Spatial and Temporal Variations of Water Quality in Hellbranch Run: A Historical Perspective

A Senior Honors Thesis

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by

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Figure 1 Hellbranch Run near Galloway, Ohio at Alton Rd.

Abstract

The Big Darby Creek west of Columbus, Ohio is a National Scenic River and is highly protected by governmental and nongovernmental agencies. A watershed tributary, Hellbranch Run, drains land that has recently seen conversion from agricultural land to urban. Urbanization can degrade streams due to increased impervious surfaces in the watershed which create pulses of sediments and pollutants to flow to streams during storm events. Study objectives are to determine and interpret the temporal and spatial dynamics of major nutrient and total suspended solids concentrations from four sites along Hellbranch Run. Sites represent different land-use catchments and upstream/downstream on the mainstem of the stream. Land-use records from 1992, 2001 and 2006 were used to compare changes in nutrient loads overtime to land-use changes. Bimonthly sampling took place from Nov. 2009 to Nov. 2010. Sampling involves measuring temperature, pH and TDS in situ in the stream. Samples were analyzed for major nutrients, including nitrate+nitrite-N, ammonium, total nitrogen, phosphate and total phosphorus concentrations. Results show total phosphorus having very high concentrations: median 398 ug/L and range (66.8 to 1,773 ug/L), whereas ammonium is closer to an environmentally acceptable level: median 52.8 ug/L, range (11.7 to 1623 ug/L). Additionally, Hamilton Ditch, a headwater draining cultivated crop, tends to have the highest concentrations of all nutrients, whereas the larger urban headwater streamreach showed lower values. Seasonal shifts exhibited a strong control on nitrate with highest values in the winter and lowest in the summer, while phosphorus shows a weaker trend with highest values in the fall. Suspended solids ranges from 4.4-612 with mean 38.5 mg/L and has lower values upstream and highest just downstream of the confluence of the two headwaters. Historical flow, nutrients and TSS data was used to estimate daily loads using the program LOADEST and the resulting

time series shows an estimated decrease in nitrate loads over the last 18 years. Knowing the current state of the water quality along Hellbranch Run is important in understanding the effects that local land-use has on it and will aid land management policy-makers.

Acknowledgements

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Introduction

The Big Darby Creek, just west of Columbus, Ohio (Figure 2) is one of the most pristine and most biodiverse streams of its size in the Midwest. It is a National and State Scenic River. It is one of the top five warm, freshwater habitats in the nation and home to several endangered species of fish and shellfish (Ohio EPA, 2006; City of Columbus, 2001). This study investigates a major tributary to the Big Darby called Hellbranch Run (Fig. 1). The Hellbranch drains land (95.8 km^2) in western Franklin County that has recently seen conversion of agricultural land to urban, especially near the city of Hilliard, Ohio (Ahn, 2007). Hellbranch Run has also undergone channelization, mainly in the two headwaters; Clover Groff Ditch (CGD) and Hamilton Ditch (HD). These headwaters once ran sinuously through swampy, poorly draining soil due to the areas clayey glacial till surficial deposits and very low gradient. In the early 1800's they were channelized to facilitate drainage and allow agricultural use of the land. The Hellbranch watershed is still primarily used for cultivated crop agriculture (near 60%, see Table 1), which is a major input of nutrients to the stream. There is also tile drainage in some of the farmland which discharges to Hellbranch Run (Riker-Coleman, 2000). In general, Hellbranch Run faces a few major threats (not in any specific order): 1) the rapid conversion of cropland to urban land, 2) the channelization of the headwaters, and 3) nutrient enrichment due to erosion and transport of agricultural fertilizers. Thus, most sections of Hellbranch Run did not meet the Ohio Environmental Protection Agencies' (OEPA) statewide biological toxicity target concentrations for major nutrients, especially poor were total phosphorus and suspended sediment, in a 2001-02 survey (Ohio EPA, 2004). Also, there was a 30% decline in fish species from 1992 to 2001 in Hellbranch Run (Miltner, White and Yoder, 2004). To protect the Big Darby's exceptional habitat, it is important that Hellbranch Run's water quality and hydrologic condition improve.

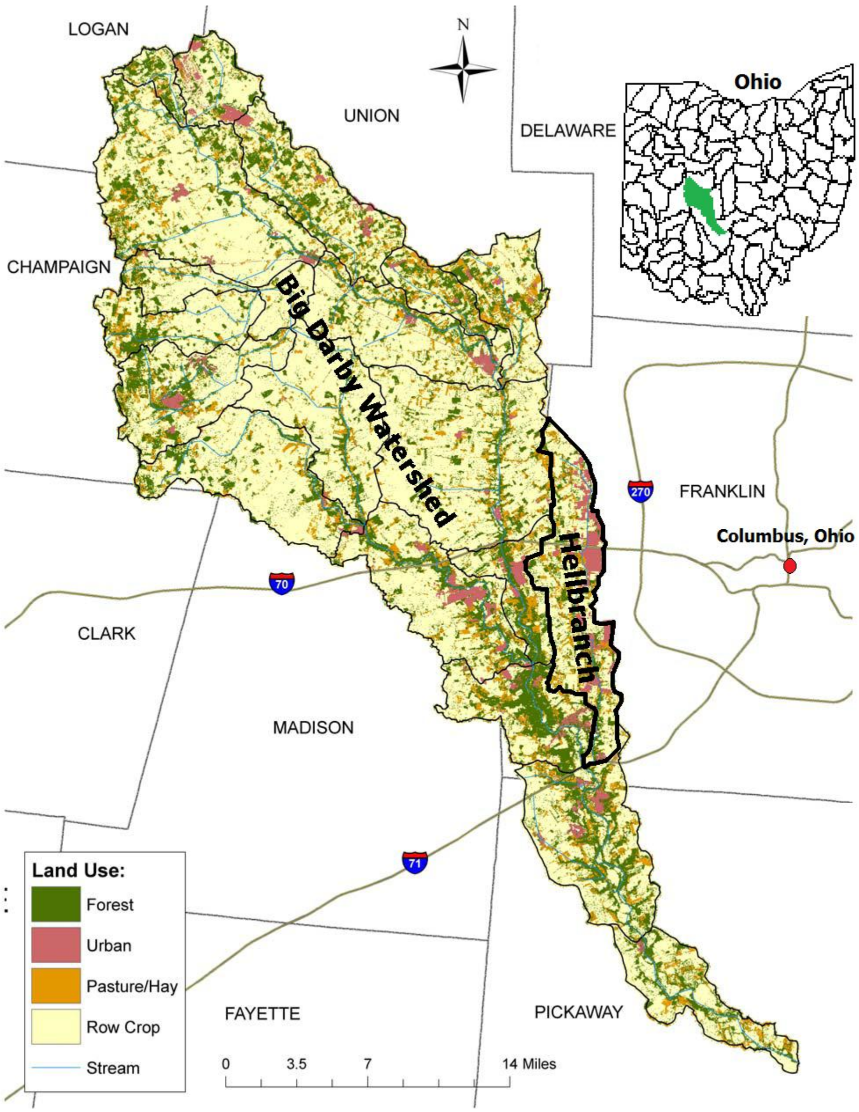

Figure 2 Map of Big Darby Creek Watershed which drains 1437 km^2 or 555 square miles of predominantly row crop. Hellbranch Run's subwatershed is highlighted; it drains 95.8 km^2 or 37 square miles. Flow direction of the Big Darby Creek is from NW to SE. Land-use map is modified from (Ohio EPA, 2006).

There are several government and non-government organizations, both locally and nationally based that have shown interest in protecting the Big Darby Watershed, and many are especially concerned for Hellbranch Run. Some include the Ohio Environmental Protection Agency (OEPA), U.S. Geological Survey (USGS), Ohio Department of Natural

Resources, the U.S. Department of Agriculture, the U.S. Department of the Interior, county/municipal/township government, the Darby Creek Association, Operation Future Association, the Ohio Sierra Club, and the Nature Conservancy. Many of these groups have contributed to stream remediation projects or other forms of protection for the stream.

