonde was secured at a fixed level, approximately 1 m below the water surface. Clearly, then, during storm events the water depth above the sensors was greater. A similar installation was used at this site previously, in 2000, 2003, and 2004 (Irvine et al., 2005a, b).

The YSI 6600 EDS datasonde was purchased specifically for this project and the sensors came with factory calibration. As a check, pH, dissolved oxygen, and turbidity were re-calibrated at the Buffalo State field station prior to installation.

Data from the YSI 6600 were uploaded to a laptop on a weekly basis (Figure 2.6). All data were edited and maintained in Excel spreadsheet format. During the weekly site

visit to upload the data, the unit and all sensors were cleaned with Kimwipes and cotton swabs, and the general operation of the unit was checked. The dissolved oxygen sensor was calibrated each week using the 100% (air) saturation method as described by the manufacturer. The dissolved oxygen membrane and electrolyte was changed at the midpoint of the project and the pH sensor also was calibrated (7 and 10 buffer) at this time. All data were graphed and reviewed on a weekly basis to identify any problem data. In general, the methodology for the sampling and YSI maintenance followed that done previously for the Buffalo River (Irvine et al., 2005a, b).

Figure 2.2 Site 1, Upper Buffalo River.

Figure 2.3 Site 2, Ohio St. Bridge.

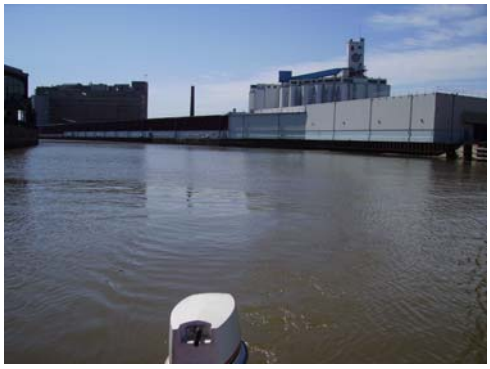


Figure 2.4 Site 3, Lower Buffalo River.

Figure 2.5 PVC tube for YSI unit, Site 2.

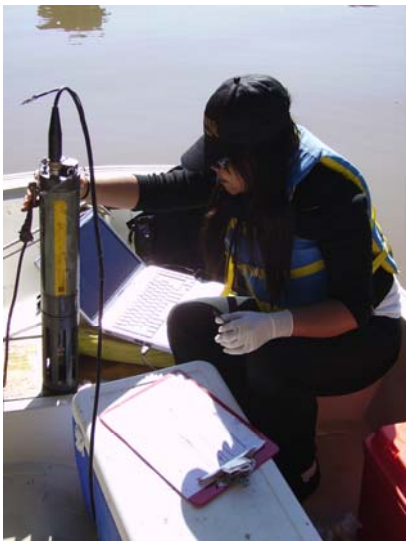


Figure 2.6 Uploading data from YSI unit.

2.3. Laboratory Methods

2.3.1. Nutrients

Total phosphorus, ammonia, and nitrate/nitrite were analyzed by Severn Trent Laboratories (STL), Amherst, NY. STL is a New York State Department of Health certified laboratory. All samples were kept refrigerated at 4 ^{o}C until analysis was started. Total phosphorus was analyzed using U.S. EPA Method 365.2, ammonia was analyzed using U.S. EPA Method 350.1, and nitrate/nitrite was analyzed using U.S. EPA Method 353.2 (U.S. EPA 1983; 1991; 1992; 1993). Reporting limits were: total phosphorus - 0.01 mg/L; ammonia - 0.02 mg/L; and nitrate/nitrite - 0.05 mg/L. QA/QC measures included matrix spikes, method blanks, and blank spikes for each batch of samples.

2.3.2. Chlorophyll a and Total Microcystins

Chlorophyll a and total microcystins were analyzed in Dr. Tom Murphy's laboratory at Environment Canada's National Water Research Institute (NWRI), Burlington, Ontario (approximately a one hour drive from Buffalo). The samples were kept on ice after collection and delivered to the NWRI laboratory the next day. The samples for chlorophyll a were analyzed according to Standard Method 10200 (APHA,

1989). The sample was filtered and the residue was extracted with acetone for spectrophotometric determinations at 663 nm, 645 nm, and 630 nm, with a detection limit of 0.1 µg/L. The samples for total microcystins were analyzed using an ELISA (Enzyme-Linked ImmunoSorbent Assay) approach with a Biorad 3550 Microplate Reader and an Envirologix microcystin plate kit (cf. Murphy et al., 2003). ELISA analysis has long been used as a less expensive and time-consuming, but accurate alternative to HPLC (high performance liquid chromatography) analysis for microcystins (Nagata et al., 1997; Domingos et al., 1999; Metcalf et al., 2000; Mathys and Surholt, 2004).

2.3.3. Phytoplankton Analysis

Phytoplankton analysis (total count and taxa identification) was done for four samples collected at Site 2 (Ohio St. Bridge). Ms. Mary Arnold did the algal enumeration and she has done similar analyses for Dr. J. Makarewicz at SUNY Brockport. Known quantities of water were poured into sedimentation chambers. At least 400 cells in transects of the settled plankton were enumerated using a Wild inverted microscope at 500x . Identifications primarily were according to Wehr and Sheath (2003), and Prescott (1962 and 1964). The number of cells per mL was determined by the formula:

$$\text{Transect count (No./mL)} = \frac{(C \bullet A)}{L \bullet W \bullet S \bullet V} \qquad [2.1]$$

where C is the number of cells counted, A is the surface area of the chamber (mm^2), L is the length of the transect (mm), W is the width of transect (mm), S is the number of transects counted, and V is the volume of sample settled (mL).

For diatom analysis, an additional quantity of each sample was boiled with 30% hydrogen peroxide, rinsed, settled and dried on coverslips. The coverslips were mounted on slides using Pleurax mounting medium (Dodd, 1987). At least 200 valves in transects of the coverslips were enumerated at 1000x using phase contrast. Identifications were based principally on Patrick and Reimer (1966), Huber-Pestalozzi (1975), and Dodd (1987). Using equation [2.1], the number of live pennate and centric diatoms per mL was

determined. The appropriate number is multiplied by the percent of the population of either a given centric or pennate species to determine the number per mL of that species.

3. RESULTS

3.1. Hydrologic Conditions During Study Period

The U.S. Geological Survey (USGS) maintains a flow gauging station on each of the three major tributaries to the Buffalo River; Cazenovia Creek, Buffalo Creek, and Cayuga Creek (Figure 1.2). Simple summation of the daily mean flow at the three gauge stations cannot provide an accurate approximation of the inflow to the top of the AOC because the gauges do not represent the entire contributing area for the three tributaries. Meredith and Rumer (1987) used a proportional-area approximation to account for the ungauged portions of the watershed in calculating the inflow to the top of the AOC:

$$Q_T = Q_G \bullet \left(\frac{A_T}{A_G} \right) \qquad [3.1]$$

where: Q_T = daily flow from the tributary to the top of the AOC (cfs or m^3s^{-1})

Q_G = daily flow at the gauge on the tributary (cfs or m^3s^{-1})

A_T = total drainage area at the mouth of the tributary (mi^2 or km^2)

A_G = drainage area upstream of the gauge (mi^2 or km^2)

The drainage areas upstream of the Buffalo, Cayuga, and Cazenovia Creek gauges are 144, 94.9, and 134 mi^2 (372.1, 245.2, 346.2 km^2), respectively. The total drainage areas for Buffalo, Cayuga, and Cazenovia Creeks are 146.2, 124.4, and 135.4 mi^2 (377.8, 321.4, 349.9 km^2), respectively (Meredith and Rumer, 1987).

The flow adjustment approach represented by equation [3.1] was used in this study to estimate daily mean flow to the top of the AOC, near Site 1, and the flow time series is shown in Figure 3.1. To facilitate timely completion of this report, it was necessary to use the provisional data supplied on the USGS website for Figure 3.1. Flow during this study was slightly higher than median flow for the period of record (approximately 63 years). Runoff events occurred during the study period, but samples were collected, to the extent possible, during non-event periods.

