Water Chemistry and Ecological Assessment

Warwick Brook (Tuxedo, NY)

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Executive Summary

A fish kill occurred in Four Corners Pond on Warwick Brook on March 13-14, 2012. The Town of Tuxedo contracted Land Use Ecological Services (LUES) to perform an assessment of the water quality conditions of Warwick Brook and review water chemistry and ecological data collected by the NYSDEC and others in order to determine likely causes of the fish kill, in particular the potential role of the Town of Tuxedo's wood chipping facility located adjacent to Caretakers Marsh and upstream of Four Corners Pond. LUES collected bi-weekly water samples at seven locations along Warwick Brook from the downstream terminus of Caretaker Marsh to the mouth of Warwick Brook at Wee-Wah Lake between June 1 and September 15, 2012. Water samples were analyzed for dissolved oxygen, biological oxygen demand, pH, nitrogen (nitrite, nitrate, ammonia, total Kjeldahl nitrogen, and total nitrogen), and phosphorus (ortho-phosphate, total phosphorus).

The sites immediately downstream of the wood chipping facility including Caretakers Marsh and the beaver dam impoundment upstream of Four Corners Pond exhibited anoxic dissolved oxygen levels (less than 0.5 mg/L) throughout the study period. Some sites in lower Warwick Brook, including Watch Tower Pond and the mouth of Warwick Brook at Wee-Wah Lake, exhibited high dissolved oxygen levels throughout the study period. Sites upstream of Four Corners Pond are chronically depleted in oxygen and these exceedingly low dissolved oxygen levels will prevent the survivorship of fish and invertebrates. The phosphorus and nitrogen concentrations throughout Warwick Brook exceed all water quality standards and recommendations put forth by the NYSDEC and the EPA. Nutrient concentrations in Caretakers Marsh and the beaver dam upstream of Four Corners Pond are exceptionally high and are indicative of a highly eutrophic and impaired water body. The high nutrient concentrations in Caretaker's Marsh relative to the reference sites strongly indicate that there is a significant outside source of nutrients and organic matter to the marsh. The Town wood chipping facility is the probable source of this subsidy, as there are no other significant nutrient sources nearby such as fertilizer-enriched runoff from agricultural fields or residential lawns or sub-surface flow from residential sanitary systems. Warm weather in early March 2012 and beaver dam breaches, resulting in hypereutrophic waters to be released downstream, provided additional stressors necessary to cause the fish kill event in the already vulnerable waters of upper Warwick Brook. The chronic impaired conditions indicate that the Warwick Brook is susceptible to fish kills during either the summer or winters months, particularly when environmental factors act to transport the oxygen depleted waters and organic matter and sediment from the upper reaches downstream.

Introduction

The Town of Tuxedo contracted Land Use Ecological Services (LUES) in May 2012 to perform an assessment of the water quality conditions of Warwick Brook and review water chemistry and ecological data collected by the NYSDEC and others in response to a fish kill in Four Corners Pond occurring on March 13-14, 2012.

Warwick Brook is a Class C stream originating in Sterling Forest. The stream channel is approximately 3.5 miles in length, largely surrounded by forested areas, and enters into Wee-Wah Lake in the Village of Tuxedo Park. The Town of Tuxedo's wood chipping facility, operated by Perfect-Cut, is located adjacent to a 26 acre emergent marsh (hereafter Caretakers Marsh) in the headwaters of the south branch of Warwick Brook. The wood chipping facility receives cut trees from the Town of Tuxedo and nearby communities. There are several impoundments, both natural (i.e. beavers) and anthropogenic, along the length of Warwick Brook. Three beaver dams impound stream waters and create open water and emergent marsh habitats on Warwick Brook downstream of Caretakers Marsh. Two beaver dam ponds are located between Long Meadow Road and Four Corners Pond and another is located on lower Warwick Brook approximately 0.9 miles upstream of Wee-Wah Lake. Two man-made ponds are located on Warwick Brook: Four Corners Pond and Watch Tower Pond. The north branch of Warwick Brook runs parallel to Ironwood Road and joins the south branch at Watch Tower Pond. Wee-Wah Lake is a Class B surface water and is used for primary contact recreation and serves as a back-up drinking water source for the Village of Tuxedo Park.

A fish kill was observed in Four Corners Pond on March 13-14, 2012. Approximately one week prior to the fish kill, the beaver ponds located between Four Corners Pond and Long Meadow Road were breached by the Palisades Interstate Parkway Commission resulting a large release of impounded water into Warwick Brook. The beaver dam breach and fish kill also coincided with an unusual period of warm, dry weather during the week preceding the fish kill. Water chemistry measurements conducted by the New York State Department of Environmental Conservation (NYSDEC) subsequent to the fish kill (March 13 and March 20-22) found very low dissolved oxygen concentrations (1.0-2.0 mg/L) at many locations of Warwick Brook between the Town wood chipping facility and Watch Tower Pond.

LUES collected bi-weekly water samples at seven locations along Warwick Brook from the downstream terminus of Caretaker Marsh to the mouth of Warwick Brook at Wee-Wah Lake between June 1 and September 15, 2012. Water sampling locations are listed in Table 1 and shown in Figure 1. Water samples were analyzed for dissolved oxygen, biological oxygen demand, pH, nitrogen (nitrite, nitrate, ammonia, total Kjeldahl nitrogen, and total nitrogen), phosphorus (ortho-phosphate, total phosphorus), and total suspended solids. In August 2012, the Town of Tuxedo requested that LUES also conduct analyses to detect copper, chromium, and arsenic throughout Warwick Brook. This request was based on reports that milled lumber was observed at the chipping facility and concern that this milled lumber may have been treated with CCA or other chemical preservation agents. Accordingly, copper, chromium, and arsenic analyses were performed on the water samples collected in the August 30 and September 14, 2012 sampling periods. The results of the water chemistry analyses were compared to NYSDEC Surface Water and Groundwater Quality Standards (NYSDEC, 2008 and 2011) and United States EPA (USEPA) Ambient Water Quality Criteria Recommendations for Lakes and Reservoirs (USEPA 2000) and Rivers and Streams (USEPA 2001) to assess the water quality conditions in Warwick Brook and any potential impacts of ecological and human health.

Water samples were also collected from the mine shaft located at the Town chipping facility, which is used as a source for water pumped onto the chip piles to cool the piles and maintain appropriate temperature for microbial breakdown of the wood biomass. In addition, water samples were also collected from three stream and pond locations outside of the south branch of Warwick Brook to serve as reference or baseline sites. The three references sites are indicated as Sites R1-R3 (Figure 1). Reference Site R-1 is located at the southwestern end of Laurel Meadow Pond; the habitat upstream of this reference location features a deciduous hardwood swamp. Reference Site R-2 is located in a stream within a deciduous hardwood swamp located downstream of Laurel Meadow Pond and a large beaver impoundment upstream of Long Meadow Road. The beaver impoundment upstream of Reference Site R-2 contains large areas of emergent marsh, with some marsh areas dominated by common reed (*Phragmites australis*) and other marsh areas dominated by broad-leaved cattail (*Typha latifolia*). Reference Site R-3 is located in a reach of eroded stream on the north branch of Warwick Brook upstream of Watch Tower Pond and downstream of a *Phragmites* marsh and beaver impoundment.