There are two major stream remediation projects on Hellbranch Run: Latham Park and Frank Park, both of which are on the CGD, the channelized headwater that now drains an increasingly urban catchment. Both remediation projects are guided by the OEPA's 2006 TMDL (Ohio EPA, 2006). The goal is to improve stream habitat, hydrologic conditions and lower nutrient loads by physically reforming the stream to restore meanders, riparian buffers/floodplains, and small wetlands (Seger, 2008). The majority of both stream remediation projects was paid for by CWA federal grants and local government funds and will total close to $0.9 million. The Frank Park stream remediation was completed in 2009 and Latham is well underway. In 2006, a model called "The Big Darby Accord" was created by local government in Franklin County, Ohio. The model gives guidelines for balancing development in the area and stream protection, it follows objectives set forth by the OEPA's TMDL and one major goal is to lower major nutrients and TSS loads from the Hellbranch to the Big Darby Creek (Ohio EPA, 2006; Sherer, Sasson and Hatmaker, 2008). The Franklin County soil and water conservation district has also purchased large tracts of land around the Hellbranch to prevent it from being developed; mainly in the southern stream reach where development pressure is weak relative to the northern sections. Another major effort is the City of Columbus' zoning overlay to protect the Hellbranch watershed from development. The overlay, adopted in 2001, requires a 100 ft riparian buffer to the mainstrem of the Hellbranch and a 75 ft buffer to both of the headwaters (to restore natural floodplains for a predicted 100 year storm). The zoning overlay also mandates 40% of land in the watershed to remain as open space and ends the practice of burying small tributary streams among other protections (City of Columbus, 2001). However, as Paul Dumouchelle of the Darby Creek Association points out, there are shortcomings with the overlay, namely 40% open land will not do enough to protect from development, and the plan is not scientifically based (Dumouchelle, 2001). The Hellbranch Run came under a very close eye from concerned organizations and governments after it showed a dramatic increase in development between the years 1992 to 2001. During this period urban land-cover grew by nearly a factor of four, rising from approximately 4.58% to 22.46% of total land-cover in the watershed (Table 1).

Goals and objectives

The goal of this research is to understand water quality dynamics of the Hellbranch Run, seasonally and spatially within different reaches of the stream. The focus is on nitrogen (N), phosphorus (P), and total suspended sediment (TSS) because, in excess, they can have a detrimental effect on stream ecology and have been found to be a major problem in this stream in the past (Ohio EPA, 2004). Major ions were also analyzed, but will not be discussed in this manuscript (raw data can be found in the appendix). The hypothesis to be tested is nitrate, total phosphorus (TP), ammonium and TSS concentrations exceed the EPA's state biological toxicity target concentrations. Also, within the overall goal, there are several key questions; how have N and P loads changed over the past 18 years? Can they be explained by land-use and hydrologic changes over time?

Concentrations of nutrients are expected to be highest in the agricultural reaches of the stream, nutrient and TSS concentrations are expected to correlate with runoff as well.

Also, over the past 18 years average loads of N and P are expected to have increased with time. These hypotheses will be analyzed using historical data from the USGS.

Literature Review

The effect of headwaters and small streams on downstream ecology has long been not fully understood (Alexander et al, 2007). Perhaps, due to this lack of knowledge, increasing development pressure, and rising agricultural needs, many small streams have been modified and degraded around the globe (Haigh, 2000). Recent findings suggest headwaters serve as a primary or significant control on downstream physical, chemical and biological water quality/hydrology and are more vulnerable than higher order streams (Ahn, 2007; Miltner, White and Yoder, 2004; Alexander et al, 2007; Haigh, 2000; Wipfli, Richardson and Naiman, 2007; Smith and Lamp, 2008; Freeman, Pringle and Jackson, 2007; Volk and Costa, 2010). Yet when compared to larger rivers, headwater streams have much less protection under current land management policies, even though they have significant influence on downstream water quality (Wipfli, Richardson and Naiman, 2007). For example; many first and second order streams are not in the jurisdiction of the CWA of the United States. This is because the CWA has jurisdiction only over navigable waters. However, in 2006 there was a U.S. Supreme Court ruling (Rapanos *v.* United States) that explicitly gave the CWA jurisdiction over low-order, non-navigable streams, but only if certain criteria are met by the stream. Namely, the stream has hydrologic permanence or the stream is found to have significant impact on downstream waters (Leibowitz et al, 2008). Both of these criteria require dedicated scientific studies to validate. Currently, the Hellbranch Run meets the CWA's drinking water standards for major nutrients and TSS; however the OEPA has made statewide biological toxicity target concentrations which are based on environmental impacts. These criteria include target concentrations for chemical constituents, e.g. NO_3^-+NO_2^--(N) among others (Ohio EPA, 1987).

Urbanization is known to cause large pulses of sediments, nutrients and pollutants to be flushed into streams when storm water meets large impervious surfaces (e.g. roads, roofs and parking lots) associated with developed areas (Hatt et al, 2004). In general, activities associated with urban land-use have been found to correlate and contribute to the degradation of surface water ecosystems by physical and chemical changes (Miltner, White and Yoder, 2004; Smith and Lamp, 2008; Hatt et al, 2004; Paul and Meyer, 2001; Hopkinson and Vallino, 1995; Barco et al, 2008; Allan, 2004). An increase in impervious surfaces in a watershed can alter the physical hydrology of a stream. Specifically, impervious surfaces have been found to cause higher peak flows during storm events which cause increased flooding frequency and magnitude, bank erosion and channel incision. Eventually a stream in an urbanizing watershed will have a growing proportion of runoff compared to baseflow (groundwater discharge to the stream) component of its total streamflow (Ahn, 2007; Hatt et al, 2004; Allan, 2004; Simon and Rinaldi, 2006; Ray, Duckles and Pijanowski, 2010). This is because less precipitation is recharging the groundwater in the watershed, and more is being transported as overland flow or runoff (Paul and Meyer, 2001; Simon and Rinaldi, 2006). This hydrologic change is significant to a streams water quality because it can change the quantity and chemical composition of water in the stream (Hatt et al, 2004; Paul and Meyer, 2001; Ray, Duckles and Pijanowski, 2010; Drever, 1987). The chemistry of groundwater is largely a function of the mineral composition of the aquifer in its flowpath, whereas the runoff waters chemical composition is related to the composition of rainwater and the surface particles it interacts with (Drever, 1987).

Channelization is known to cause stagnation of water during low flows, resulting in very low oxygen levels and a poor habitat (Hopkinson and Vallino, 1995). During high flows, the banks may be incised, due to the abrasion of fast flowing particles (Simon and Rinaldi, 2006). Steep channel banks can diminish flooding frequency, cause oversized stream cross-sectional area and result in the accumulation of silt and clay in the channel depending on the flow capacity of the stream and sediment input rate (Simon and Rinaldi, 2006). These accumulated fine-grained particles are known to have high surface area and to readily adsorb nutrients to be leached to the stream or groundwater, or transported in pulses during high flow events (Volk and Costa, 2010; Simon and Rinaldi, 2006; Wallace et al, 1995).

Major nutrients such as nitrogen (N) and phosphorus (P) are essential for plant and animal growth, however, nutrient enrichment or eutrophication is now seen as the largest impairment to surface water quality in the United States (U.S. Environmental Protection Agency, 1996). Nitrogen and phosphorus are often limiting nutrients, and an abundance of N and P especially inorganic forms such as nitrate, ammonium and phosphate can cause excessive growth among primary producers and can result in lowered levels of dissolved oxygen, fish kills, toxic algal blooms, and they can be toxic to aquatic organisms (Ohio EPA, 1987; Correll, 1999; Biggs, 2000; Moore et al, 2004; Redfield, 1958). Numerical criteria for target concentrations of nutrients in Ohio's lakes and streams have been determined by the OEPA. These criteria are found empirically, based on biological response; see (Ohio EPA, 1987). However there is no law enforcing these concentrations in Ohio. High levels of nitrates in drinking water pose a human health risk as well; the CWA drinking water standard is 10 mg/L. For example high concentrations of nitrates in drinking water from groundwater wells have been linked to infant methemoglobinemia (blue baby syndrome), among other health issues and diseases (Knobeloch et al, 2000). Application of agricultural fertilizers, usually containing inorganic nitrate, phosphate, ammonium, or organic N and P (i.e. manure), is often the main input of nutrients to streams in agricultural or developed watersheds; however sewage effluent, burning of fossil fuels (emits NO_x and N_2O), energy production and many industrial activities introduce nutrients to the environment (Galloway et al, 2004; Zublena, Baird and Lilly, 1991; Arheimer and Liden, 2000; Driscoll et al, 2001).

There are several studies that investigate the control of land-use and seasons on N and/or P loading for various streams, e.g. (Arheimer and Liden, 2000; Clark et al, 1992; Domagalski et al, 2008; Pieterse, Bleuten and Jorgensen, 2003; Reynolds, Emmett and Woods, 1992; Renwick et al, 2008; Udawatta et al, 2002; Shields et al, 2008; Lenat and Crawford, 1994; Tong and Chen, 2002).

As human population has risen, along with demand for crops and livestock, fertilization has helped increase crop yields. However, findings suggest that 70% of the fertilizers and feed applied to farms in the US is either lost to soil storage or transported to surface or groundwater (Daniel, Sharpley and Lemunyon, 1998). Implementing best management practices (BMPs) to reduce this large amount of residual N and P to water resources is only part of the solution.

Nitrogen (and P to a lesser extent) is mobile in groundwater, and neither of them can be indefinitely stored in soils, so total N and P input and output rates from farms and watersheds needs to be seriously addressed (Daniel, Sharpley and Lemunyon, 1998). The nitrate molecule is negatively charged and does not adsorb readily to soil particles. This is because most silicate minerals have negative charges on their surfaces, due to weathering and cation release. Thus, nitrate is very mobile in groundwater, and groundwater pollution of nitrate is common (Hudak, 2000). Also, because most P output is associated with just a few large storm events, soil erosion and transport processes are highly related to P transport. An additional water quality problem associated with ammonium (NH_4^+) is acidification of waters, when NH_4^+ is oxidized by bacteria to NO_3^- (Driscoll et al, 2001).