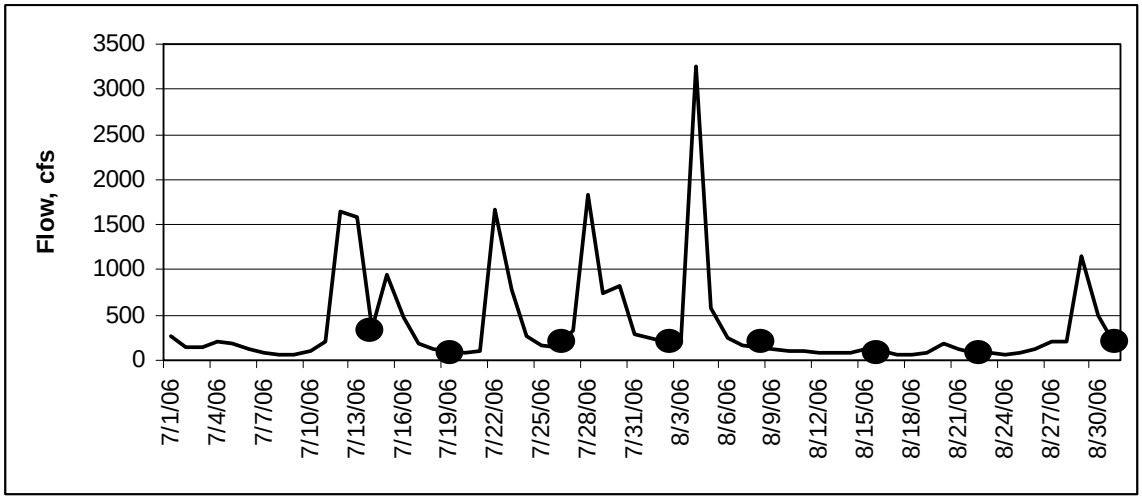


Figure 3.1 Daily mean flow to the top of the AOC; sample dates are represented by:● Conversion from cfs to m^3s^{-1}, multiply cfs by 35.315.

3.2. Nutrients and Chlorophyll a

The results of the nutrient analysis are shown in Table 3.1 while the results of the chlorophyll a analysis are shown in Table 3.2 and Figure 3.2. A duplicate sample was collected at the Ohio St. Bridge on 8/31/06 and the results were: total phosphorus, <0.01 mg/L; nitrate/nitrite, 0.3 mg/L; ammonia, 0.1 mg/L; and chlorophyll a, 2.2 µg/L.

Table 3.1 Nutrient Results

Sample Date	Upper Buffalo River			Ohio St. Bridge			Lower Buffalo River		
	T. Phos. mg/L	NO3/NO2 mg/L	Ammonia mg/L	T. Phos. mg/L	NO3/NO2 mg/L	Ammonia mg/L	T. Phos. mg/L	NO3/NO2 mg/L	Ammonia mg/L
7/14/2006	0.11	0.52	0.079	0.16	0.39	0.19	0.05	0.26	0.16
7/20/2006	0.097	0.025	0.05	0.081	0.36	0.15	0.063	0.4	0.17
7/27/2006	0.073	0.025	0.066	0.079	0.25	0.13	0.099	0.25	0.1
8/2/2006	0.005	0.025	0.064	0.005	0.24	0.2	0.038	0.22	0.16
8/9/2006	0.065	0.11	0.06	0.061	0.28	0.22	0.026	0.23	0.24
8/16/2006	0.089	0.084	0.12	0.016	0.14	0.24	0.03	0.25	0.26
8/23/2006	0.005	0.17	0.085	0.005	0.18	0.25	0.01	0.2	0.28
8/31/2006	0.024	0.32	0.083	0.028	0.28	0.28	0.005	0.25	0.26
Mean	0.059	0.160	0.076	0.054	0.265	0.208	0.040	0.258	0.204
Std. Dev.	0.042	0.177	0.022	0.053	0.083	0.051	0.031	0.061	0.065

Table 3.2 Chlorophyll a Results, µg/L

Sample Date	Upper Buffalo River	Ohio St. Bridge	Lower Buffalo River
7/14/2006	7.4	3.3	6.2
7/20/2006	14.8	3.8	5.5
7/27/2006	8.4	5.7	4.8
8/2/2006	11.7	3.1	12.5
8/9/2006	12.9	2.5	13.1
8/16/2006	9.4	2.8	7.3
8/23/2006	14.4	3.4	8.4
8/31/2006	4.3	1.9	3.1
Mean	10.4	3.3	7.6
Std. Deviation	3.7	1.1	3.6

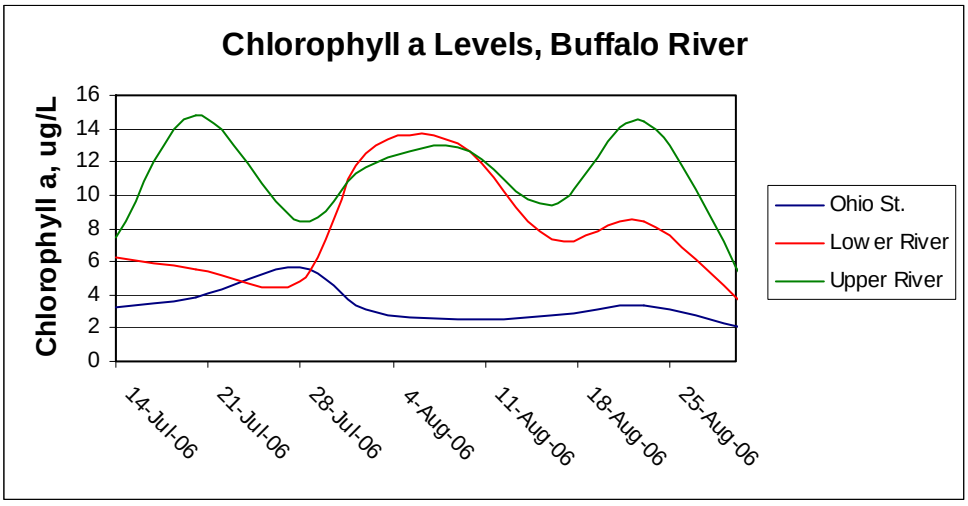


Figure 3.2 Chlorophyll a results.

3.3. Total Microcystin

The results of the total microcystin analysis are shown in Table 3.3. A duplicate sample was collected at the Ohio St. Bridge on 8/31/06 and the resulting level was 0.008 µg/L.

Table 3.3 Total Microcystin Levels, µg/L

Sample Date	Upper Buffalo River	Ohio St. Bridge	Lower Buffalo River
7/14/2006	0.011	0.021	0.025
7/20/2006	0.041	0.023	0.012
7/27/2006	0.012	0.065	0.045
8/2/2006	0.050	0.020	0.259
8/9/2006	0.044	0.048	0.322
8/16/2006	0.041	0.018	0.100
8/23/2006	0.061	0.090	0.113
8/31/2006	0.015	0.008	0.012
Mean	0.034	0.037	0.111
Std. Deviation	0.019	0.029	0.118

3.4. Phytoplankton Abundance and Taxa Identification

Total phytoplankton abundance at the Ohio St. Bridge (Site 2) for each of the four sample dates is summarized in Table 3.4 and abundance by taxa is presented in Appendix 1. The distribution of algal population, by division, is shown in Figure 3.3.