Under natural conditions, the waters of emergent marshes can have low dissolved oxygen concentrations (less than 2 mg/L) due to the high rates of microbial decomposition of decaying vegetation (Kadlec and Knight, 1995). Similarly, lower dissolved oxygen concentrations have been observed in streams downstream of beaver impoundments compared to streams without beavers (Bledzski et al., 2011). Due to the potential for natural wetlands and beaver ponds to reduce dissolved oxygen in water bodies, reference sites were selected that are within or downstream of natural marshes or beaver ponds. This was done to facilitate comparison with Caretakers Marsh and the beaver impoundments downstream of Caretakers Marsh. The use of these selected reference sites shall provide insight into the potential impacts of the Town chipping facility on the water chemistry of the immediately adjacent marsh and downstream beaver ponds, as compared to marshes and beaver pond outfalls that are not directly downsteam of the Town facility.

Methods (Sampling Procedures and Laboratory Analysis)

Water Sample Collection

Water samples were collected bi-weekly from June 1 to September 15, 2012. Stream water samples were collected from straight reaches of the stream having uniform flow, having a uniform and stable bottom contour, and where constituents were well-mixed along the cross section. Water samples were collected far enough above and below confluences of streamflow or point sources of contamination to avoid sampling a cross section where flows are poorly mixed or not unidirectional. Water samples were collected from stream reaches with unidirectional flow (i.e. without eddies). If eddies were present within the stream channel, samples were only collected from portions of stream cross-section with unidirectional flow. Water samples collected from ponds within Warwick Brook or reference marshes (Lower Four Corners, Watch Town Pond, and Reference Sites 1 and 2) were collected from the pond/marsh shoreline in 0-2.5' of water. Samples were collected 0.75-1.0' below water surface. During stream and pond water sample collection, the collector waded out to at least knee depth, being careful to limit, as much as possible, disturbance of the sediments. Mine water was collected from the surface of the mine shaft and approximately 2.5 ft from the edge of the shaft edge.

Dissolved oxygen, pH, and temperature measurements were conducted in the field with a YSI Pro20 multi-function meter (dissolved oxygen and temperature) and a YSI pH 100 waterproof pH Tester. The meters were warmed up for 15 minutes before attempting measurement. The probes were suspended in the water column for at least 30 seconds to equilibrate before measurement. The meter was calibrated

for dissolved oxygen measurements according to manufacturer's standards prior to each monitoring event. The pH meter was also calibrated prior to each monitoring event using standard pH buffer solutions (pH 4.01, 6.86).

The technician then collected water samples with a wide mouth, 4 liter plastic sampling bottle. The technician again waded into the stream to at least knee depth, but slightly (2-4 m) upstream of the location of the YSI and pH measurements. The large water sample was divided into separate aliquots for analysis (i.e. individual bottles were not filled in succession directly from the water column as different water masses may have been encountered due to flow).

For nutrient analysis, immediately after collection, sample water was placed into a new 500 mL plastic bottle (after rinsing with sample water) containing 1 mL of sulfuric acid (4.5 Normal) to preserve the samples. Nutrient samples were filtered in the laboratory prior to analysis. Sample water collected for biological oxygen demand and total suspended solids analysis was placed in a new 1 L translucent plastic bottle, after rinsing, leaving a small air-space to aid in laboratory mixing. All water samples were placed on ice (to maintain a temperature of 4°C) until delivery to the lab where they were refrigerated until analysis.

Laboratory Analysis
Table 2 summarizes the laboratory tests that were employed to analyze the collected water samples. Samples were hand-delivered to the testing laboratory (EcoTest Laboratories, North Babylon NY) within 12 hrs of collection. All necessary chain of custody documentation was completed.

Results and Discussion

Dissolved Oxygen and Biochemical Oxygen Demand
Oxygen is critical for the survival and reproduction of aquatic life. Aquatic organisms may die of the amount of oxygen dissolved in water falls below a critical threshold and chronically low dissolved oxygen levels will lead to the disappearance of aquatic life from impaired water bodies. Dissolved oxygen concentrations were extremely low at the two sampling locations furthest upstream and closest to the Town wood chipping facility (Caretakers Marsh and the Beaver Dam upstream of Four Corners Pond) with dissolved oxygen concentrations never exceeding 0.5 mg/L between June 1 and September 15, 2012, as shown in Figure 2a. Dissolved oxygen concentrations generally increased with increasing distance downstream from Caretakers Marsh. Only the mouth of Warwick Brook at Wee-Wah Lake exhibited consistently high dissolved oxygen concentrations (greater than 7.0 mg/L) throughout the study period. A seasonal trend of declining dissolved oxygen throughout the summer months with a slight increase in dissolved oxygen in the late August and September was observed at most of the Warwick Brook sites, Figure 2a, except the two upstream locations (Site 1 and 2) and lower Warwick Brook location (Site 6). This decline in dissolved oxygen concentration in the summer months is due to 1) the higher water temperatures, as warm waters have less capacity to retain dissolved oxygen than cooler waters, and 2) the decomposition of organic matter and respiration of microbes which consumes the dissolved oxygen in the water. In general, the three reference locations exhibited a similar trend of reduced dissolved oxygen levels as the summer progressed with slightly increased levels at the end of the study period (Figure 2b).

NYSDEC Surface Water Quality Standards indicate that dissolved oxygen levels less than 5.0 mg/L (minimum daily average) or 4.0 (at any time) are considered not suitable for supporting warmwater (i.e. non-trout) fish communities (NYSDEC 2008). The sites immediately downstream of the wood chipping

facility including the Long Meadow Road crossing and the beaver dam adjacent to Long Meadow Road exhibited anoxic dissolved oxygen levels (less than 0.5 mg/L) throughout the study period. These sites are chronically depleted in oxygen and these exceedingly low dissolved oxygen levels will prevent the survivorship of fish and invertebrates. The severely depleted oxygen levels observed at these locations are consistent with the bioassessment performed by Watershed Assessment Associates (2012), which found benthic invertebrates to be nearly absent from Warwick Brook just upstream of Four Corners Pond and which characterized the biological conditions of this reach of Warwick Brook as "very poor".

The two sampling locations in Four Corners Ponds exhibited large fluctuations in dissolved oxygen concentration throughout the study and periods of low dissolved oxygen concentration (i.e. below 5.0 mg/L) which are likely to have adverse effects of the survivorship and growth of fish and invertebrates. Large fluctuations in dissolved oxygen concentration at these sites are likely due to the presence of accumulated organic sediments in Four Corners Pond and large quantities of suspended and dissolved organic matter in the waters of Four Corners Pond due to downstream transport from Caretakers Marsh and the two beaver impoundments. Microbial metabolization of the organics in the sediments and water column of Four Corners Pond drives the variation in dissolved oxygen in Four Corners Pond. Watch Tower Pond maintained dissolved oxygen concentrations above NYSDEC standards (5.0 mg/L) throughout much of the study period. A pond aerator is continuously operated in Watch Tower Pond and certainly improves the oxygen availability in the pond's waters. Downstream of Watch Tower Pond, the sampling location in lower Warwick Brook (Site 6) had dissolved oxygen concentrations below 5.0 mg/L throughout much of the study period. As stated previously, both emergent marshes and beaver impoundments can adversely impact dissolved oxygen concentrations through the decay of marsh vegetation (Kadlec and Knight, 1995) or the accumulation of organic sediments upstream of the impoundment (Bledzski et al., 2011). The mouth of Warwick Brook at Wee-Wah Lake (Site 7) maintained high dissolved oxygen concentrations (above 7.0 mg/L) throughout the study period, as the flowing of turbulent waters along the rocky stream bed aerated the stream between Sites 6 and 7 (Figure 2a).