Phosphate (PO_4^{-3}) has a strong charge and tends to adsorb to fine grain particles, especially those with cations such as: Fe^{+3}, Al^{+3}, Ca^{+2}, and Mn^{+2} or reactive iron oxide/hydroxide minerals. Due to its reactivity and sorptive nature, phosphate is less mobile than NO_3^- in groundwater and is commonly correlated to TSS concentrations (Drever, 1987; Uusitalo et al, 2001; Borggaard, 1983; Barber, 2002). Ammonium is typically oxidized or assimilated biologically very quickly, and does not tend to accumulate in soil or waters (Drever, 1987; Butturini and Sabater, 1998). Nutrients NO_3^-, PO_4^{-3}, and NH_4^+ are major components of topically applied fertilizers, therefore streams in agricultural catchments tend to show high concentrations.

Sediment erosion and transport to streams are natural processes; however anthropogenic activities have greatly increased the rates of soil erosion. Till farming and urbanization among other activities are processes that expose surface sediment and allow it to be transported during rain events (Paul and Meyer, 2001; Kosmas et al, 1997; Lindstrom, Nelson and Schumacher, 1992; Evans and Seamon, 1997). High erosion rates introduce large TSS yields to streams, and can impair stream water quality. High turbidity waters are uninhabitable for many species of aquatic life, they have been found to clog fish gills, and sedimentation of stream beds can create a loss of habitat. As previously stated, if accumulation of sediment occurs in a stream channel, these fine-grained particles tend to adsorb nutrients (Allan, 2004; Simon and Rinaldi, 2006; Wallace et al, 1995; Barber, 2002; Forstner, 1987; Volk and Costa, 2010).

Scientific studies already completed on the Hellbranch Run include: (Ohio EPA, 2006; Ahn, 2007; Riker-Coleman, 2000; Ohio EPA, 2004; Miltner, White and Yoder, 2004; Dumouchelle, 2008; Jones and Raab, 2011). The scope of each range from; investigating stream flow gains and losses, to fish and insect counts, to modeling land-use change in the entire Big Darby watershed, and how it relates to the change in total impervious surfaces. Here are some of their findings: Hellbranch Run is the most urbanized watershed of all the Big Darby subwatersheds and it has shown a 15% increase in its peak flow from 1992 to 2007 (Ahn, 2007). There was a 30% loss in fish species from 1992 to 2001. Hellbranch Run had the highest levels of Total Kjeldahl Nitrogen (organic N plus ammonia and ammonium) of all streams sampled in the Big Darby Creek (Ohio EPA, 2004). Hellbranch Run contributed to bacteria concentrations and decreased dissolved oxygen levels in the Big Darby Creek. Big Darby Creek had a significantly higher total phosphorus (TP) concentration downstream of the Hellbranch (Ohio EPA, 2004).

Geology and Hydrogeology

The underlying geology in the Hellbranch Run watershed is comprised of Silurian-Devonian dolomite and limestone bedrock, specifically, the Lockport Dolomite, Bass Islands Group Dolomites and the Columbus Limestone. There is also some shale and minor sandstone present. The bedrock dips approximately 13 ft per mile to the east (Riker-Coleman, 2000). The Wisconsinan glaciation scoured the area carving many valleys in the carbonate bedrock that were later filled with glacial till, and outwash sand and gravel (Dumouchelle, 2008). There is a high percentage of clay and silt in Ohio's glacial till, which makes for low hydrologic conductivities in many glacial surficial deposits (Riker-Coleman, 2000). The till in the study area is part of the Darby Plains physiographic area. The area is very flat, although some relief is provided from ground moraines and erosion (Dumouchelle, 2008; Brockman, 1998). The glacial deposits in the area in general are heterogeneous, mostly unsorted till, but there are some lenses of sand and gravel which have higher hydrologic conductivities. Thickness of overlying glacial till and outwash deposits in the study area ranges from 50 ft or less up to 330 ft (Riker-Coleman, 2000; Dumouchelle, 2008). The limestone and dolomite bedrock is the main aquifer that discharges to the Hellbranch and groundwater yields are as high as 250 gpm above 300 ft (Jones and Raab, 2011). Additionally, the glacial deposits in the watershed yield 5-25 gpm and act as a partially confining layer (Ohio EPA, 2006). The headwater areas have lower stream gradients (8 – 10 ft per mile) compared to downstream on the Hellbranch where the average gradient is 11 ft per mile (Riker-Coleman, 2000; Krolczyk, 2001). Recent findings have shown Hellbranch Run is a gaining stream over its full length, yet it loses flow over several short reaches (Dumouchelle, 2008).

Methods

Study Sites

Water samples were collected at four locations on Hellbranch Run (Figure 3); from both of the headwaters HD at Feder Road which drains predominantly cultivated cropland, and CGD at Broad Street which drains mostly low density urban land. The other sampling sites are on the mainstem of Hellbranch at Alton Road (M2) and at the USGS stream gage station # 03230450 at Lambert Road, near Harrisburg, Ohio (M1), see Figure 3. The gage at M1 drains 92.7 km^2 of land in the 95.8 km^2 watershed. The M2 site was chosen to represent the mainstem after the mixing of the two headwaters and to compare concentrations to downstream. The HD drains roughly 14 km^2 of land, of which greater than 85% is cultivated crop and 15% pasture/hay or developed land (from aerial photographs from Franklin County's Auditor, and national land cover database maps). Conversely the CGD drains close to 23 km^2 and is close to 65% developed land, mostly low density urban, in the City of Hilliard, Ohio, and the remaining land is largely used for cultivated crop agriculture (Figure 3).

Land-use data from the National Land Cover Database (NLCD) was used to investigate land-use in the watershed for the years 1992, 2001 and 2006 (Table 1). The NLCD data was created by a consortium of organizations including the USGS, EPA, National Oceanic and Atmospheric Administration (NOAA), and the U.S. Forest Service (USFS).

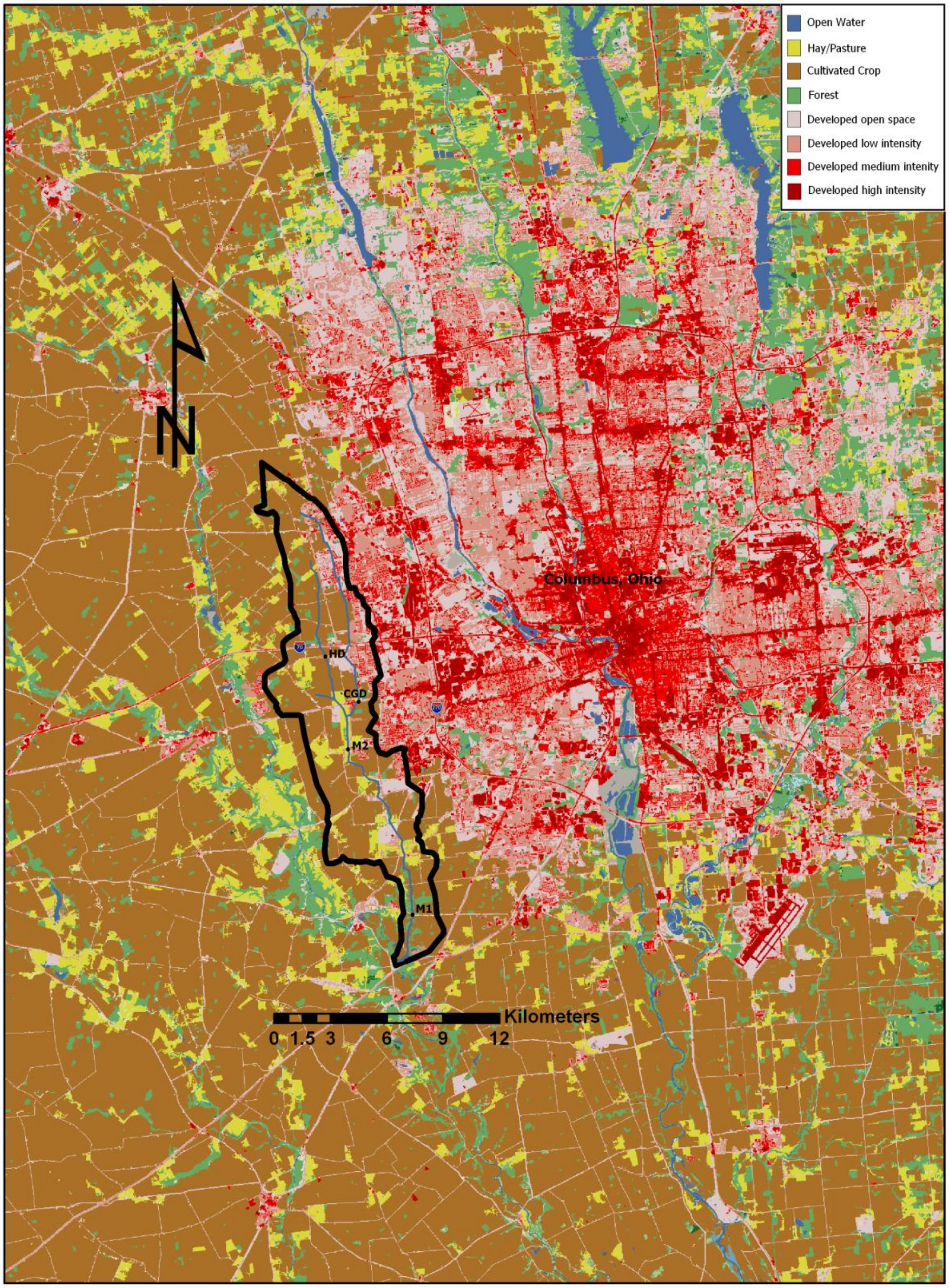

Figure 3 Map showing the Hellbranch Run Watershed and its proximity to Columbus, Ohio. Sampling locations M1, M2, CGD and HD are also included. The background map is the 2006 land-use-land-cover dataset, available from the NLCD. The purpose here is to show the sampling locations, although the legend shows specific land-use categories. For a better view of specific land-uses in the Hellbranch watershed see figure 3.