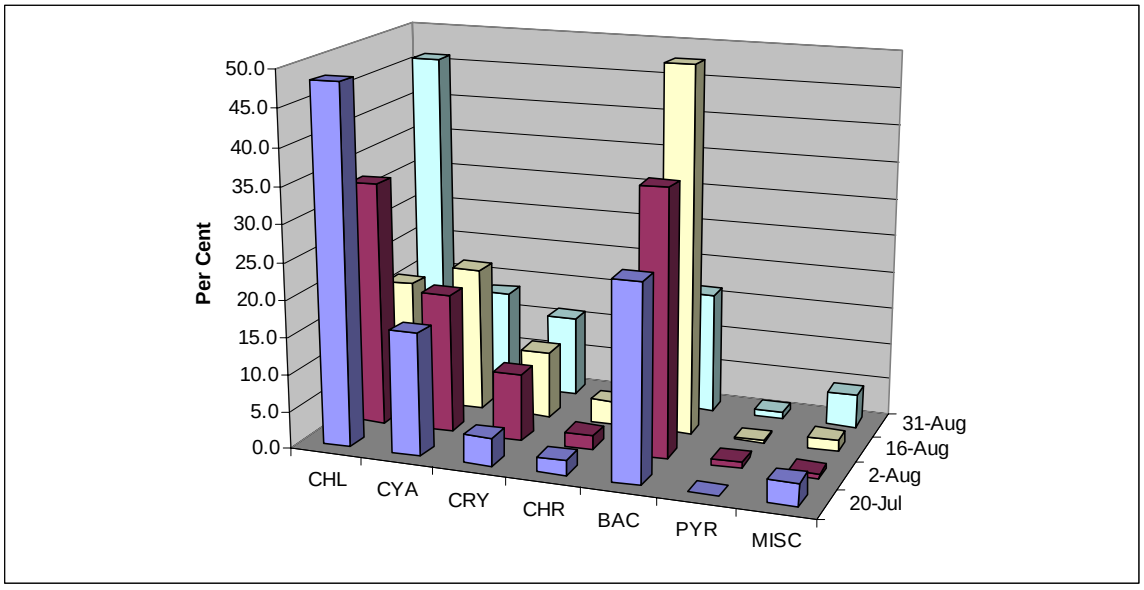


Figure 3.3 Algal population distribution (as a per cent of total population count), by division; CHL – Chlorophyta; CYA – Cyanobacteria; CRY – Cryptophyta; CHR – Chrysophyta; BAC – Bacillariophyta; PYR – Pyrrophyta; MISC – miscellaneous algae, not accurately identified.

Table 3.4 Total Phytoplankton Abundance, cells/mL

Sample Date	7/20/06	8/2/06	8/16/06	8/31/06
Abundance	3,379	2,861	2,304	3,082

3.5. YSI Datasonde Results

The results of monitoring temperature, pH, conductivity, dissolved oxygen, turbidity and fluorescence (chlorophyll a) at the 15 minute time steps are shown in Appendix 2. To visualize general trends, the weekly mean values are plotted in Figure 3.4 and the means and standard deviations of the weekly data are presented in Table 3.5.

New York State guidelines for dissolved oxygen in Class C, non-trout waters state "…the minimum daily average shall not be less than 5.0 mg/L and at no time shall the DO concentration be less than 4.0 mg/L. Daily mean dissolved oxygen levels were calculated and 50 of the 56 days monitored had a daily mean value less than 5.0 mg/L. Based on the 15 minute time step data, the dissolved oxygen level was less than 4.0 mg/L 56% of the time.

As a check on the precision of the YSI fluorescence measurements in representing chlorophyll a levels, the mean of the weekly sample values for chlorophyll a (Table 3.2) can be compared to the mean of the fluorescence measurement taken at the same time. The mean of the chlorophyll a from Table 3.2 was 3.3 μg/L and the mean from the fluorescence measurements was 3.5 μg/L.

A duration curve was developed for the turbidity data collected in this study and is presented in Figure 3.5. Based on this duration curve, turbidity was ≤40 NTU 55.7% of the time; ≤30 NTU 32% of the time; and ≤20 NTU 11.3% of the time. The duration curve includes storm event and non-event data. Because of increased erosion and sediment transport, turbidity is higher for storm events. During the summer of 2006, dry weather turbidity at the Ohio St. Bridge site typically was in the range of 27 NTU (see week of 8/16/06-8/23/06, Appendix 2).

Table 3.5 Summary Data, Weekly Means and Standard Deviations (in brackets), YSI Datasonde

Week Ending	Temp., C	Cond., mS/cm	pH	D.O., mg/L	Turbidity, NTU	Chlorophyll a, µg/L
7/14/06	23.72 (0.67)	0.45 (0.041)	7.54 (0.09)	4.60 (1.1)	25.9 (17)	3.7 (2.4)
7/20/06	25.39 (0.88)	0.33 (0.014)	7.54 (0.091)	3.69 (0.85)	41.1 (29.7)	4.11 (1.06)
7/27/06	24.89 (1.28)	0.354 (0.026)	7.56 (0.064)	4.05 (0.63)	52.4 (38.8)	4.14 (1.51)
8/2/06	24.71 (0.83)	0.33 (0.02)	7.62 (0.05)	4.73 (0.53)	80.9 (60.5)	4.81 (1.70)
8/9/06	24.95 (1.09)	0.29 (0.05)	7.55 (0.12)	4.04 (0.84)	176 (170)	7.55 (4.43)
8/16/06	24.31 (0.34)	0.31 (0.02)	7.48 (0.026)	4.07 (0.27)	55.1 (26.5)	4.36 (1.01)
8/23/06	24.18 (0.35)	0.39 (0.02)	7.47 (0.04)	3.04 (0.49)	27.7 (7.0)	2.1 (0.72)
8/31/06	23.3 (0.88)	0.48 (0.02)	7.52 (0.06)	3.46 (0.76)	40.1 (26.9)	1.69 (0.99)

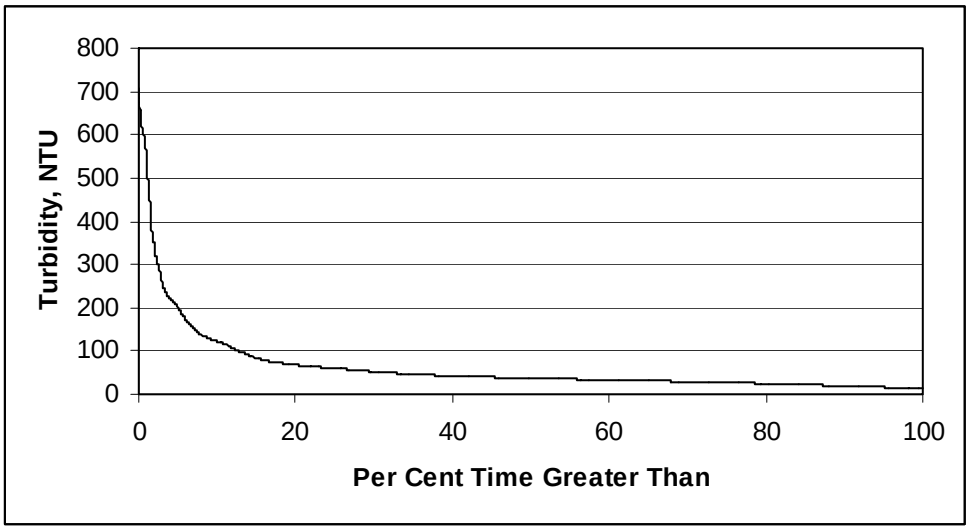
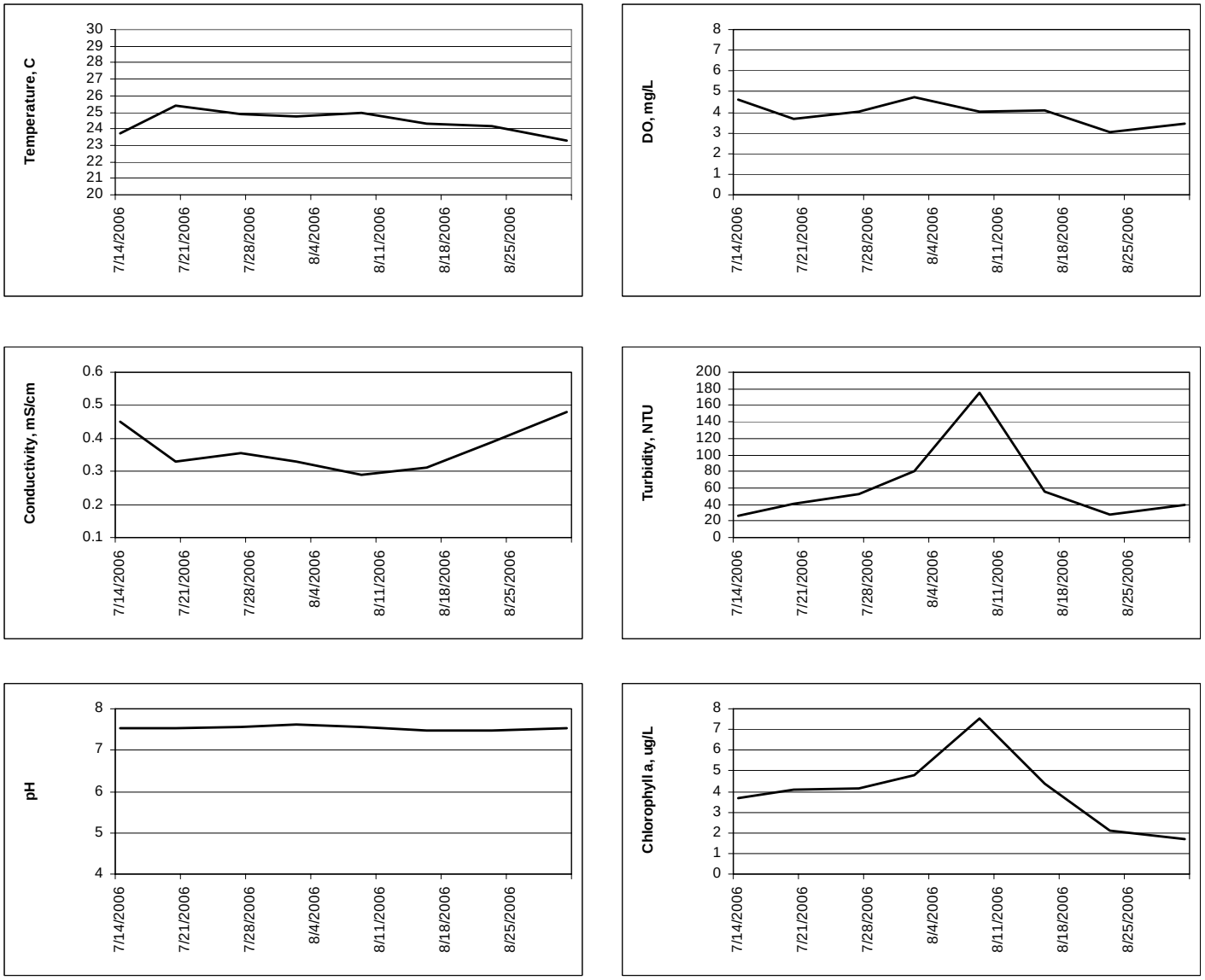