The three reference locations exhibited adequate dissolved oxygen concentrations in the early summer but declining oxygen availability throughout the summer. All reference sites were within or adjacent to vegetated freshwater wetlands or beaver impoundments; accordingly, the low dissolved oxygen in the late summer months is expected for these high productivity habitats. While dissolved oxygen concentrations between 1.75 and 5.0 mg/L were observed throughout much of June to August (Figure 2a), these habitats maintained dissolved oxygen concentrations that were substantially higher than Caretakers Marsh and the beaver impoundment upstream of Four Corners Pond (less than 0.5 mg/L) (Figure 2b).

The oxygen availability within the Warwick Brook system was also assessed by quantifying Biochemical Oxygen Demand (BOD). BOD represents the amount of dissolved oxygen in the lake or stream waters that would be consumed during the aerobic decomposition of the organic compounds in the lake or stream water by microorganisms. There are no New York State standards for the evaluation of BOD values. BOD values in natural aquatic ecosystems range from 0.5-3.0 mg/L, while waters that are impacted by municipal or industrial wastes can exceed 30 mg/l (EPA 1997). High BOD levels, equal to or greater than 10 mg/L, in Caretakers Marsh and the beaver impoundment upstream of Four Corners Pond were observed throughout the study period (Figure 3). BOD was exceptionally high, over 30 mg/L, in these sampling locations and at the outflow of Warwick Brook at Four Corners Pond between during the June 1 and June 15 sampling periods. BOD values at these locations were generally over 10 mg/L and declined, albeit irregularly, throughout the study period. Only Watch Tower Pond

and sampling locations downstream of Watch Tower Pond exhibited BOD concentrations consistently below 5.0 mg/L. BOD concentrations at the three reference sites exceeded 3.0 mg/L on only one occasion.

The exceedingly high BOD concentrations in Caretakers Marsh and the upper reaches of Warwick Brook, especially in the early summer, indicate that these waters contained large quantities of dissolved and suspended organic matter. Metabolization of this dissolved organic matter by microbial organisms extract all or a large proportion of the available oxygen in the surface waters. The consistent decrease in BOD with increasing distance from Caretakers Marsh may suggest that this marsh is exporting large quantities of dissolved and suspended organic matter downstream. As shown on Figure 3, at many locations in Warwick Brook, BOD declined throughout the study period. Insufficient data is available to explain this seasonal decline in BOD, but it may be related to a seasonal decrease in stream flow volume and water level in Warwick Brook as high flow volumes occur in the spring and early summer and flow volumes decrease through the summer as seasonal droughts and soil water deficits occur.

Nutrients (Phosphorus and Nitrogen)

A direct cause of the low dissolved oxygen conditions and high BOD concentrations in upper Warwick Brook from Caretakers Marsh to Four Corners Pond is the excessive nutrient concentrations. While nutrients are essential to healthy biological productivity in surface waters, excessive concentrations of nutrients cause unhealthy levels of algal and plant growth and can adversely affect the water quality and ecological health of lakes, ponds, and streams. A decline in water quality resulting from excessive biological productivity stimulated by nutrient loading is referred to as eutrophication.

New York State has narrative water quality standards for nitrogen and phosphorus indicating that the maximum limits are "none in amounts that will result in growths of algae, weeds, and slimes that will impair the waters for their best usages" (NYSDEC, 2008). The NYSDEC has also provided a water quality guidance value of 20 µg/L (or .02 mg/L) for phosphorus (total phosphorus) for class AA, A, and B surface waters (NYSDC, 2011). New York has an existing water quality guidance value of 10 mg/L for nitrate-nitrogen for Class A surface waters and "none that will result in growths of algae, weeds, and slime that will impair use" for Class B, C, and D waters. Guidance documents published by the US EPA provide ambient water quality recommendations for lakes and reservoirs indicating that total phosphorus concentrations below 0.08 mg/L and total nitrogen concentrations below 0.24 mg/L are necessary to avoid the adverse effects of eutrophication (US EPA, 2000). For rivers and streams, the US EPA has recommended that total phosphorus concentrations below 0.10 mg/L and total nitrogen concentrations below 0.38 mg/L be maintained to avoid the adverse effects of eutrophication (US EPA, 2001). As will be discussed below, the phosphorus and nitrogen concentrations in much of Warwick Brook substantially exceed these water quality standards and/or recommendations. Average values for the water chemistry parameters at each of the Warwick Brook sampling locations and reference sites are presented in Tables 3 and 4.

Total nutrient concentrations at the downstream end of Caretakers Marsh and the beaver dam adjacent to Long Meadow Road averaged 0.99-2.33 mg/L (total phosphorus) and 8.4-17.7 mg/L (total nitrogen) (Figures 4 and 5). These values exceed New York State and US EPA nutrient standards and recommendations by for total phosphorus and total nitrogen by 12-115 times or 22-75 times, respectively. Recent studies by the NYSDEC have indicated that total phosphorus concentrations greater 0.065 mg/L are associated with eutrophic conditions (Smith et al. 2007). Accordingly, Caretakers Marsh and upper reaches of Warwick Brook are highly eutrophic.

Nutrient concentrations progressively decreased in Warwick Brook with increasing distance from Caretakers Marsh. Total phosphorus concentrations averaged 0.22 and 0.11 mg/L in the Upper and Lower Four Corners Pond locations, respectively (Table 3). Phosphorus was high in early June (ranging from 0.3-0.6 mg/L), but was less than 0.05 mg/L throughout much of the summer before increasing to 0.1-0.4 again in the late summer (Figure 4). Total nitrogen concentrations remained high in Four Corners Pond throughout the summer, and ranged from 2.1-7.2 mg/L from late May to mid-September. Similar to phosphorus concentrations, total nitrogen concentrations were highest in the early June and late August (Figure 5). However, total nitrogen concentrations (averaging 4.72 and 4.02 mg/L in Upper and Lower Four Corners Pond locations) remained well above regulatory standards and recommendations throughout the entire study period in Four Corners Pond. Fluctuations in nutrient concentrations in Four Corners Pond are likely due to 1) uptake in nutrients by photosynthetic algae and plants in the mid-summer (mid-June through mid-August) and 2) variation in water flow in Warwick Brook with possible more organic matter and nutrients exported from Caretakers Marsh into Four Corners Pond in the late spring and fall due to seasonal variation in steam flow volume.

Watch Tower Pond and lower Warwick Brook generally exhibited total phosphorus concentrations below the 0.08 and 0.10 mg/L US EPA recommendations and the 0.065 mg/L recommended threshold for nutrient impairment by Smith et al. (2007). Watch Tower Pond only exceeded these criteria during the June 1 sampling period. Lower Warwick Brook (Site 6) exhibited total phosphorus concentrations of 0.13-0.16 in the late spring and late summer, but was typically below these criteria. The mouth of Warwick Brook at Wee-Wah Lake never exceeded the US EPA recommendations for total phosphorus (the highest observed value was 0.08 mg/L on June 15, 2012). The three reference sites located outside of the south branch of Warwick Brook never exceeded the US EPA or Smith et al. (2007) recommendations for total phosphorus during the study period.

Similar to total phosphorus, the total nitrogen concentrations at Watch Tower Pond and lower Warwick Brook were lower than the Four Corners Pond and Caretakers Marsh sites. However, total nitrogen concentrations at Watch Town Pond (1.1-4.0 mg/L) and lower Warwick Brook (0.3-1.2 mg/L) exceeded EPA recommendations for lakes and ponds (0.24 mg/L) throughout the study period. In contrast to total phosphorus, the three reference sites also exceeded this standard throughout much of the study period, as Reference Site R1 (Laurel Meadow Pond) ranged between 0.3-1.4 mg/L, Reference Site R2 ranged between 0.1-0.9 mg/L, and Reference Site R3 (North Branch of Warwick Brook) ranged between 0.2-1.2 mg/L. The mouth of Warwick Brook at Wee-Wah Lake had the lowest total nitrogen concentrations of all the Warwick Brook sampling locations, but was higher than the reference locations and the EPA recommendations for rivers and streams (0.38 mg/L).