The NLCD data was created using Landsat Thematic Mapper satellite data with 30m spatial resolution. A detailed explanation of how the data was created and its accuracy can be found in (Homer et al, 2004). For year 2006, the Hellbranch Run watershed total land-use is approximately comprised by 59% cultivated crop, 24% developed, 10% hay/pasture, and 7% forested (Table 1). The vast majority of urban land is in the CGD catchment, but there is some light development in the south east areas of the watershed. Unlike many Ohio streams its size, Hellbranch does not lie below a reservoir.

Land-use variations over time for the entire Hellbranch Run Watershed				
Land – Use Type	1992 % land-cover	2001 % land-cover	2006 % land-cover	% change of total land-use from 1992 to 2006
Open Water	0.13	0.24	0.24	+0.11%
Developed, Open Space	ND	9.57	10.05	ND
Developed, Low Intensity	2.91	10.48	10.94	+8.03%
Developed, Medium Intensity	1.67**	2.41	2.63	+0.96%
Developed, High Intensity	ND	0.08	0.09	ND
Barren Land	ND	0.03	0.02	ND
Deciduous Forest	6.90	5.55	5.50	-1.4%
Evergreen Forest	0.08	0.04	0.04	-0.04%
Mixed Forest	0.00	0.01	0.01	+0.01%
Herbaceous	1.71**	1.42	1.39	-0.32%
Hay/Pasture	20.63	9.93	9.92	-10.71%
Cultivated Crops	65.38	60.19	59.11	-6.27%
Woody Wetlands	0.52	0.02	0.02	-0.5%
Emergent Herbaceous Wetlands	0.08	0.04	0.04	-0.04%

Table 1 Land-use data for Hellbranch Run Watershed, data acquired using ArcMap. A shapefile from an outline of the Hellbranch Watershed was used to clip the NLCD land-use, land-cover data layers for each year shown above. **The 1992 data set was made using a different mapping land-cover classification system compared to 2001 and 2006. For comparison purposes the developed, medium intensity category was replaced with the 1992 data categories of; residential high intensity plus commercial/industrial/transportation. Similarly, the category of herbaceous was replaced with the 1992 data category of recreational grasses.

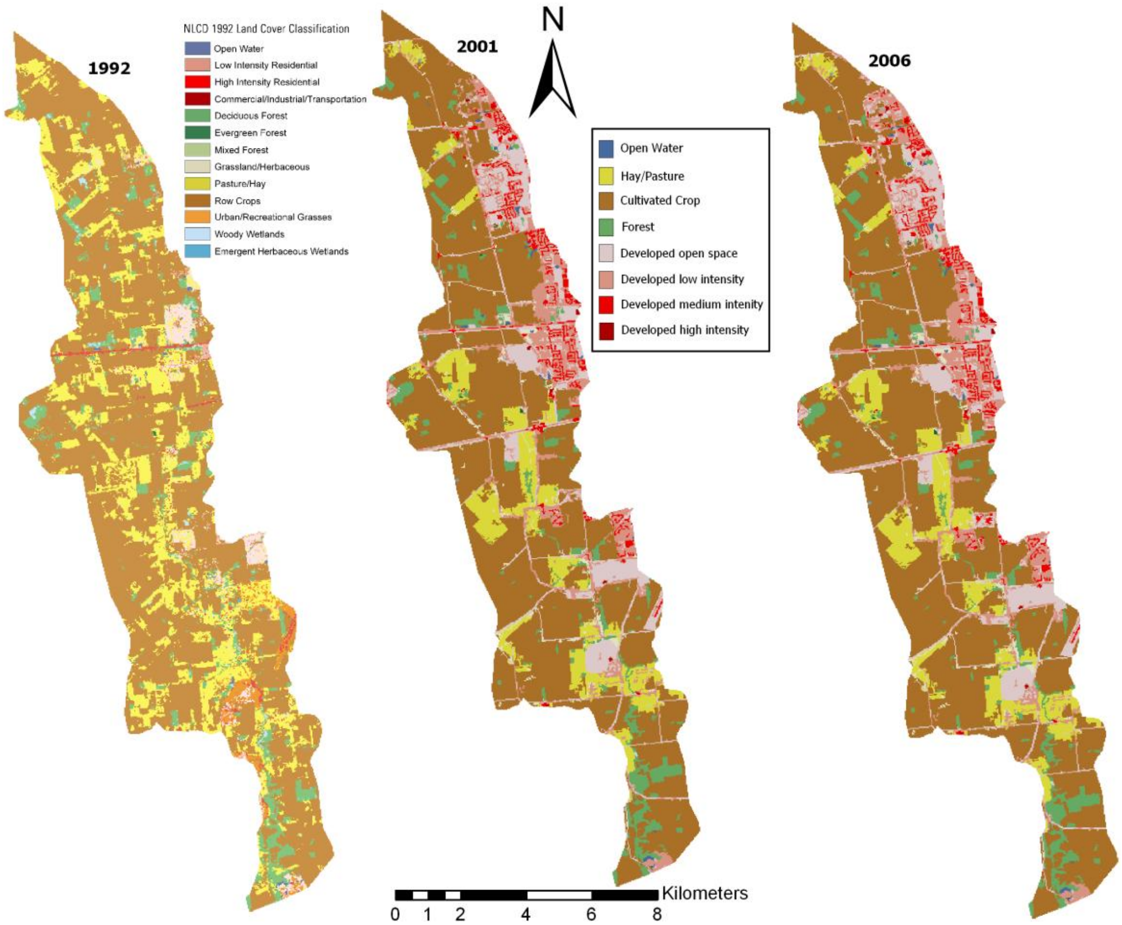

Figure 4 Land-use maps for the Hellbranch Run watershed for 1992, 2001 and 2006. Map data from the NLCD, notice the rapid increase in urban land from 1992 to 2001 in the northeast portion of the watershed, near Hilliard, Ohio.

Sampling Techniques

Sampling took place nearly every two weeks over the course of one year starting in November 2009 and ending in November 2010. However, due to travel obligations there are some gaps in the data. In total there were 21 samples taken at each site, for a total of 84 samples. Sampling dates were chosen to collect a range of flow conditions, i.e. during high and low flows. Sampling was done by hand, taking a liter of water from the stream with a Fisher scientific polypropylene nalgene bottle being held below the surface of the water. This sampling technique may have created a bias towards lower TSS measurements due to lower flow velocities near the banks of the stream. Each bottle was washed with the stream water three times before taking a sample. Each bottle that was used including the hand pump filtering system used was washed with deionized water three times before each sampling. All samples were filtered at the sampling site through a Whatman 0.45 micron glass microfiber filter, using a hand pump filtering system. Each sample bottle was put on ice in a dark cooler while in the field to prevent nutrient decomposition, and nutrient samples were then immediately placed in a freezer whereas major ion samples were stored in a refrigerator at the Byrd Polar Research Center in Columbus, Ohio. To measure TSS each filter was weighed before and after use to an accuracy of 0.0000g, they were dried under a laminar flow hood overnight prior to weighing. A Thermo Scientific Orion 5 Star Meter was used to measure stream and ambient temperature, pH, and conductivity in situ in the stream.