Figure 3.5 Turbidity duration curve for Ohio St. Bridge site.

3.6. QA/QC Results

Laboratory QA/QC guidelines were met for all nutrient analyses for the samples from the first six weeks of the project. The hold time was exceeded for the total phosphorus analysis of the 8/23/06 samples. The matrix spike recovery was high for the total phosphorus analysis of the 8/23/06 and 8/31/06 samples. The total phosphorus data for these weeks was within expected range and the data were retained for this report.

Figure 3.4 Weekly mean data, YSI datasonde.



Precision was determined using the relative per cent difference (RPD) from the laboratory measurements of the field duplicates collected on 8/31/06:

$$RPD = \frac{(C_1 - C_2) \bullet 100}{(C_1 + C_2)/2} \qquad [3.2]$$

where C_1 is the larger of the two observed values and C_2 is the smaller of the two observed values. The RPD values for the individual analytes are summarized in Table 3.6. Generally, RPD values <35% are acceptable (Irvine, 1997). The RPD for total phosphorus from this project was higher than that for a Cazenovia Creek project (11%), but the nitrate/nitrite RPD from this project was lower than the Cazenovia Creek project (11%)(Irvine, 1997).

Table 3.6 RPD Values, This Study

Total Phosphorus	NO3/NO2	Ammonia	Total Microcystin	Chlorophyll a
23.7	1.7	23.7	0	3.7

4. DISCUSSION

4.1. Trophic Status Based on Nutrient and Chlorophyll a Levels

As noted in Sections 1.2.1 and 1.2.2, there are a number of ways to assess the trophic status of a waterbody and in this section several alternatives are examined: a) threshold levels for total phosphorus and chlorophyll a identified from the literature; b) reference reach approach for comparisons of total phosphorus, nitrate/nitrite, and chlorophyll a; and c) the 25th percentile approach for the median of the general stream population.

A summary of threshold levels for total phosphorus and chlorophyll a, compiled from the literature and focusing only on North America, is provided in Table 4.1. As noted by Walker et al. (2006), there is considerable variability in these threshold levels, particularly for total phosphorus. In comparing the mean total phosphorus levels at the sample sites in the Buffalo River AOC (Table 3.1) with the threshold levels from Table 4.1, a conclusion regarding trophic status clearly may depend on the threshold level chosen. For summary purposes, it was decided to use the moderately low threshold of 42 μg/L. The mean levels of total phosphorus from all sites in the AOC are greater than this threshold. However, the sample variability also must be considered and to do this, one sample t-tests were conducted with the threshold value of 42 μg/L. The one-sample t-tests showed that the mean total phosphorus levels from the sites were not significantly different from the 42 μg/L threshold (α=0.05). The one-sample t-tests also showed that the mean chlorophyll a levels from the sites were not significantly greater than 8 μg/L and in fact, the mean chlorophyll a level at Site 1 was significantly less than 8 μg/L (α=0.05).

Irvine (1997) conducted a baseline water quality survey in support of the Erie County Department of Environment and Planning's Cazenovia Creek Watershed Management Project. Samples were collected at 12 sites from the headwaters to the mouth of Cazenovia Creek during four storm events and two dry weather periods. Site 8 (Allen Road bridge at Domes) represented the upstream control for the west branch of

Table 4.1 Nutrient and Chlorophyll a Threshold Levels

TP, µg/L	TN, µg/L	Chlorophyll a, µg/L	Comment	Source
42	300	8	Defines eutrophic boundary	Van Nieuwenhuyse and Jones, 1996 (quoted in U.S. EPA, 2000a)
70		15	TP level based on experiments to keep Chlorophyll a <15 µg/L, a nuisance action level	State of Oregon guidelines (quoted in Walker et al., 2006)
25	70	10	Oligotrophic-mesotrophic boundary	Table 8, various sources (quoted in Walker et al., 2006)
75	1.5	30	Mesotrophic-eutrophic boundary	Table 8, various sources (quoted in Walker et al., 2006)
42	290	8	Nutrient levels to keep Chlorophyll a ≤8 µg/L,	Dodds and Welch, 2000
40	900		Median level from U.S. rivers	Dodds and Welch, 2000
20	300		Guideline set for Clark Fork Voluntary Nutrient Reduction Program, Montana	Dodds and Welch, 2000
50			Water quality guideline for Illinois	Quoted in Walker et al., 2006
100			Water quality guideline for New Jersey	Quoted in Walker et al., 2006
30	200		Water quality guidelines for Ohio, warmwater habitat for large rivers; nitrogen in nitrite/nitrate rather than TN	Quoted in Walker et al., 2006
		40	Water quality guideline for North Carolina, non-trout streams	Quoted in Walker et al., 2006
10-35 (annual mean)		Mean: 2.5-8; Max: 8-25	Mesotrophic lake characteristics	Vollenweider and Kerekes, 1982
35-100 (annual mean)		Mean: 8-25; Max: 25-75	Eutrophic lake characteristics	Vollenweider and Kerekes, 1982
20-35			Mesotrophic trigger range for lakes or rivers; conservative approach	Canadian Council of Ministers of the Environment, 2006
25-75			Mesotrophic trigger range for rivers and streams, suggested and depending on lake receiving water quality	Environment Canada, 2004
30			To avoid excessive plant growth in rivers	Ontario Ministry of Environment and Energy, 1999
50			Protection of freshwater aquatic life, guideline for Alberta	Environment Canada, 2004
50			Water quality guideline for Manitoba	Environment Canada, 2004

Cazenovia Creek while Site12 represented the upstream control for the east branch of Cazenovia Creek. For Site 8, the mean (n=2) total phosphorus level was 15 μg/L and the mean nitrate/nitrite level was 305 μg/L, while for Site 12 the mean (n=2) total phosphorus was 65.5 μg/L and the mean nitrate/nitrite was 685 μg/L. Analysis for chlorophyll a was not done. Based on this limited control reach data set it can be concluded, with some caution, that the Buffalo River AOC data are within the same range as the control sites.