Interestingly, inorganic forms of nitrogen, i.e. nitrate and nitrite, comprised a small proportion of the total nitrogen observed in the Warwick Brook sites compared to estimates of organic forms of nitrogen (i.e. total Kjeldahl nitrogen) (Table 3). This is consistent with the decaying organic matter as the nutrient source to Warwick Brook and with the low dissolved oxygen availability which impedes the oxidation of organic forms of nitrogen, i.e. ammonia or dissolved organic matter, into inorganic forms (i.e. nitrite or nitrate). In addition, relatively lower proportions of inorganic nitrogen, specifically nitrate, may be caused by the uptake and use of nitrate by algae in the spring and summer months.

The phosphorus and nitrogen concentrations throughout Warwick Brook exceed all water quality standards and recommendations put forth by the NYSDEC and the EPA. The nutrient concentrations in Caretakers Marsh and the beaver dam upstream of Four Corners Pond are exceptionally high and are indicative of a highly eutrophic and impaired water body. As shown in Table 3, the mean total

phosphorus and total nitrogen values in Caretakers Marsh and the beaver dam Pond are 1.13-2.66 mg/L and 8.38-17.74 mg/L, respectively. In comparison, the mean total phosphorus and total nitrogen concentrations in the three reference locations were less than 0.5 mg/L and 0.58-1.03 mg/L, respectively. Emergent marshes and freshwater wetlands, such as Caretakers Marsh and Reference Sites R1 and R2, typically have high levels of biological production and can export organic matter and nutrients to downstream waters. However, the exceptionally high nutrient concentrations in Caretaker's Marsh relative to the reference sites strongly indicate that there is a significant outside source of nutrients and organic matter to the marsh. The Town wood chipping facility is the probable source of this subsidy, as there are no other significant nutrient sources nearby such as fertilizer-enriched runoff from agricultural fields or residential lawns or sub-surface flow from residential sanitary systems.

Arsenic, Copper, and Chromium

This study was intended to evaluate the potential causes of the March 2012 fish kill event in Four Corners Pond. Accordingly, the study has focused on environmental factors typically contribute to acute fish kill events, such as low dissolved oxygen and nutrient loading. The additional sampling for copper, chromium, and arsenic was performed at the behest of the Town of Tuxedo after reported observations of milled lumber at the chipping facility. Water samples collected by LUES did not provide any evidence of these heavy metals in the waters of Warwick Brook waters downstream of Caretakers Marsh; however, this sampling only consisted of two sampling dates (August 30 and September 15, 2012). Concentrations of copper, chromium, and arsenic were at or below the detectable limits of the analytical equipment. Importantly, the detectable limits of the analytical equipment were lower than the NYSDEC standards for the protection of water quality and human health in surface and groundwaters (NYSDEC, 2008).

Other groups have conducted water chemistry testing for one or more of these heavy metals. A surface water sample from Wee-Wah Lake was collected on May 9, 2012 by the Village of Tuxedo Park prior to the opening of the lake for recreational activities in the summer. The water sample was analyzed by Environmental Labworks (Marlboro, NY). Arsenic, copper, and chromium concentrations were at or below the detectable limits of the analytical equipment. Again, the detectable limits of the analytical equipment were lower than the NYSDEC standards for the protection of water quality and human health in surface and groundwaters. Water samples collected and analyzed by Weston and Sampson (Poughkeepsie, NY) and reviewed by Dr. James Hayes found elevated arsenic concentrations (15.9 µg/L) in a water sample from Caretakers Marsh on July 16, 2012. The absence of sampling data in this report on copper and chromium prevents a conclusion whether the elevated arsenic is due to contamination from treated (CCA) timber or some other anthropogenic or natural source. The finding of an elevated arsenic concentration within Caretakers Marsh suggests that additional arsenic/copper/chromium sampling should be conducted to 1) determine if the Weston and Sampson reading is an isolated occurrence or indicative of a more widespread area of contamination within Caretaker Marsh and 2) determine if these metals are being exported from Caretakers Marsh into Warwick Brook.

pH

pH is a measure of the concentration of hydrogen ions in water and is a measure of the acidity of water. The pH scales ranges from 0 to 14, with values of 7.0 considered neutral, values less than 7.0 considered acidic, and values greater than 7.0 considered basic. Average pH values ranged between 6.63 and 8.13 in the Warwick Brook with no consistent trends during the study period. There was a slight trend towards increasing pH (more basic) in locations farther from the wood chipping facility. Average values through the June-September study period are presented in Table 5. Review of water quality data

collected by the NYSDEC (March 13-22, 2012) shortly after the fish kill event indicated several lower pH values (5.0-5.5) in sites closest to the wood chipping facility, but no values less than 6.5 at downstream locations in Warwick Brook. In this study, no values less than 6.5 were observed at the downstream end of Long Meadow Marsh between June-September 2012. Similarly, the Watershed Assessment Associates Report (2012) found pH values between 7.33-7.74 in Warwick Brook between Four Corners Pond and Wee-Wah Lake.

It is likely that pH in the upper Warwick Brook is lower (more acidic) in the winter months due to the effects of tannic acid (produced during the breakdown of wood biomass). In the summer months, higher pH (more basic) conditions may occur as the photosynthetic activity of phytoplankton consumes dissolved CO_2 in the waters of Warwick Brook; reduced CO_2 results in higher pH in aquatic systems through the carbonate-pH buffering system. Repeated sampling of the pH of the mine shaft water at the location of Town wood chipping facility found slightly acidic values between 6.5 and 6.9, but within NYSDEC water quality standards. The Weston and Sampson/ Hayes sampling found more acidic waters (3.26) in the Scotts Mine Shaft located on the northwest side of Long Meadow Road. It was beyond the scope of this project to evaluate differences in mine shaft water between different historic shafts, it is certainly unknown how well these areas are connected or mixed. However, considering the low pH of the Cook Mine shaft observed by Weston and Sampson and J. Hayes, it is advisable that 1) periodic monitoring of the pH of the Town chipping facility mine shaft be conducted to ensure that pH values remain within acceptable limits through the rest of the year and 2) that the potential for direct discharge of Cook Mine water to Caretakers Marsh or Warwick Brook be evaluated.

Foam

There has been considerable discussion of the cause of the orange- or brown-colored foam that has been observed in upper Warwick Brook. Foam formation can be the result of natural processes, but may also be caused by or exacerbated by pollution. In the case of Warwick Brook, the foam formation is likely connected to the high nutrient loading and high concentrations of organic matter in and downstream of Long Meadow Marsh. Foam can form in natural freshwater systems with very high organic content. The foam is formed by the accumulation of organic compounds at the water surface. Due to differences in the physical and chemical characteristics of these compounds and water, the presence of these compounds facilitates the formation of bubbles and foam as turbulence or wind action introduces air into the water. Brown-colored foam is likely the result of suspended solids and tannins in the streamwater. High concentrations of tannins are normally found in aquatic systems in heavily forested areas; the large quantities of wood at the chipping facility most likely contribute additional tannins to the Warwick Brook system. Orange-colored foam is likely the result of oxidized iron compounds becoming entrained in the foam and/or the effects of iron-oxidizing bacteria. Iron-oxidizing bacteria are likely to be present in the anoxic sediments in Caretakers Marsh and marshes in the headwaters and margins of the beaver ponds. The mining history of the Sterling Forest area suggests the abundance of iron compounds in streams draining the watershed may be likely. Iron concentrations in the We-Wah Lake water sample were not above NYSDEC standards for protection of water and human health. It is possible that seasonal patterns in foam formation will be observed with increased foam observed in the late fall and winter, as plant and algal biomass produced in the summer months decomposes. In addition, the tendency for turbulent waters to produce foam is greater in salt water or waters with large concentrations of inorganic ions. Thus, if Warwick Brook receives significant quantities of road salt during the winter months, the applied salt may increase the potential for foam formation in downstream portions of Warwick Brook.