Laboratory Analysis

Major nutrients were analyzed at the School of Earth Sciences geochemistry lab at The Ohio State University, Columbus, Ohio. Nutrients analyzed included NO_3^- + NO_2^--N, NH_4^+-N, and total N (TN) in mg/l, also PO_4^{-3}, and TP as PO_4^{-3} in ug/L. Total N is the sum of NO_3^- + NO_2^- -N, NH_4^+-N and dissolved organic nitrogen (DON) and total P is a combination of three forms of phosphorus: orthophosphates, polyphosphates, and organic phosphorus. From this data, DON in mg/L and TP as P and dissolved organic P (DOP) in ug/L were calculated as DON = TN - (NO_3^- + NO_2^- + NH_4^+-N) and DOP= TP - PO_4^{-3}. To analyze the nutrient samples the Skalar SAN++ automated nutrient analyzer was used following the instructions from the manufacturer. Samples were analyzed for major cations: Na^+, K^+, Mg^{2+}, Ca^{2+} and major anions: Cl^-, and SO_4^{-2} by ion chromatography (Welch et al, 1996). A Dionex DX-120 (Sunnyvale, CA) was used for the major ion analyses. This instrument uses a single piston, isocratic pump with constant flow rate set at 1.2 mls per minute and an electrical conductivity detector. For the cation analyses, a Dionex IonPac CS12A analytical column (4x250mm) and a CG12A guard column (4x50mm) was used. The eluent is 0.13% methanesulfonic acid solution. A CSRS Ultra Cation Self-Regenerating Suppressor was used. For the anions, a Dionex IonPac AS14 analytical column (4x250m) and an AG14 guard column (4x50mm) were used. The eluent is a 1.0 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 solution. An ASRS Ultra Anion Self-Regenerating Suppressor was used. Alkalinity was not determined by titration; however it can be calculated from the charge balance of major cations minus anions.

Statistical Analysis

ArcGIS 9.3 was used to analyze land-use, land-cover maps from the National Land Cover Database (NLCD) for years 1992, 2001, and 2006. The land-use for each year of data was calculated in ArcMAP, by creating a shapefile for the Hellbranch Watershed and clipping it out of the NLCD map layer. Aerial photographs from the Franklin County auditor were also used to estimate recent changes in land-use from 2006-2010 in the CGD and HD. The USGS program LOADEST was used to estimate daily mean concentrations for missing data and create a time series of loads (Runkel, Crawford and Cohn, 2004). The program utilizes linear, logarithmic and trigonometric functions to create a regression model to fit data to known flow and time values. For a detailed explanation, see the user's manual (Runkel, Crawford and Cohn, 2004). The USGS stream gage on Hellbranch Run near Harrisburg, Ohio (site M1) has supplied instantaneous discharge data every 15 minutes beginning in 1992 (Runkel, Crawford and Cohn, 2004). Concentrations and loads were estimated with LOADEST for the period of 01/01/1993 to 12/31/2010 using daily average streamflow, and historical nutrient data courtesy of the USGS, and those from this study for:

NO_3^- + NO_2^- -N, TP, and TSS. LOADEST input data included n=308 for TP, n=84 for NO_3^- + NO_2^- -N and n=269 for TSS. LOADEST was allowed to pick the appropriate model for each data set. Output residual data were also analyzed to determine if the residuals were normally distributed, in order to display the correct output data (for a detailed explanation see Runkel, Crawford and Cohn, 2004). The web application "WHAT" created at Purdue University was used for hydrograph analysis and baseflow separation. Streamflow data were retrieved from the USGS instantaneous data archive for the gage at Hellbranch Run near Harrisburg, Ohio. The recursive digital filtering method was used for all hydrograph separations (Lim et al, 2005). Microsoft excel 2003 and Mathematica 7 were also used for statistical analysis.

Results & Discussion

Hydrograph Analysis

Using historical streamflow data from 01/01/1993 through 12/31/2010 and the hydrograph separation program "WHAT", the daily mean baseflow was found to be 18.7 cfs and median 9.2 cfs (Lim et al, 2005). The base flow index (BFI) for the 18 year period is 0.48, i.e. streamflow is comprised of 48% baseflow and 52% runoff components. The yearly BFI ranges from 0.41 in calendar year 2000 to 0.53 in calendar year 2002. There is no obvious trend in the Hellbranch's BFI over the past 18 years (Table 2). Figure 5 is representative of a typical hydrograph for Hellbranch Run.

Base Flow Index for Hellbranch Run from 1993-2010	
Calendar Year	**BFI**
1993	0.49
1994	0.46
1995	0.48
1996	0.48
1997	0.49
1998	0.46
1999	0.49
2000	0.41
2001	0.47
2002	0.53
2003	0.51
2004	0.47
2005	0.45
2006	0.49
2007	0.45
2008	0.47
2009	0.52
2010	0.50
Total	**0.48**

Table 2 Baseflow index for each year of available flow data from the USGS, BFI calculated using hydrograph separated data from WHAT (Lim et al, 2005).

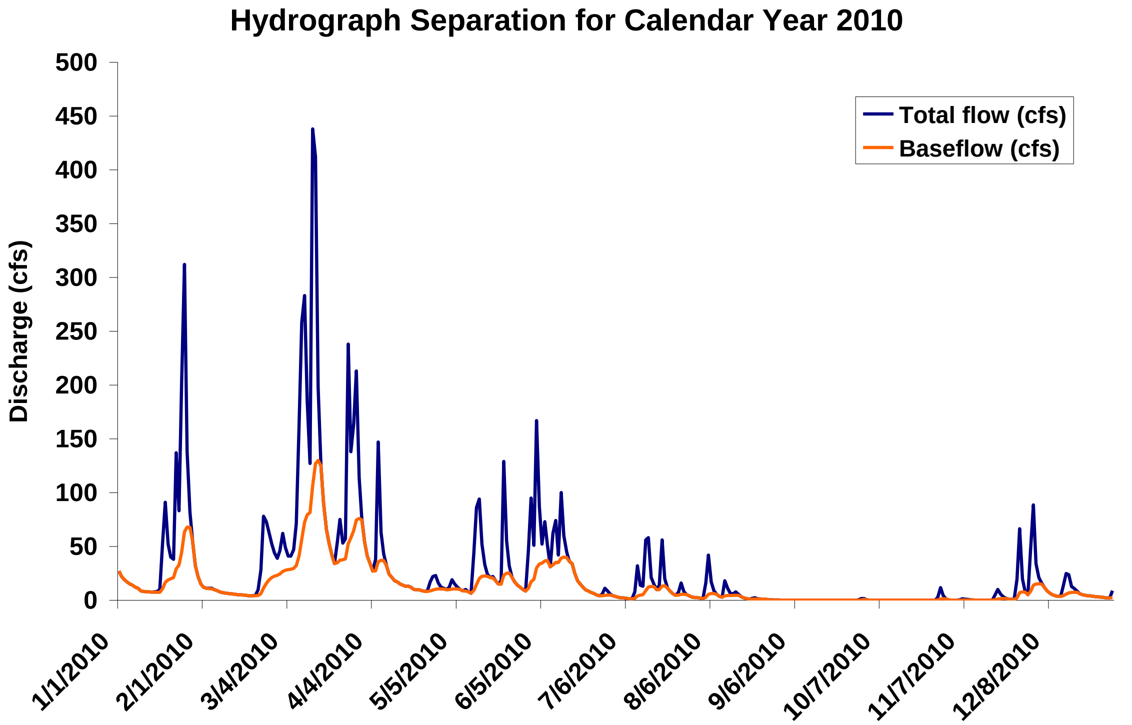

Figure 5 Hydrograph for calendar year 2010, showing baseflow (lower line) and the total flow using data collected at the USGS gage on Hellbranch Run. Notice the stream has very low flow (not detectable) in the fall. Some stream lengths downstream on Hellbranch did not have hydrologic connectivity in the late fall.

The winter provides the highest flows, typically in January, and the lowest flows tend to be during late summer and fall when precipitation is low, temperatures are high and baseflow is low (Figure 6 and Table 3).

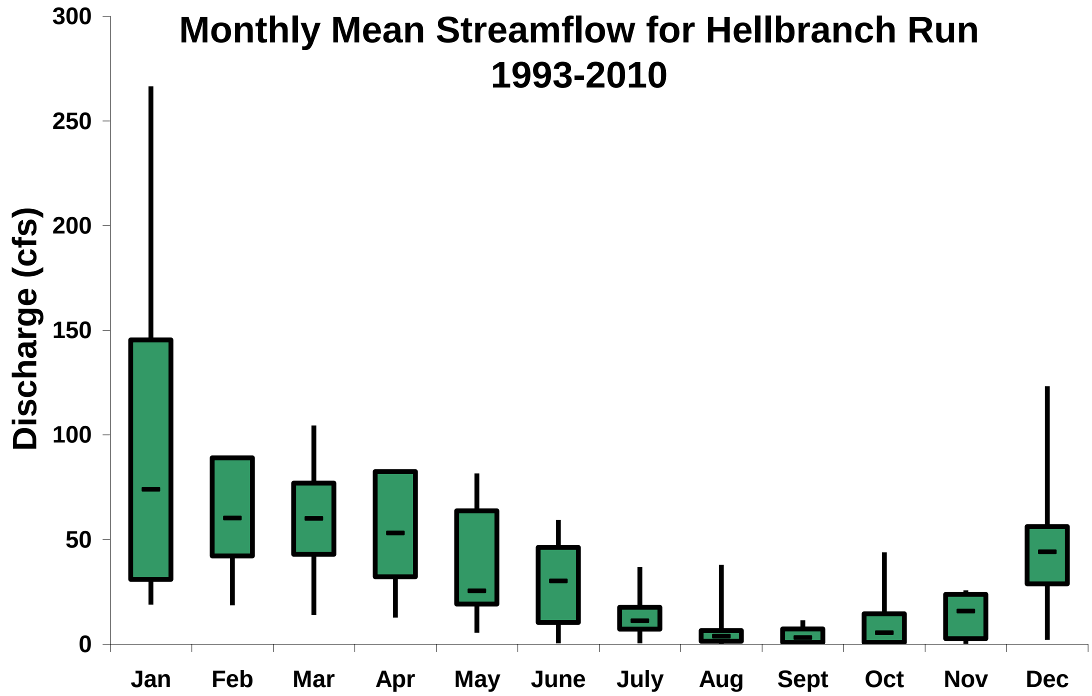

Figure 6 Box plot for monthly mean streamflow for Hellbranch Run. Daily average streamflows were used to calculate mean monthly discharge for each month in the 1993-2010 record, only monthly means are used in this plot. Here error bars represent maxima and minima, the box is the inter-quartile range and the dash in the box is the median. N=18 for each box.