Following the procedure recommended by U.S. EPA (2000b), three median values representing the summer (June, July, August), fall (September, October, November), and spring (March, April, May) seasons were determined for water quality parameters from rivers in the New York State Department of Environmental Conservation's (NYSDEC) Niagara River and Lake Erie Drainage Basin, as defined under the RIBS (Rotating Intensive Basin Studies) program (NYSDEC, 1997; 2005). A total of 16 streams (and 79 samples) were included in this analysis and data reflected sampling in 1993-94 and 2000-2001. The exception to this sample timeframe was that data collected at the Ohio St. Bridge on the Buffalo River also reflected limited sampling in 1995, 1997, 1998, and 1999. The reference condition for the Buffalo River watershed (located in the Eastern Great Lakes and Hudson Lowlands, Level III Ecoregion) was then determined as the 25th percentile of the distribution of the 16 median values and results for the three seasons are summarized in Table 4.2. The mean value of total phosphorus for the three sample sites in the Buffalo River exceeds the 25th percentile of the median values in the Niagara River and Lake Erie Drainage Basin for the summer season (0.0173 mg/L (17.3 μg/L)). The mean value of nitrate/nitrite for the three sample sites in the Buffalo River were less than the 25th percentile of the median values in the Niagara River and Lake Erie Drainage Basin for the summer season (0.277 mg/L (277 μg/L)). It also is worth noting that the mean total phosphorus level for the Ohio St. Bridge site from the RIBS data is not significantly different from the mean level in this study (α=0.05) based on a non-pooled two sample t-test.

Gartner Lee Limited (2006) compiled total phosphorus data for 667 streams and rivers in the Canadian Mixed Wood Plains ecozone in developing an approach to establish guidelines for Canada. The Mixed Wood Plains essentially represented

Southern Ontario and in essence, this study followed the U.S. EPA ecoregion approach. Gartner Lee Limited (2006) reported that the mean total phosphorus level for the 667 streams and rivers was 0.079 mg/L (79 µg/L) with a standard deviation of 0.093 mg/L (93 µg/L). It was noted that the higher total phosphorus levels in the Mixed Wood Plains (as compared to the more northerly Boreal Shield ecozone) was related to thicker soils, a calcareous geology, and anthropogenic activity. It appears that Gartner Lee Limited (2006) used the 25th percentile of all data from the Mixed Wood Plains rivers (rather than the 25th percentile of the medians of the watersheds) to recommend a total phosphorus guideline. This guideline was identified as 0.027 mg/L (27 µg/L).

Table 4.2 Water Quality Guidelines for Buffalo River AOC Based on 25th Percentile of Median River Values

	Spring Season	Summer Season	Fall Season
Total Phosphorus	0.0138	0.0173	0.0125
Nitrate/Nitrite	0.398	0.277	0.256
Turbidity	1.48	2.63	2.29
Conductivity	295	387	387
Dissolved Oxygen	10.2	7.5	9.5
pH	7.7	7.8	7.7

Units – Total phophorus, nitrate/nitrite, dissolved oxygen in mg/L; turbidity in NTU; conductivity in µS/cm

The Minnesota Pollution Control Agency (2003) examined the relationships between nutrient levels and phytoplankton abundance in a number of watersheds using the ecoregion framework. As part of this assessment, generalizations were made to characterize watershed responses. For example, the characteristics of low nutrient, minimally impacted streams that require protection to maintain high water quality were identified. Other stream categories included: moderate nutrient concentrations requiring a "slight reduction" approach; nutrient rich requiring a BOD reduction approach; nutrient rich and high algal response streams; and streams with high nutrients and low algal response. The Minnesota Pollution Control Agency (2003) considered the Crow River to be an example of a low nutrient, high quality stream, where mean total phosphorus levels in the summers of 1999 and 2000 were in the range of 0.032 to 0.059 mg/L (32 to 59

μg/L). This certainly is within the range of the data for the Buffalo River. Mean turbidity for the Crow River ranged between 2.5 and 4 NTU. The Blue Earth River was an example of a nutrient rich river with a high algal response. Mean total phosphorus levels for this river (summers of 1999 and 2000) ranged between 0.192 and 0.248 mg/L (192-248 μg/L); mean turbidity ranged between 31 and 68 NTU; and mean chlorophyll a ranged between 0.041 and 0.101 mg/L (41-101 μg/L). These values of total phosphorus and chlorophyll a are higher than those observed in the Buffalo River and it also can be argued the turbidity for the Blue Earth River was higher. Finally, the Red River was an example of a high nutrient, low algal response waterbody. Summer mean values in 2000 were in the range of 0.208-0.602 mg/L (208-602 μg/L) for total phosphorus; 0.026-0.038 mg/L (26-38 μg/L) for chlorophyll a; and 27-151 NTU for turbidity. It was suggested that the high turbidity (Minnesota water quality guideline is 25 NTU) suppressed algal growth in the Red River (see also, Walker et al., 2006). A similar argument could be made for the Buffalo River. However, nutrient levels and turbidity levels are not as high as the Minnesota example. As noted in Section 3.5, dry weather turbidity levels at the Ohio St. Bridge in 2006 were in the range of 27 NTU. Flow in the summer of 2006 was higher than median and in general, turbidity is higher with higher flows. Irvine et al. (2005b) noted that mean dry weather turbidity (1 m depth) at 10 sites along the Buffalo River in the summers of 2003 and 2004 was in the range of 10-24 NTU. While additional evaluation could be done, at this point it does not appear that turbidity would have a major impact on algal abundance in the Buffalo River.

4.2. Presence of Undesirable Algae – Levels of Microcystin

The levels of total microcystin as shown in Table 3.3 were below the WHO guideline of 1 μg/L for microcystin-LR. Microcystin-LR would be contained within the total microcystin results and as such, data in Table 3.3 is conservative relative to the WHO guideline. Levels in Table 3.3 were higher than those reported for Lake Ontario by Makarewicz et al. (2006), but within the same range as levels reported for sites at Presque Isle and Wendt Beach in Lake Erie (Murphy et al., 2003). Levels in Table 3.3 were lower than those reported for western Lake Erie and Sandusky Harbor, as reported by Boyer

(2006) and considerably lower than the levels that resulted in the posting of Hamilton Harbor in 2001 (Murphy et al., 2003). Based on the levels of total microcystin presented in Table 3.3, it can be concluded that microcystin and associated algal species are not a concern at this point in time, although periodic monitoring should continue.

4.3. Phytoplankton Abundance and Taxa Identification

4.3.1. Total Abundance

The total abundance of phytoplankton ranged between 2,304 and 3,379 cells/mL at the Ohio St. Bridge site (Table 3.4). Makarewicz and Lewis (2002) reported total phytoplankton levels at two sites on Eighteenmile Creek to range between 9,547 and 36,157 cells/mL in June through August, 2000. Total abundance for Yanty Creek (considered a relatively unimpacted watershed on the south shore of Lake Ontario) was 62,845 cells/mL in a June sample and 15,094 cells/mL in an August sample, while total abundance for a site on the Oswego River was 26,863 cells/mL in an August sample (Makarewicz and Lewis, 2002). Phytoplankton abundance for six rivers in Argentina had phytoplankton densities ranging between 50 and 188,475 cells/mL (Mercado, 2003). del Giorgio et al. (1991) found that phytoplankton densities generally increased in the downstream direction, in response to sewage inputs to a river, with maximum values reaching 46,000 cells/mL.

The low total phytoplankton abundance on the Buffalo River is consistent with the relatively low chlorophyll a levels. The chlorophyll a levels on Eighteenmile Creek were in the 0.9-1.5 μg/L range, while total phosphorus was 113.6-127.6 μg/L and turbidity was 0.94-1.23 NTU (Makarewicz and Lewis, 2002). Given the variability inherent in phytoplankton enumeration, it might be concluded that the algal abundance between the Buffalo River and Eighteenmile Creek are not dissimilar. It is interesting that the total phosphorus levels on Eighteenmile Creek are higher than the Buffalo River, while turbidity is lower. Again the question as to whether turbidity on the Buffalo River is somewhat suppressing algal productivity could be considered, but probably is not a major issue.