Eutrophication and the March 2012 Fishkill

As stated previously, the Town wood chipping facility is the likely source for the excessive nutrient concentrations in Caretakers Marsh and Warwick Brook. As wood biomass is broken down by microbial action in the chip piles, organic compounds, such as carbohydrates, tannins and lignin (also known as phenolics) and nutrients are leached from the piles. These organic compounds are likely transported from the wood chipping facility into Caretaker Marsh by 1) infiltration of rainfall into the chip piles, entraining of organic compounds leached from the wood into the infiltrated rainwater, and sub-surface flow of water with high organic matter content into the adjacent marsh; 2) entraining of organic compounds leached from the wood into the mine water pumped onto the chip piles and sub-surface flow into the marsh; and 3) surface runoff during heavy rainfall events transporting coarse and fine woody particulates and the above-described dissolved organic compounds and nutrients directly downslope into the adjacent marsh.

Organic compounds, such as carbohydrates and phenolics, are metabolized by microorganisms and, therefore, contribute substantially to the oxygen depletion observed in Caretakers Marsh and upper Warwick Brook. The nutrients stimulate the growth and production of freshwater algae and marsh plants; when the algae and plants die, the biomass is metabolized by various detritivores and microorganisms which also consumes oxygen and contributes to the anoxia observed within the marsh and upper brook. Another potential adverse impact of the high organic compound content and low dissolved oxygen availability in Caretakers Marsh is that these conditions may increase the solubility and mobility of trace metals, such as iron, aluminum, and arsenic, and may increase the export of these metals from the marsh (Reuter and Perdue, 1977).

The exceedingly low dissolved oxygen concentrations within the upper Warwick Brook make this system susceptible to fish kill events throughout much of the year. Several factors that typically trigger fish kill events include 1) sudden periods of warm temperature, 2) the die-off of a large algal bloom, and/or 3) pulses of high organic content water caused by runoff or stream discharge after a large rain event. High temperatures contribute to fish kill events as warm waters accommodate less dissolved oxygen than cooler waters. Thus, freshwater lakes and ponds are typically more prone to fish kill events in the summer months due to the combined effects of the increased oxygen demand from the decomposition of large quantities of algae and the reduced capacity of the stream/pond water to hold dissolved oxygen. However, fish kills may also occur in freshwater lakes and ponds during the winter months. Winter fish kills typically occur during cold, harsh winters when a lake or pond is covered by a thick layer of ice and snow. Ice and snow prevent light from reaching algae and aquatic plants, the vegetation dies due to the absence of light, and the decomposition of the dead plant biomass consumes the available dissolved oxygen. If oxygen depletion is severe enough, extensive mortality of a lake or pond's fish populations may occur. Due to the mild winter and absence of ice cover in Four Corners Pond at the time of the March 2012 event, this is clearly not the immediate cause of this fish kill. Thus, the March 2012 fish kill was likely influence by factors that are more typically associated with summer fish kills such as warm temperatures and increased oxygen demand.

The hypereutrophic state of the Caretakers Marsh and the upper reaches of the south branch of Warwick Brook is the principal contributing factor to the March 2012 fish kill. However, several other factors likely contributed to the fish kill. An unusually warm and dry period preceded the March 2012 fish kill in Four Corners Pond, as shown in Table 6. During the preceding week (March 6-12), the average daily high temperature was 59.9 °F (15.5°C). This is 10°F above the long-term average daily high temperature of 41.0 °F (5.0 °C) for the second week of March. The warm temperature likely stimulated microbial metabolism of the new organic matter and resulted in reduced the capacity of the pond water's to hold

dissolved oxygen. In addition, the beaver dam located upstream of Four Corners Pond was breached in the week preceding the fish kill. Beaver ponds accumulate large quantities of sediments (Naiman et al. 1988) and have significant impacts on the water quality characteristics of downstream waters. Stream reaches below beaver ponds have been observed to have higher water temperatures, lower dissolved oxygen concentrations, and higher dissolved organic carbon and nitrate- and ammonium-nitrogen concentrations (Bledzki et al. 2011) than stream reaches without beaver ponds. The breaching of a beaver dam can result in a sudden release of sediments and floodwaters downstream and can have adverse effects on downstream water quality. For example, an experimental beaver dam breach in western Massachusetts found that turbidity and water temperature increased significantly (more than 5-7 °C) between 400-2000m downstream of the breached dam (Bledzki et al. 2011).

Summary

The findings of this water chemistry monitoring clearly indicate that Caretakers Marsh and the upper reaches of the south branch of Warwick Brook have highly eutrophic conditions resulting in chronic oxygen depletion and adverse impacts on water quality and ecological habitat. Some sites in lower Warwick Brook, including Watch Tower Pond and the mouth of Warwick Brook at Wee-Wah Lake, exhibited high dissolved oxygen levels throughout the study period. It is most likely that the Town wood chipping facility has been the source of additional nutrients and organic matter that have caused the eutrophic and oxygen depleted conditions in Caretakers Marsh and upper reaches of the south branch of Warwick Brook. Warm weather of early March 2012 and beaver dam breaches provided the additional stressors necessary to cause the fish kill event in the already vulnerable waters of upper Warwick Brook. The chronic impaired conditions indicate that the Warwick Brook is susceptible to fish kills during either the summer or winters months, particularly when environmental factors act to transport the oxygen depleted waters and organic matter and sediment from the upper reaches downstream.

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Figure 1: *Sampling Locations for Warwick Brook Water Chemistry Assessment*
Bi-weekly water samples were collected from seven locations on Warwick Brook downstream of the Town wood chipping facility between May 30 and September 15, 2012. Water samples were collected from three reference location outside of Warwick Brook: Laurel Meadow Pond, Long Meadow Road Outfall, and North Ironwood Road. Water samples were also collected from the mine shaft at the Town wood chipping facility.