A time series of total flow in $m^3 y^{-1}$ and total yearly precipitation shows the trend overtime for total yearly flow, which is mainly a function of total precipitation (Figure 7).

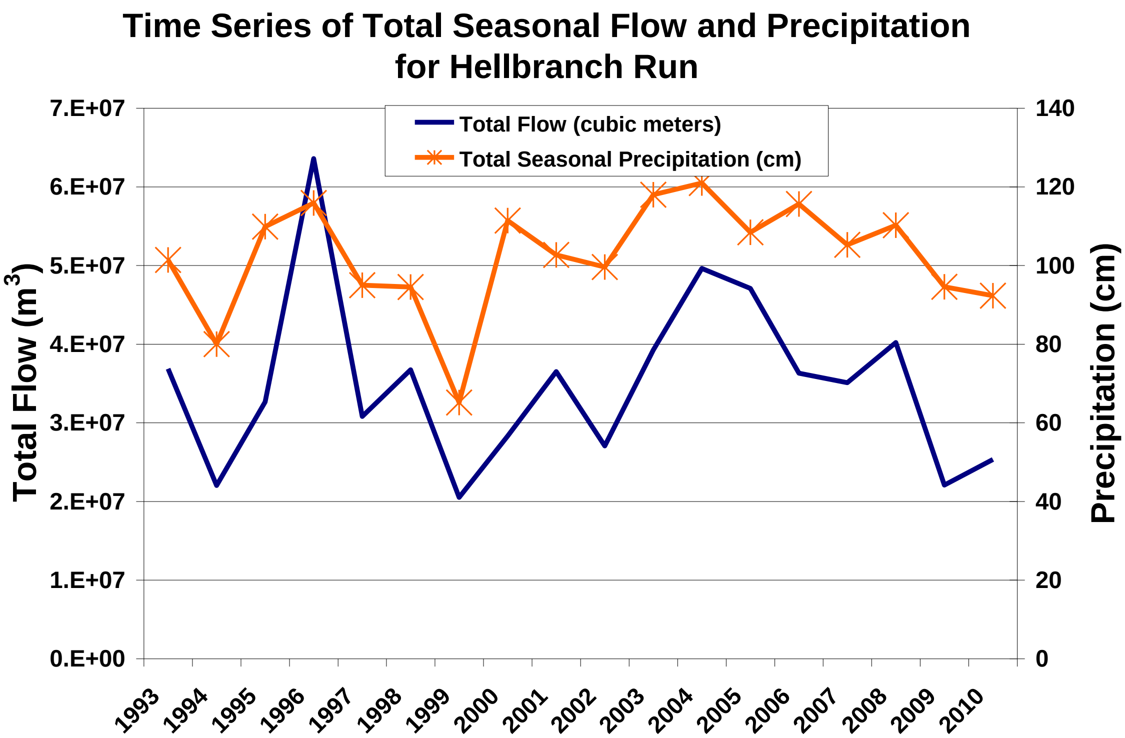

Figure 7 Time series showing total yearly flow and total precipitation using precipitation records for years 1993-2010 attained courtesy of the Central Ohio Rain Gage Network (CORN). Yearly flow was calculated using daily average flows, for each day in the time period.

A streamflow cumulative distribution graph is another way to visualize the percentage of a streams groundwater discharge component and runoff component and how these proportions change with wet and dry conditions (Figure 8).

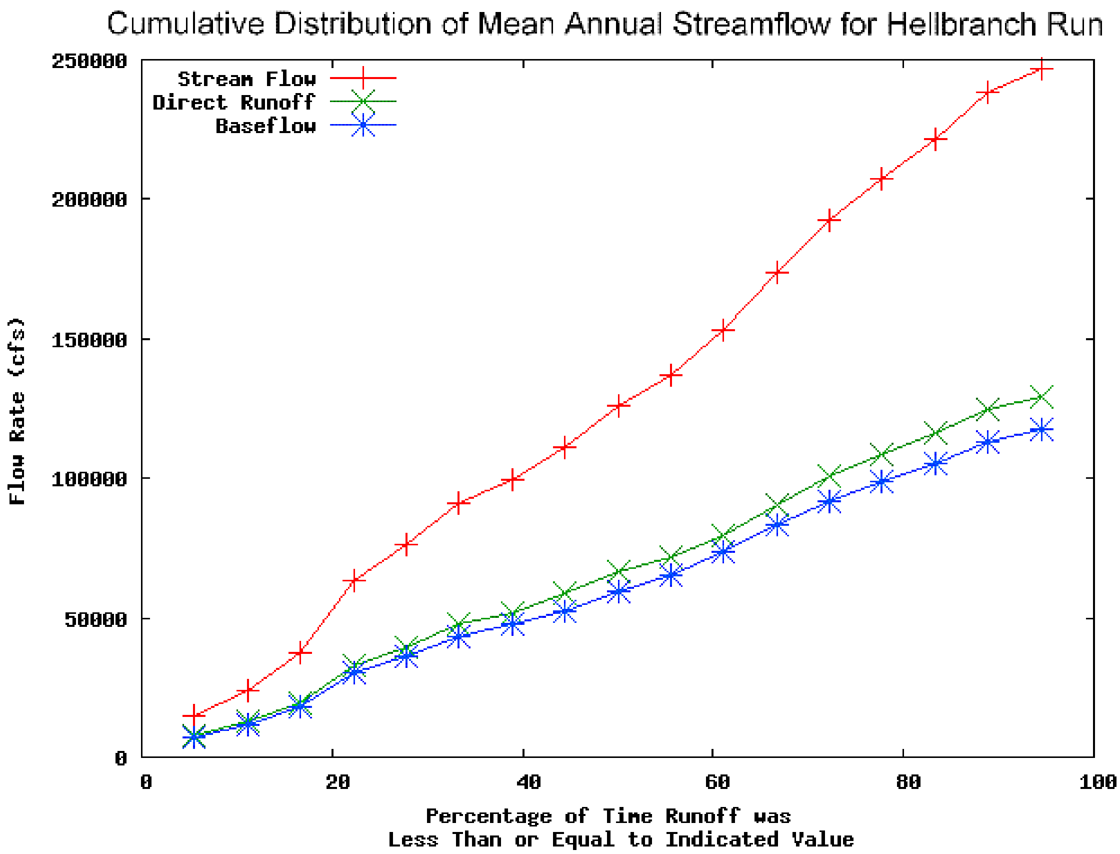

Figure 8 Cumulative distribution function of mean annual streamflow, estimated mean annual surface runoff, and estimated mean annual base flow for Hellbranch Run calculated using "WHAT"(Lim et al, 2005). The x-axis represents the ranked values of flow, with the lower values to the left representing the lowest flows ever recorded (driest times) and moving to the right on the x-axis represents higher flows and wetter conditions.

Figure 9 shows the cumulative flow distribution for the Little Darby Creek at West Jefferson Ohio. Although, the Little Darby has a larger drainage area of 419.6 km^2 compared to the 92.7 km^2 of the Hellbranch, they share characteristics: 1) they are both major tributaries in the Big Darby Creek watershed and thus get similar amounts of precipitation, 2) they both drain predominantly cultivated crop land, and 3) neither lie below a reservoir. However, the Little Darby has much less developed land compared to the Hellbranch. Notice in Figure 9 the Little Darby typically has a larger baseflow component than runoff (BFI for period from 1993-2010 is 0.58) as compared to the Hellbranch. Increased urbanization and impervious surfaces in watersheds (e.g. Hellbranch) can eventually lead to a smaller baseflow component of total streamflow. Consequently this may lead to more variable stream chemistry, temperature, and decreased stream water levels especially in the dry season, all of which contribute to degradation of aquatic habitat (Hatt et al, 2004; Paul and Meyer, 2001).