4.3.2. Population Structure

As noted in Section 1.2.3, it is generally believed that phytoplankton population structure reflects its physical and chemical environment, but researchers have not yet reached consensus as to the best metrics to characterize impacts to structure. This report takes a weight of evidence approach and examines a number of different metrics.

One of the simplest measures of population structure is species richness. Species richness at the Ohio St. Bridge site was: 79 (7/2/06); 76 (8/2/06); 61 (8/16/06); and 85 (8/31/06). By comparison, species richness was 59 for the Eighteenmile Creek sites; 32-34 for Yanty Creek; and 107 for the Oswego River (Makarewicz and Lewis, 2002). The result for the Oswego River may represent a mix of species from harbor, lake, and river environments and therefore was higher than a strictly river habitat. This situation is possible for the Ohio St. Bridge site, as flow in the Buffalo River is impacted by Lake Erie water levels and lake water can flow up the river (Irvine et al., 1992). However, the Ohio St. Bridge site is far enough upstream that this impact should be minimal. In a survey of published studies on 67 rivers throughout the world, Rojo et al. (1994) found that the average species richness in temperate rivers was around 126, but also was highly variable, with a standard deviation of 94. Approximately 40% of the temperate rivers surveyed had a species richness of 80 or less. Species richness on the upper Mississippi River in Minnesota was greatest in the summer months, with maximum values around 50 (Kromer Baker and Baker, 1981).

Barbour et al. (1999) noted that species richness is predicted to decrease with increasing pollution because many species are stressed, although it also was noted that habitats may be naturally stressed by low nutrients, low light, or other factors. Willen (2001) found that as anthropogenic enrichment of total phosphorus was reduced species richness increased. However, del Giorgio et al. (1991) concluded that there were only small decreases in species richness at the more polluted sample locations in their study of a river in Argentina. Ponader and Charles (2003) found that multi-metric indices were better than simple community metrics, such as species diversity, as indicators of nutrient conditions. Hurlbert (1971) was harsher, suggesting that species diversity is an ecologically meaningless concept. The Kentucky Department for Environmental

Protection (2002) concluded that species diversity has been used with some success as an indicator of sewage pollution, but the success of the diversity index depends upon careful application and interpretation.

The Shannon-Weaver Index of Diversity frequently is used to assess algal population structure and is a function of both the number of species in a sample and the distribution of individuals among those species (Barbour et al., 1999; Kentucky Department for Environmental Protection, 2002; Graham et al., 2004). Using this index, $H' = 0$ when only one species is present and H' is a maximum when all individuals are evenly distributed among S species:

$$H' = -\sum\left(\frac{n_i}{N} \bullet \ln\frac{n_i}{N}\right) \qquad [4.1]$$

Where n_i is the number of cells of each species and N is the total count of all phytoplankton. The maximum diversity is a calculated as:

$$H_{\max} = \ln S \qquad [4.2]$$

Where S is the total number of species observed on a sample date. The evenness (E) of the plankton community can be calculated by comparing the actual diversity to the maximum diversity:

$$E = \frac{H'}{H_{\max}} \qquad [4.3]$$

The value of E ranges from 0 to 1, with values closer to 1 representing greater community evenness. It is thought that the value of E will decrease with increasing trophic status (U.S. EPA, 2000a).

Table 4.3 summarizes the values of H' and E for the Ohio St. Bridge site, based on cell numbers. In comparison, Makarewicz and Lewis (2002) reported evenness values of 0.319 to 0.447 for two sites on Eighteenmile Creek, 0.46-0.576 on Yanty Creek, 0.307

for one site on the Oswego River, and 0.639-0.758 for a nearshore site on Lake Ontario. In Crystal Bog, a humic lake in Wisconsin, Graham et al. (2004) found the H′ value ranged between 0.5 and 3.0, while the value of E ranged between 0.1 and 0.8. There was clear seasonality in the Wisconsin data, with the highest values occurring in August through October. Villena and Romo (2003) concluded that algal community structure in a Mediterranean lake exhibited an increasing equal contribution of algal groups and a reduction in volume of some species indicative of organic pollution in response to lower total phosphorus levels due to a reduction of sewage discharge. However, there was not a statistically significant change in the H´ value from samples before and after sewage diversion. In contrast, Willen (2001) found that as anthropogenic enrichment of total phosphorus was reduced evenness increased. Results for the Buffalo River suggest that the phytoplankton population exhibits a good level of species diversity and evenness.

Table 4.3 Summary of Shannon-Weaver Index Calculations, Ohio Street Bridge Site

Sample Date	H′	E
July 20, 2006	3.02	0.69
August 2, 2006	3.6	0.82
August 16, 2006	2.34	0.57
August 31, 2006	3.7	0.83

A number of studies specifically have focused on the distribution of the diatom population to assess phytoplankton health (e.g. Rott et al., 1998; Barbour et al., 1999; Fore and Grafe, 2002). Diatoms are differentiated from soft algae because their cell walls are made of silica that some have likened to a “glass house”. Diatoms have a yellow-brown chloroplast (rather than green) that enables them to photosynthesize. Rojo et al. (1994) reported that diatoms tend to be the dominant division of phytoplankton in temperate rivers although green algae could be important in some rivers. Figure 3.3 shows that diatoms were the dominant division for the Buffalo River in two of the four sample weeks, but were secondarily important to chlorophyta in the other two weeks.

There are two different groups of diatoms, the pennates, which are typified by bilateral symmetry and the centrics which have radial symmetry (Graham and Wilcox,

2000). It has been suggested that the ratio of centrics to pennates might be used to differentiate environmental conditions and in general as nutrient and pollutant levels increase, the C:P ratio also increases (del Giorgio et al., 1991; Ponader and Charles, 2003). The C:P ratios for the Buffalo River were 25.2 on 6/20/06; 0.53 on 8/2/06; 29.8 on 8/16/05; and 1.0 on 8/31/06, and as such these results are inconclusive with respect to environmental conditions.

Table 4.4 summarizes the results of the environmental condition classification based on the scheme presented by Lowe (1974) which examines the presence of specific diatoms. Rott et al. (1998) updated diatom-based classification schemes for trophic status and pollution tolerance in a study of the Grand River, Southern Ontario. Results for the Ohio St. Bridge site using the approach of Rott et al. (1988) are summarized in Table 4.5.

Table 4.4 Environmental Conditions Based on Diatom Presence

Sample Date	Summary of Results
7/20/06	9 species characteristic of eutrophic conditions; 1 species characteristic of saproxenous conditions; 19 species unclassified
8/2/06	12 species characteristic of eutrophic conditions; 1 species characteristic of saproxenous conditions; 26 species unclassified
8/16/06	5 species characteristic of eutrophic conditions; 1 species characteristic of saproxenous conditions; 20 species unclassified
8/31/06	7 species characteristic of eutrophic conditions; 1 species characteristic of saproxenous conditions; 1 species characteristic of oligotrophic to eutrophic conditions; 16 species unclassified

Table 4.5 Frequency of Diatom Species by Trophic Status and Saprobic Water Quality Class (Classification Based on Species Identified by Rott et al. (1998))

	Trophic Status						Saprobic Water Quality Class			
Sample Date	2	3	4	5	6	7	s	t	t-ht	ht
7/20/06	1	1	2	3	1		2	3		3
8/2/06			3	4	1	2	2	7		1
8/16/06	1	1	1	3		2	2	4		1
8/31/06			1	4	1	1	1	4		2

Trophic Status codes: 2 – oligotraphentic to mesotraphentic; 3 – mesotraphentic; 4 – mesotraphentic to eutraphentic; 5 – eutraphentic; 6 – hypereutraphentic; 7 – oligotraphentic to eutraphentic. Saprobic Water Quality Class codes: s – sensitive; t – tolerant; t-ht – moderately to highly tolerant; ht- highly tolerant