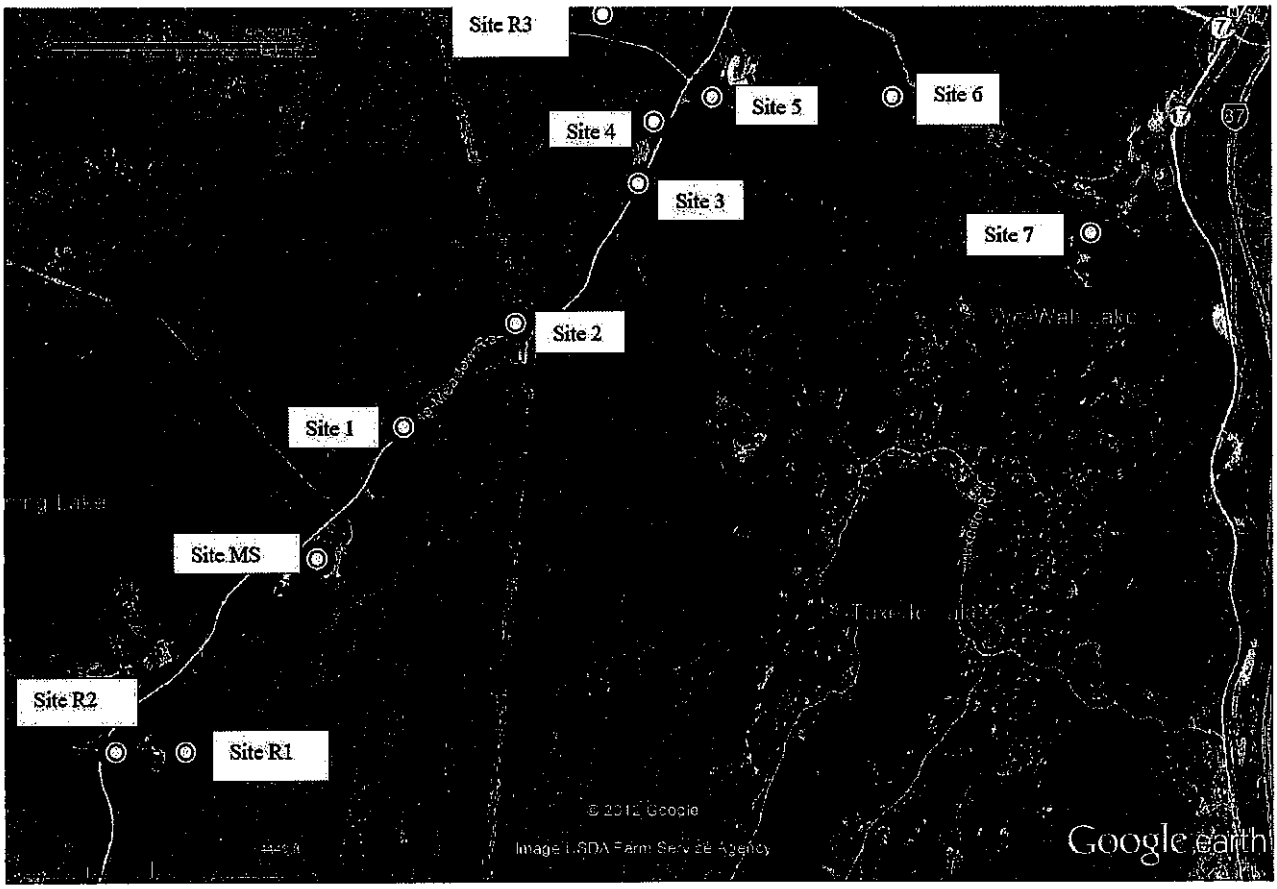


Figure 2: *Dissolved oxygen concentrations in Warwick Brook and three reference locations.* **(a)** Bi-weekly measurements of dissolved oxygen were conducted at seven locations between Caretakers Marsh and the mouth at Wee-Wah Lake. **(b)** Bi-weekly measurements of dissolved oxygen at three reference sites located outside of the south branch of Warwick Brook. Measurements were conducted between June 1 and September 15, 2012 with a YSI Pro20 multi-function meter. The NYSDEC surface water quality standard for instantaneous measurements of dissolved oxygen for warmwater fisheries (4.0 mg/L) is indicated on both Figure 2a and 2b.

Figure 2a: Dissolved Oxygen Concentrations in Warwick Brook from June-September 2012

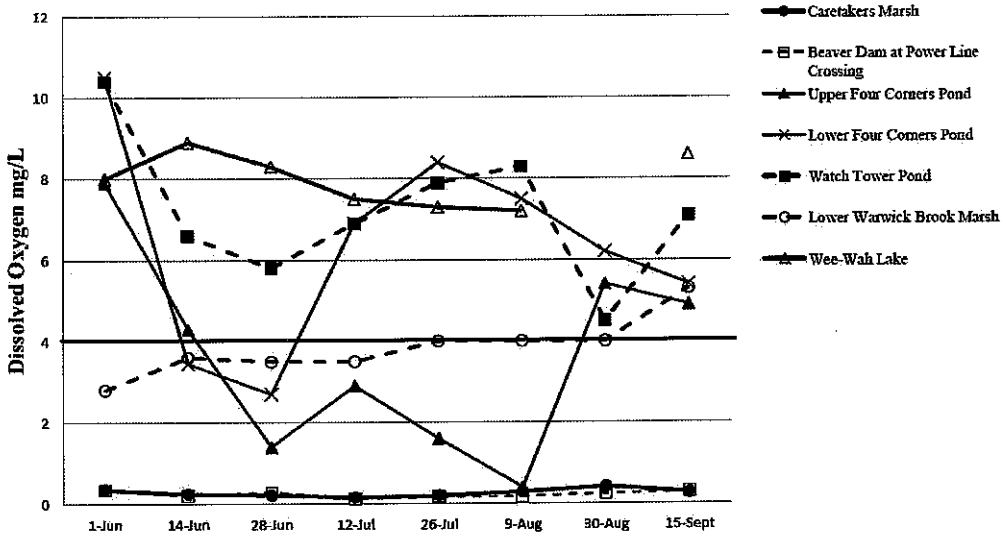


Figure 2b: Dissolved Oxygen Concentrations at Reference Sites from June-September 2012

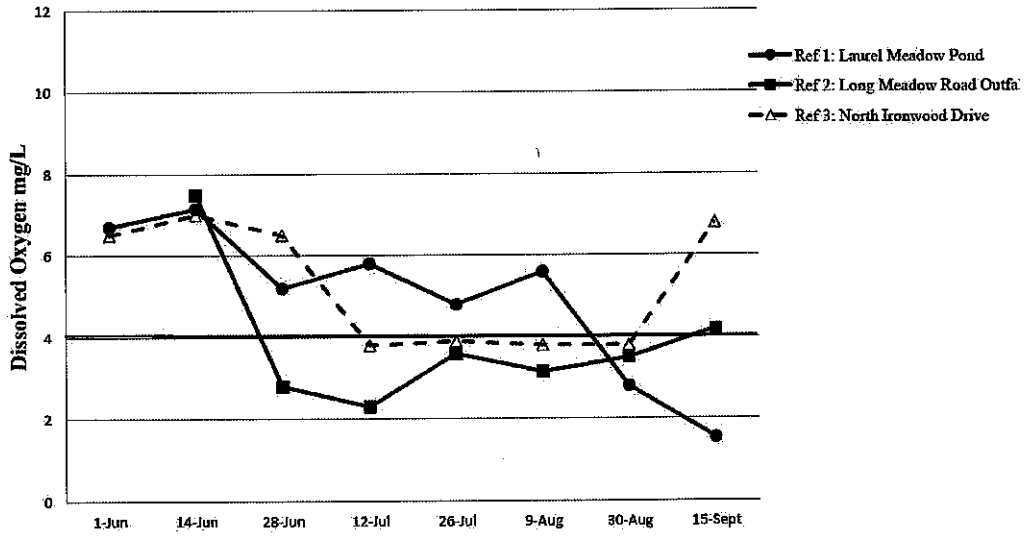


Figure 3: *Biochemical Oxygen Demand (BOD) in Warwick Brook.* Bi-weekly measurements of biochemical oxygen demand (BOD) were conducted at seven locations between Caretakers Marsh and the mouth at Wee-Wah Lake between June 1 and September 15, 2012.