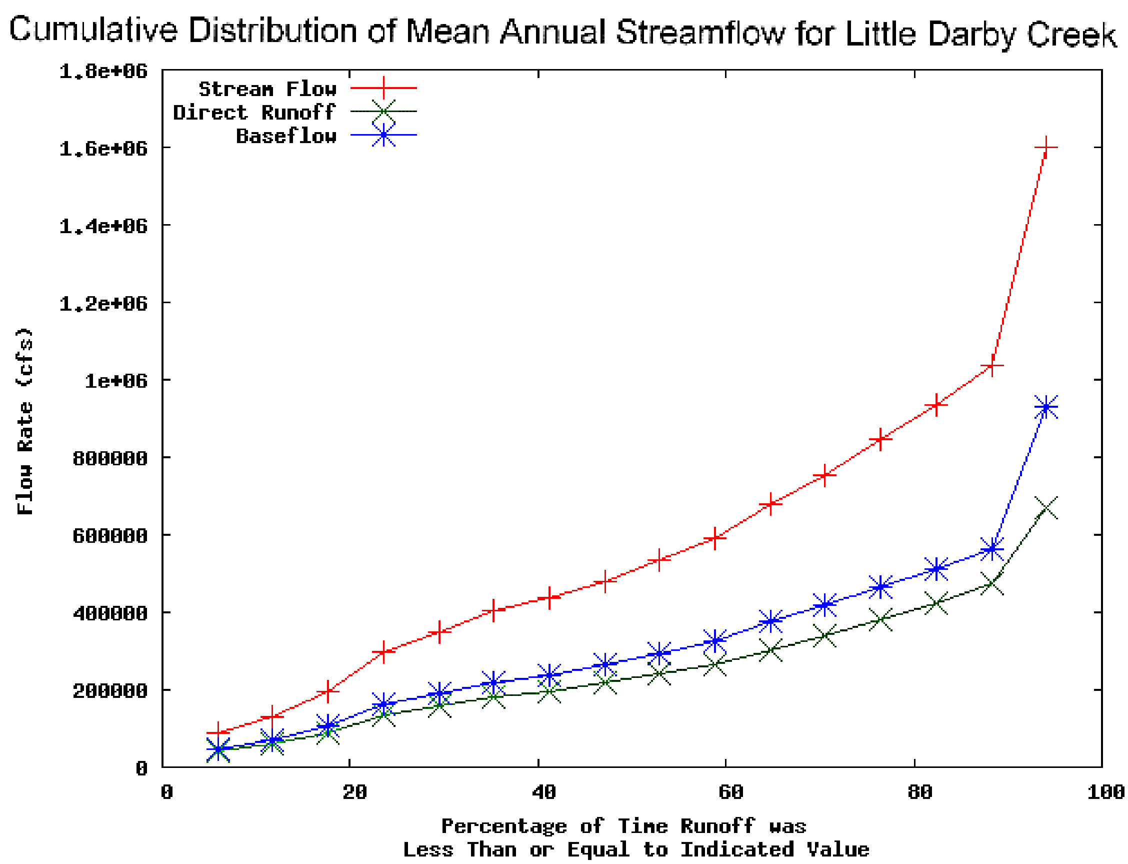

Figure 9 Cumulative distribution function of mean annual streamflow, estimated mean annual surface runoff, and estimated mean annual base flow for the Little Darby Creek at West Jefferson, Ohio.

Major Nutrients and TSS

Load duration curves were calculated for $NO_3^- + NO_2^-$ -N, TP and TSS using historical USGS data and data from this study (from 1992 through 2010). Please note, all graphs that refer to target concentrations or loads are based on OEPA's biological criteria set forth for the Hellbranch Run in the Big Darby Creek TMDL published in 2006, but were also verified by personal communication in 2010 (Ohio EPA, 2006). Results show that NO_3^- + NO_2^- -N is typically found well above the OEPA biological toxicity target concentration of 0.5 mg/L with a median of 2.5 mg/L (see Fig. 9). The curve shows that nitrate has a very weak correlation with total streamflow and the pearson correlation coefficient between NO_3^- + NO_2^- (N) and total streamflow is r=0.36.

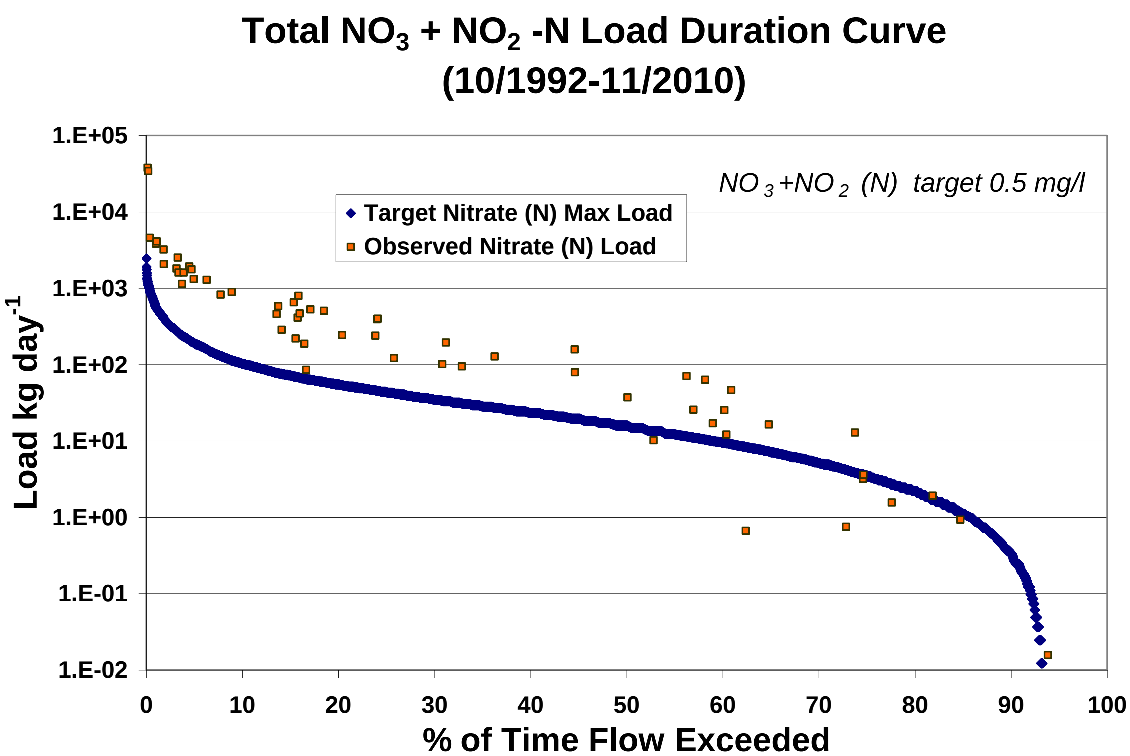

Figure 10 Load duration curve for nitrate + nitrite as N using historical nutrient data collected by the USGS plus this studies' data (n=84), and streamflow data recorded at USGS gage station 03230450 (site M1). Daily flows were ranked and the allowable loads were calculated using the OEPA biological toxicity target concentration of 0.5 mg/L. Note that N loads are almost always above the target load regardless of flow.

There were no strong correlations of nitrate with runoff; instead there is a strong correlation of NO_3^- + NO_2^- (N) with baseflow. The pearson correlation coefficient for the relationship between baseflow and NO_3^- + NO_2^- (N) at site M1 is r=0.728, R^2=0.53 which is a statistically significant relationship with $p<0.01$ and n=21 (Figure 11). This suggests there is some input of residual nitrate that is stored in the glacial deposits or sediments near the stream. The tile drains in some of the farmland could also play a role in increased nitrates during baseflow conditions. Although groundwater pollution of nitrate is common, it cannot be concluded here due to lack of data. However, in some areas of the watershed where the glacial deposits are thin and comprised of sand or gravel lenses, there is a possibility nitrate could make it down to the underlying carbonate aquifer (Riker-Coleman, 2000). If the nitrates' flowpath does reach the carbonate aquifer, it is particularly vulnerable to nitrate contamination. This is because carbonate aquifers tend to have high hydrologic conductivity due to large openings in the aquifer and the carbonate material has little sorptive capacity (Drever, 1987).