Results from Table 4.4 and 4.5 indicate that the algal population at Ohio St. Bridge has mixed characteristics, with some species representing a less polluted and less nutrient rich mesotrophic condition and other species representing a more polluted and nutrient rich eutrophic condition. *Cyclotella meneghiniana* has been reported to prefer nutrient rich and higher turbidity environments, with a broad pollution tolerance (Rott et al., 1988; del Giorgio et al., 1991; Rojo et al., 1994) and this species was in the top five in cell abundance for two of four sample dates. However, the *Cyclotella meneghiniana* percentage of the total population on those two dates (7/20/06 and 8/2/06) was relatively low at 5.4% and 4.7%, respectively. *Gomphonema parvulum* also has been associated with more polluted, higher nutrient sites (Rott et al., 1988; Fore and Grafe, 2002; Mercado, 2003) and was present at low levels (0.009-0.12% of total population) in three of four weeks. Shero (1995) suggested that *Nitzchia spp*. broadly are abundant in rivers that are middle to high in nutrients, middle to high in conductivity, and alkaline in pH. *Nitzchia palea* is a specific example that is associated with more polluted, higher nutrient sites (Fore and Grafe, 2002; Mercado, 2003) and was present at low levels (0.054-1.5% of total population) in three of four weeks. *Cyclotella atomus*, which has been associated with eutrophic conditions (Fore and Grafe, 2003) was present (0.33-1.9% of total population) in all four sample weeks. On the other hand *Meridion circulare*, characteristic in low conductivity streams (Rott et al., 1988) was present (0.15% of total population) in one of four weeks, while *Gomphoneis olivacea*, characteristic of low orthophosphate (Rott et al., 1998) was present (0.009-0.09% of total population) in two of four weeks. *Aphanizomenon flos-aquae* is a blooming cyanobacteria that can create nuisance and low dissolved oxygen conditions in rivers (Kromer Baker and Baker, 1981; Moreno et al., 2005) and the Great Lakes, although levels in Lake Erie declined considerably between 1970 and 1983-85 (Makarewicz and Bertram, 1991). *Aphanizomenon flos-aquae* was not observed in any of the samples from the Ohio St. Bridge. Although the microcystin toxin was detected in all samples, *Microcystis spp.* algae, which is most commonly thought to produce the toxin, was not detected in any of the samples. It is possible that other algae, such as *Planktothrix agardhii* and *Anabaena flos-aquae* can produce microcystin (Carmichael and Bent, 1981; Keil et al., 2002; Laub

et al., 2002; Tonk et al., 2005). *Planktothrix agardhii* was observed in three of the four Ohio St. Bridge samples while *Anabeana spp.* was observed in one sample.

Meaningful, direct comparison cannot be made of the taxa characteristics in this study and the studies by Martin (1991) and Shero (1995) because the earlier studies focused on periphyton collection. It is interesting to note that for a similar sample date of late July, Shero (1995) showed 10 species in common with this study.

A number of indices that specifically consider diatom population structure and environmental conditions have been developed and by 2000, the Biological Diatom Index (IBD), including support software and databases, was well-established at the national level in France (Prygiel, 2002). Ponader and Charles (2003) evaluated three European-developed indices, the Trophic Diatom Index (TDI), the IBD, and the Specific Polluosensitivity Index (IPS) for rivers in New Jersey. These indices showed good correlation with total phosphorus and chlorophyll a levels, as well as the percentage of urban land use. Ponader and Charles (2003) also noted that because these indices were developed in Europe, some important North American diatom species could not be considered in the calculation because data on pollution sensitivity consistent with the indices were not available. The Commonwealth of Kentucky (2002) has begun to develop a multi-metric index approach, as have Wang et al. (2005), but more work remains to be done to assess the effectiveness of such approaches.

To evaluate the impact of water quality on the diatom population structure for the Bufalo River, we used the TDI approach outlined by Kelly and Whitton (1995):

$$TDI = \frac{\sum a_j s_j v_j}{\sum a_j v_j} \qquad [4.4]$$

Where a_j is the abundance (cells/mL) of species j in the sample, s_j is the pollution sensitivity of species j, on a scale of 1-5, and v_j is the indicator value on a scale of 1-3. Values of s_j and v_j were taken from Kelly and Whitton (1995), but this work represented a river in England, and therefore not all diatom species from the Buffalo River could be included in the calculation. The value of the TDI can range from 1 (clean water) to 5 (high nutrient and/or organic polluted water).

Results of the TDI calculations for the Buffalo River were: 7/26/06 – 4.8; 8/2/06 – 3.6; 8/16/06 – 3.0; 8/31/06 – 3.6. The mean TDI of the four sample dates was 3.8. For comparison purposes, the TDI also was calculated for two sites on Eighteenmile Creek, using the data provided by Makarewicz and Lewis (2002) from three sample dates (June, July, August) in 2000. Site 1 was near the mouth of the river adjacent to a small marina in Olcott, NY and impacted by Lake Ontario waters, while Site 2 was in a flooded river valley, upstream of Olcott, downstream of the Burt dam, and unimpacted by Lake Ontario waters. The mean TDI for the three sample dates at Site 1 on Eighteenmile Creek was 4.5 and for Site 2 was 4.4. Kelly and Whitton (1995) reported the mean TDIs for an example river in England were 4.18 for a site upstream of a sewage treatment plant and 4.63 for a site downstream of the plant. It was noted that the upstream site also experienced some eutrophication stress due to higher nutrient levels.

The Pollution Tolerance Index (PTI) is an alternative to the TDI and is calculated as (after Commonwealth of Kentucky, 2002):

$$PTI = \frac{\sum (n_i t_i)}{N} \qquad [4.5]$$

Where n_i is the number of individuals in species i, t_i is the tolerance value of species i, and N is the total number of individuals from all species used in the calculation. The pollution tolerance ratings are based on those proposed by Palmer (1969; 1977) and for this study range between 1 and 5. If no tolerance value was available for the species, it was excluded from the calculation in equation [4.5]. There are two important differences between the TDI and PTI. First, the PTI considers all taxa, not just diatoms. Second, the tolerance rating of the PTI is inverse to the to pollution sensitivity rating of the TDI; for the PTI a number near 1 indicates most tolerant taxa, while a number near 5 indicates a predominance of sensitive taxa.

The PTI values for the Buffalo River ranged between 2.9 and 3.6. It is important to note that tolerance values were available for less than half the species enumerated in the Buffalo River samples and more work needs to be done on quantifying tolerance ratings if the PTI is to be used as a stand-alone index.

The TDI and PTI results for the Buffalo River are consistent with the results presented in Tables 4.4 and 4.5 as well as the qualitative discussion of indicator species above. The TDI and PTI results suggest that the Buffalo River is not pristine, exhibiting some environmental stress, but similarly it is does not have an excessive eutrophication or organic pollution problem.

4.4. Continuous Water Quality Monitoring with the YSI

It is generally understood that excessive growth of primary producers, including phytoplankton, will lead to a depletion of dissolved oxygen, under the conditions of eutrophication (e.g. Walker et al., 2006). The dissolved oxygen levels measured at the Ohio St. Bridge (Site 2) are generally are lower than prescribed by state guidelines (see Section 3). The frequency of time for which dissolved oxygen did not meet guidelines in 2006 is consistent with sampling done in 2000, 2003, and 2004 (Irvine et al., 2005a, b). However, as noted by Irvine et al. (2005a, b), the low dissolved oxygen in the river is related to a combination of factors including stratification in the river at low flows that can reduce aeration, high sediment oxygen demand, long residence times due to system hydraulics (dredging increases channel cross sectional area and residence time), and moderate to low background biochemical oxygen demand. Combined sewer overflows appear to have minimal impact on dissolved oxygen levels (Jaligama et al., 2004; Irvine et al., 2005a). It can be concluded that phytoplankton abundance is not sufficiently high to negatively impact dissolved oxygen levels.