Figure 3: Biochemical Oxygen Demand in Warwick Brook from June-September 2012

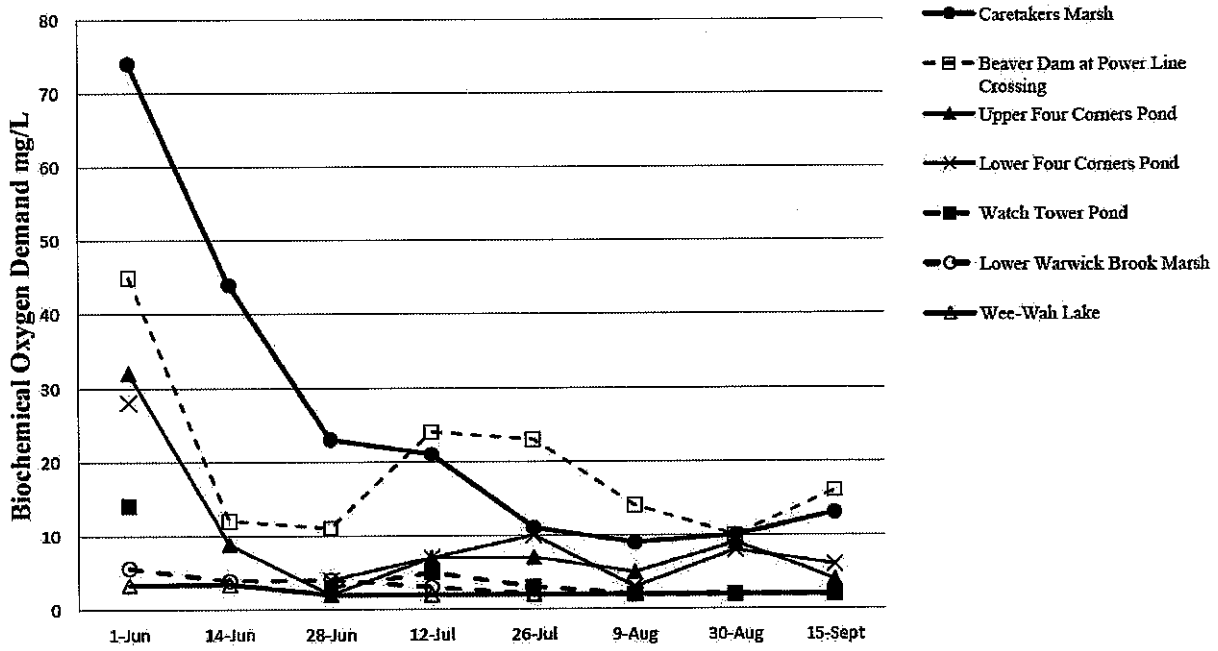


Figure 4: *Total Phosphorus in Warwick Brook.* Bi-weekly measurements of total phosphorus were conducted at seven locations between Caretakers Marsh and the mouth at Wee-Wah Lake between June 1 and September 15, 2012.

Figure 4: Total Phosphorus Concentrations in Warwick Brook from June-September 2012

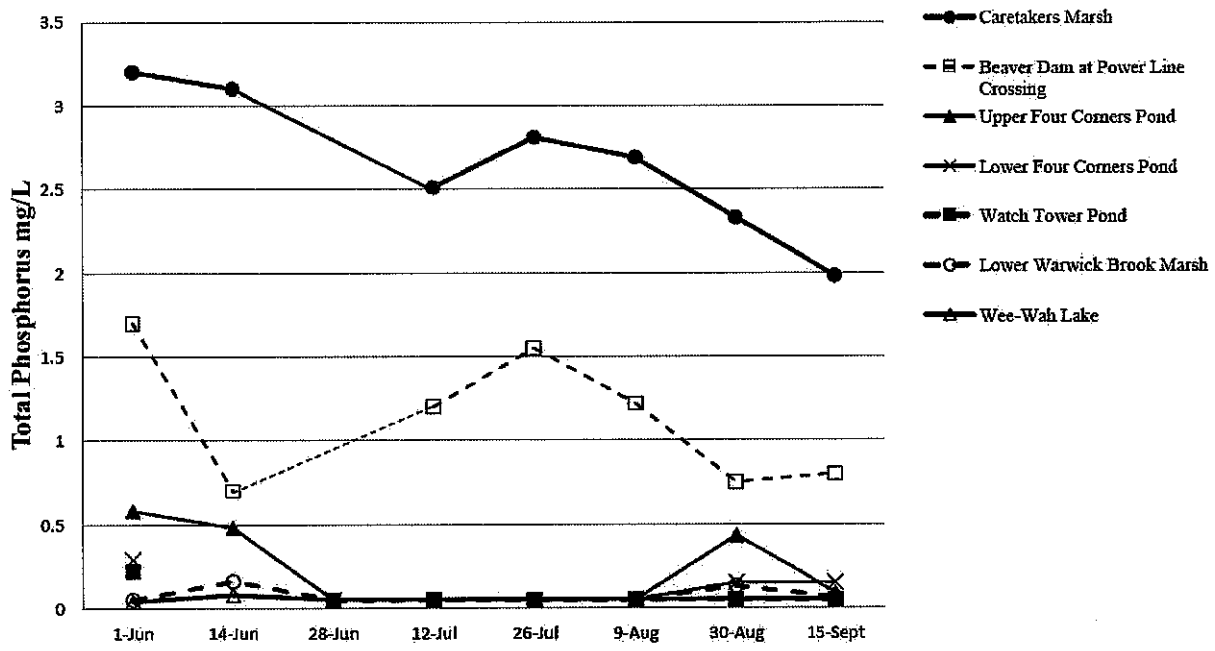


Figure 5: *Total Nitrogen concentrations in Warwick Brook and three reference locations.* **(a)** Bi-weekly measurements of total nitrogen were conducted at seven locations between Caretakers Marsh and the mouth at Wee-Wah Lake. **(b)** Bi-weekly measurements of total nitrogen at three reference sites located outside of the south branch of Warwick Brook

Figure 5a: Total Nitrogen in Warwick Brook from June-September 2012

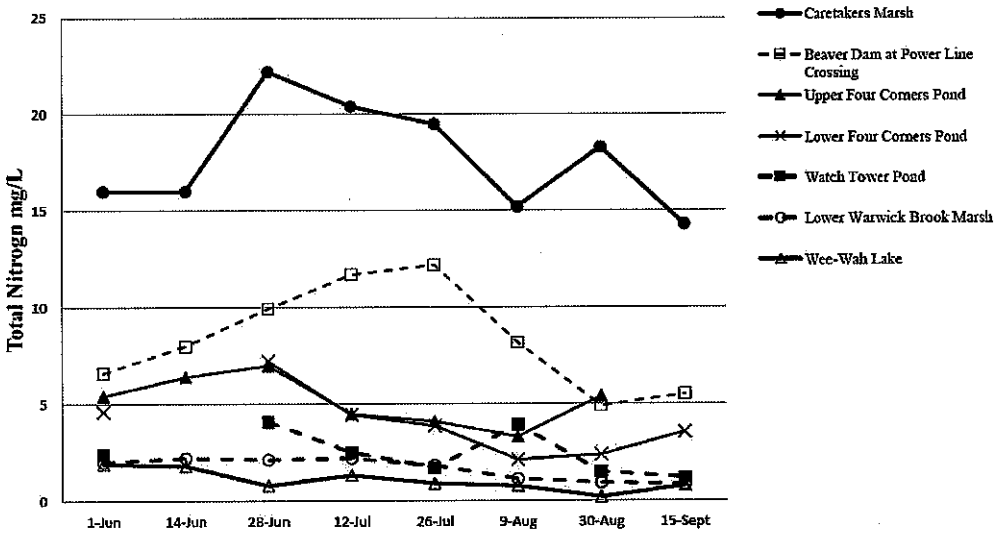
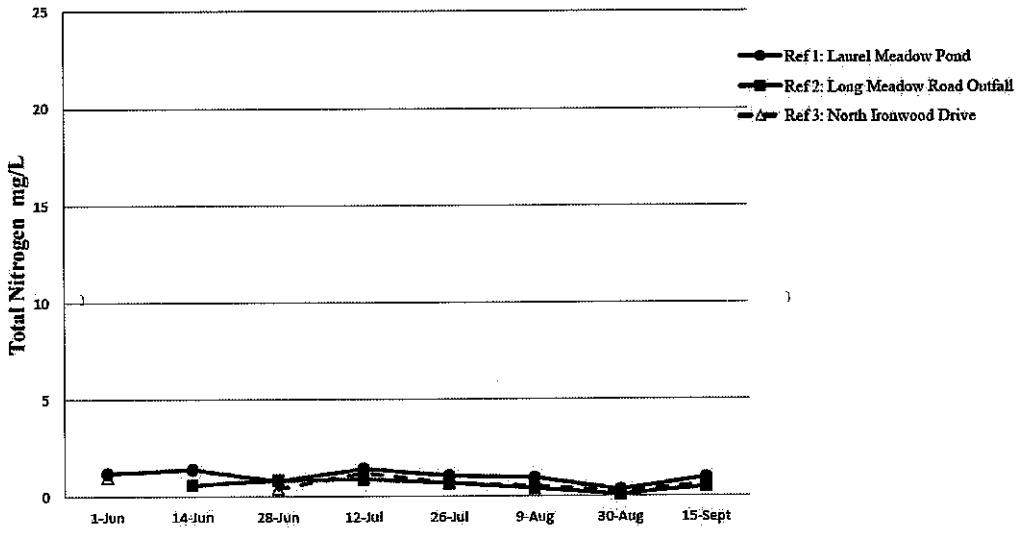


Figure 5b: Total Nitrogen Concentrations at Reference Sites from June-September 2012



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Site #	*Location*
1	Downstream Terminus of Caretakers Marsh at Long Meadow Road
2	Outfall of Beaver Impoundment adjacent to Power Line Clearing
3	Outfall of Warwick Brook into Four Corners Pond (Upper Four Corners Pond)
4	Four Corners Pond Surface Water Upstream of Impoundment (Lower Four Corners Pond)
5	Outfall of south branch of Warwick Brook into Watch Tower Pond (Watch Tower Pond)
6	Lower Warwick Brook
7	Mouth of Warwick Brook at Wee-Wah Lake
MS	Mine Shaft Located at Town Wood Chipping Facility
R1	Reference Site 1: Laurel Meadow Pond
R2	Reference Site 2: Long Meadow Road Outfall
R3	Reference Site 3: North Ironwood Drive

Table 2: *Analytical Methods Utilized for Warwick Brook Water Chemistry Assessment (EcoTest Laboratories, North Babylon NY)*

Water Chemistry Parameter	*Analytical Method*
Total Phosphorus	EPA Method 365.3, SM 4500-PE
Ortho-phosphate	EPA Method 365.3, SM 4500-PE
Total Nitrogen	EPA Method 351, 353, M 4500-NC
Nitrogen, Kjeldahl	Standard Method S204500NORB, EPA 351.2
Ammonia	Standard Method S204500NH3C, EPA 350.1
Nitrate + Nitrite	EPA Method 353.2
Total Suspended Solids	Standard Method S182540D
BOD	Standard Method S185210B
Arsenic / Chromium / Copper	EPA Method 200.7

Table 3: *Average Phosphorus Parameters for Warwick Brook Between Caretakers Marsh and Wee-Wah Lake and Three Reference Locations Between June and September, 2012.*

Site #	*Location*	*Total Phosphorus (mg/L ± SD)*	*Ortho-Phosphate (mg/L ± SD)*
1	Caretakers Marsh	2.66 ± 0.43	2.46 ± 0.60
2	Beaver Dam at Power Lines	1.13 ± 0.40	0.89 ± 0.28
3	Upper Four Corners Pond	0.22 ± 0.23	0.13 ± 0.12
4	Lower Four Corners Pond	0.11 ± .09	0.09 ± 0.09
5	Watch Tower Pond	0.07 ± 0.64	0.07 ± 0.04
6	Lower Warwick Brook	0.08 ± 0.04	0.10 ± 0.08
7	Wee-Wah Lake	0.05 ± 0.01	< 0.05
R1	Laurel Meadow Pond	< 0.05	< 0.05
R2	Long Meadow Road Outfall	< 0.05	< 0.05
R3	North Ironwood Drive	< 0.05	< 0.05
MS	Mine Shaft	0.12 ± .01	0.08 ± .03

Table 4: *Average Nitrogen Parameters for Warwick Brook Between Caretakers Marsh and Wee-Wah Lake and Three Reference Locations Between June and September, 2012.*

Site #	*Location*	*Total Nitrogen (mg/L ± SD)*	*Total Kjedahl Nitrogen (mg/L ± SD)*	*Ammonia (mg/L ± SD)*	*Nitrate (mg/L ± SD)*
1	Caretakers Marsh	17.74 ± 2.80	17.56 ± 2.63	17.74 ± 2.80	8.89 ± 2.08
2	Beaver Dam at Power Lines	8.38 ± 2.72	8.22 ± 2.54	2.61 ± 0.75	0.23 ± 0.34
3	Upper Four Corners Pond	4.78 ± 1.60	4.58 ± 1.64	0.98 ± 0.94	0.23 ± 0.31
4	Lower Four Corners Pond	4.02 ± 1.70	3.93 ± 1.55	0.58 ± 0.53	0.15 ± 0.14
5	Watch Tower Pond	2.47 ± 1.15	2.05 ± 0.92	0.44 ± 0.57	0.43 ± 0.65
6	Lower Warwick Brook	1.65 ± 0.60	1.48 ± 0.51	0.42 ± 0.25	0.20 ± 0.17
7	Wee-Wah Lake	1.05 ± 0.58	0.67 ± 0.44	0.14 ± 0.05	0.40 ± 0.19
R1	Laurel Meadow Pond	1.03 ± 0.35	0.98 ± 0.31	0.17 ± 0.10	0.12 ± 0.09
R2	Long Meadow Road Outfall	0.58 ± 0.28	0.52 ± 0.22	0.20 ± 0.18	0.12 ± 0.08
R3	North Ironwood Drive	0.68 ± 0.34	0.63 ± 0.27	0.17 ± 0.08	0.12 ± 0.08
MS	Mine Shaft	2.10 ± 1.96	2.00 ± 1.99	0.55 ±1 .01	0.17 ± .22

Table 4: *pH Values for Warwick Brook Between Caretakers Marsh and Wee-Wah Lake and Three Reference Locations Between June and September, 2012.*

Site #	*Location*	*Mean pH (± SD)*
1	Caretakers Marsh	6.63 ± .09
2	Beaver Dam at Power Lines	6.89 ± .20
3	Upper Four Corners Pond	7.59 ± .24
4	Lower Four Corners Pond	8.13 ± .39
5	Watch Tower Pond	7.91 ± .44
6	Lower Warwick Brook	7.33 ± .07
7	Wee-Wah Lake	7.88 ± .16
R1	Laurel Meadow Pond	6.55 ± .40
R2	Long Meadow Road Outfall	6.57 ± .42
R3	North Ironwood Drive	7.34 ± .19
MS	Mine Shaft	6.66 ± .16

Note: NYSDEC Water Quality Standard for pH- 6.5-8.5

Table 5: *Air Temperature Prior to March 13-14, 2012 in Four Corners Pond*

Time Period	*Average Daily High Temperature*	*Long-Term Average Temperature*
March 7-13, 2012	59.0 (±9.9) °F	41.0 °F

Notes: Air Temperature Records from Sloatsburg, NY (obtained from www.weatherunderground.com)