A diurnal pattern in dissolved oxygen may be observed in rivers, particularly during dry, low flow periods, since algae and rooted plants can deliver oxygen to the water through photosynthesis (e.g. Irvine, 2003). The dissolved oxygen levels would be expected to rise from the morning and peak in late afternoon/early evening. At night, aquatic organisms continue to respire, consuming oxygen, and therefore the dissolved oxygen levels begin to decline through to the next morning (Mitchell and Stapp, 1995; Walker et al., 2006). Irvine et al. 2005b found a diurnal pattern occurred principally during dry periods (June through July) at two sites in shallower water upstream of the dredged channel. One site was located near the mouth of Cazenovia Creek and the other

site was located on the Buffalo River at the Seneca St. Bridge, upstream of Cazenovia Creek. Irvine et al. 2005b generally did not observe a diurnal pattern at the Ohio St. Bridge and similarly there is no strong diurnal signal for the 2006 sample period.

Storm events have a clear impact on water quality in the river. In general, turbidity increases with increased sediment erosion and transport (cf. Lewis, 1996; Sun et al., 2001; Davies-Colley and Smith, 2001; Irvine et al., 2002; Pfannkuche and Schmidt, 2003) while conductivity frequently exhibits a dip (Irvine et al., 2005a, b). Constituents from chemical weathering of soils and bedrock may predominantly enter rivers in temperate, humid climates via groundwater inputs (Marsh, 1991; Morisawa, 1968). As such, conductivity and dissolved solids concentration would be greater during baseflow conditions, when the principal hydrologic input is groundwater and may become diluted by stormwater runoff (Walling and Webb, 1980). Tomlinson and De Carlo (2003) observed a dilution effect for conductivity during storms in their monitoring of streams in Hawaii, as did Irvine (2003) in a study of the Allegheny River, PA, and Irvine et al. (2005a, b) for the Buffalo River in 2000, 2003, and 2004. Irvine et al. (2005b) also observed that during the drier summer months when the dredged channel becomes nearly stagnant, dissolved oxygen might increase during storms, as part of the flushing associated with increased flow, although this was not always the case. Similar patterns for turbidity, conductivity, and dissolved oxygen can be identified at the Ohio St. Bridge from the 15 minute time step data plotted in Appendix 2.

The chlorophyll a levels generally increase in association with the higher turbidity levels during storm events (e.g. 7/13/06; 7/18/06; 7/29/06; 8/5/06; 8/24/06). One explanation for this increase in chlorophyll a is that periphyton is entrained along with river bed erosion from the shallow water areas above the dredged channel (Walker et al., 2006).

5. CONCLUSION

5.1. BUI #8 Eutrophication and Undesirable Algae

Based on a literature review, threshold levels of 42 μg/L TP and 8 μg/L chlorophyll a were chosen as a guideline for the Buffalo River. These levels generally could be considered as representing the division between a eutrophic and mesotrophic river, but it must be noted that threshold levels reported in the literature exhibit considerable variability. The mean level of TP and chlorophyll a from the Buffalo River samples were not significantly greater (α=0.05) than the selected threshold levels.

Samples collected at two Cazenovia Creek headwater sites (west branch and east branch) were used to represent reference reach (i.e. relatively un-impacted control site) levels of TP and nitrate/nitrite. Recognizing that the reference reach sample set was small (n=2 for each site), the mean levels of TP and nitrate/nitrite from the Buffalo River sites were in the same range as the reference reaches. An alternative reference reach approach, suggested by the U.S. EPA (2000a), was used in which the 25th percentile for medians of regional stream data defined the nutrient criteria. The mean TP levels in the Buffalo River were greater than the 25th percentile of the medians of 16 rivers in the same ecoregion (RIBS data), while the mean nitrate/nitrite levels were less than the 25th percentile of the medians.

A qualitative review of the literature showed that Buffalo River nutrient and chlorophyll a levels were similar to those reported for "low nutrient, high quality streams" (e.g. Minnesota Pollution Control Agency, 2003). The total abundance of phytoplankton, based on direct count, was relatively low in samples collected from the Ohio Street Bridge Site which is consistent with the low chlorophyll a and fluorescence (YSI 6600) measurements.

Total microcystin (algal toxins) levels were used as an indicator of potential risk to fish, wildlife, or human health due to the presence of undesirable algae. Total microcystin was detected in all Buffalo River samples, but at levels well below the WHO guideline. *Microcystis spp.* algae were not observed in the water samples, but low levels of other microcystin-producing algae (e.g. *Planktothrix agardhii, Anabaena flos-aquae*) were observed.

5.2. BUI #13 Degradation of Phytoplankton

The phytoplankton species richness in the Buffalo River was relatively high for this region, as was the Shannon-Weaver Index of Diversity. Generally, it is believed that lower species richness and Shannon-Weaver values will be observed with increasing trophic status. The C:P ratios for the four samples were highly variable and of little use for environmental interpretation in this study. Qualitatively, the assessment of indicator species showed taxa that represented eutrophic and poorer water quality conditions were mixed with taxa that represented less nutrient-rich, mesotrophic conditions.

Two simple indices also were calculated using the population data. The Trophic Diatom Index (TDI) has values that range between 1 (clean water) and 5 (nutrient rich and/or organic polluted water) with results for the Buffalo River being in the 3.0-4.8 range. By comparison, the TDI values at two sites on Eighteenmile Creek, NY were in the 4.4-4.5 range, while a eutrophic river in England, impacted by a sewage treatment plant, had a TDI value of 4.63. The second index considered was the Pollution Tolerance Index (PTI). Pollution tolerance values for individual species in the PTI ranged between 1 and 5. An important difference between the PTI and TDI is that the tolerance rating of the PTI is *inverse* to the to pollution sensitivity rating of the TDI; for the PTI a number near 1 indicates most tolerant taxa, while a number near 5 indicates a predominance of sensitive taxa. The PTI values for the Buffalo River ranged between 3.0 and 3.2, while the PTI values for two sites on Eighteenmile Creek, NY ranged between 2.3 and 3.6.

5.3. General Water Quality Considerations

The fluorescence measurements from the YSI 6600 EDS datasonde were similar to the laboratory measurements of chlorophyll a. Based on the YSI measurements, the weekly average chlorophyll a (calculated from 15 minute time step measurements) ranged between 1.69 and 7.55 μg/L. The total abundance counts (cells/mL) from the algal enumerations were relatively low and as noted in Section 5.1 this was consistent with the low chlorophyll a levels and fluorescence readings.

Dissolved oxygen levels in the middle section of the Buffalo River frequently were less than state guidelines for this class of river, a finding which is consistent with previous studies. Low dissolved oxygen levels primarily are impacted by the hydraulics of the Buffalo River and are not the result of high nutrient and algae levels.

Turbidity can be high in the Buffalo River during storm events (in some cases exceeding 1,000 NTU), but during dry weather in 2006 turbidity at the Ohio Street Bridge site was in the range of 27 NTU. Dry weather turbidity levels in the range of 10-24 NTU were observed in the summers of 2003 and 2004. It appears unlikely that the turbidity levels are high enough to suppress algal abundance, given the nutrient levels in the river, but this should be investigated in more detail.

5.4. Recommendations

The weight of evidence suggests that the Buffalo River AOC does not have a eutrophication problem at this time, but nutrient levels are sufficiently high that implementation of watershed BMPs and water quality monitoring should be continued. Based on the microcystin analysis as an indicator, the AOC also does not have a problem with undesirable algae. It is suggested that BUI #8 can be de-listed.

The weight of evidence is a little less clear for BUI #13. Reference criteria and endpoints have not been established specifically for the Great Lakes, although this is a SOLEC objective. Many studies that have assessed plankton population structure in a lotic environment focused on periphyton rather than phytoplankton. There is a need for further research on standardized population structure indices and their environmental interpretation. The phytoplankton population structure appears to reflect the suburban/urban environment. There appears to be some anthropogenic impact as reflected by the TDI and PTI and presence of certain indicator species, but these impacts do not seem to indicate extreme stress. It is suggested that BUI #13 can be de-listed, but periodic monitoring of the phytoplankton population should be undertaken.

Ultimately, the Buffalo River Remedial Advisory Committee must decide whether the weight of evidence approach taken in this study provides reasonable guidance in making de-listing decisions. A number of individual indices, threshold

criteria, and river reach approaches were examined in this report. While a specific multi-metric index or threshold nutrient level is appealing in its simplicity, it may not be possible at this time to identify a single, most appropriate criterion.

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