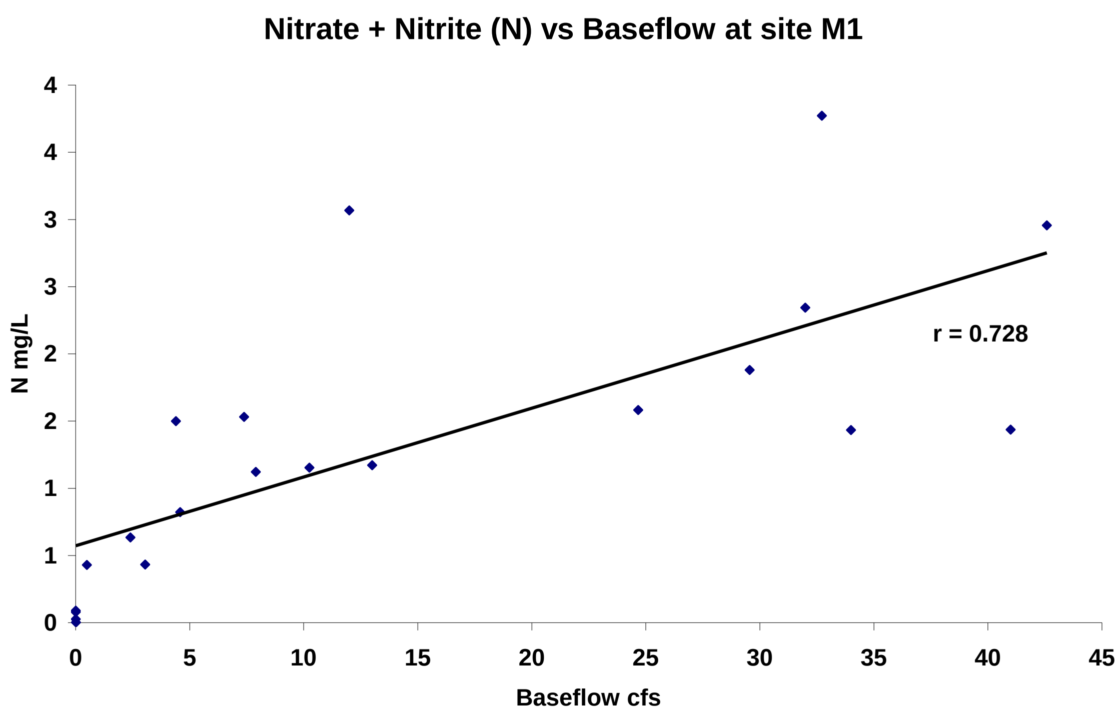

Figure 11 Graph showing nitrate-nitrite (N) vs. baseflow at site M1 (at the USGS gage), with pearson correlation coefficient r=0.728, n=21.

Total P daily loads are more variable; showing many daily loads close to an order of magnitude above and below the target concentration of 0.08 mg/L (Figure 12). However, all but one sample collected in this study had a TP concentration above the OEPA's target. Total P was found to have a moderate correlation with total streamflow r=0.58. Suspended sediment loads are generally below the OEPA target of 28 mg/L except for during the top 10% of ranked flows which represent large storms (Figure 13). TSS also has a moderate correlation with total streamflow r=0.58.

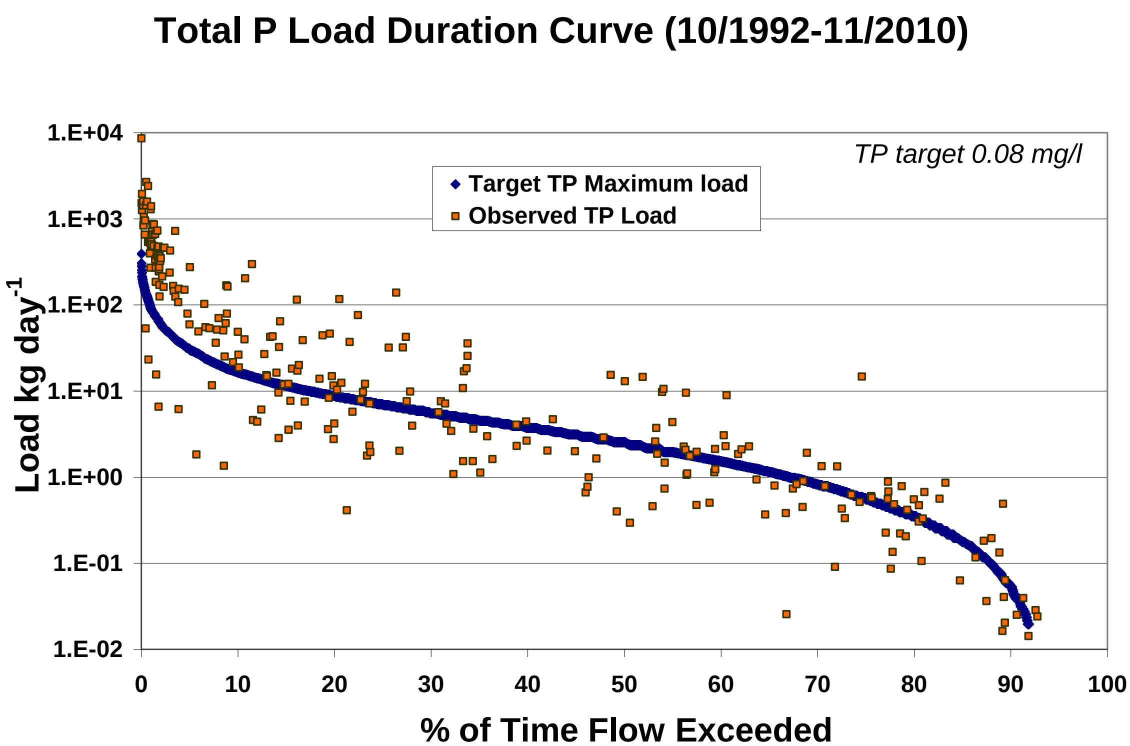

Figure 12 Load duration curve for TP using historical nutrient data collected by the USGS plus this studies data, and streamflow data recorded at USGS gage station 03230450. Daily flows were ranked and the allowable loads were calculated using the OEPA biological toxicity target concentration of 0.08 mg/L.

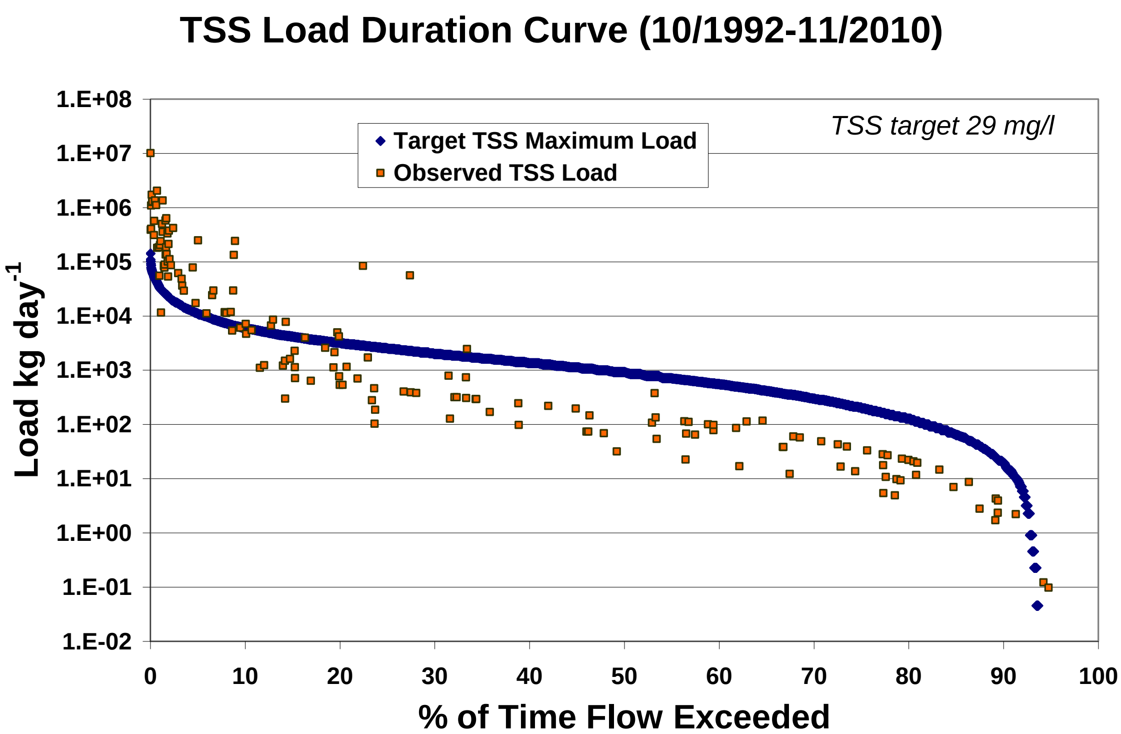

Figure 13 Load duration curve for TSS using historical nutrient data collected by the USGS plus this studies data (n=136), and streamflow data recorded at USGS gage station 03230450. Daily flows were ranked and the allowable loads were calculated using the OEPA biological toxicity target concentration of 29 mg/L. Notice higher loads occur during the top 10% highest flow conditions.

There is a distinct seasonal trend on $NO_3^- + NO_2^-$ -N concentrations that can be seen in Figure 14, where N is highest during the wet season (winter) and lowest in the dry season (autumn). Notice HD has higher mean concentrations for any given season. Also, nitrate concentrations exceed the OEPA's biological toxicity target concentration of 0.5 mg/L most of the year at all locations on the stream except for part of the time in the fall or late summer. Seasonally, nitrate is significantly higher (using a t test where α=0.05) in the winter compared to autumn for each sampling location within all seasons (Figure 14). This could be due to cooler temperatures in the winter which can limit N uptake biologically and biological activity in general. Also, denitrification rates of nitrate (removal) have been found to be lower during oxic conditions (Rysgaard et al, 1994). These oxic conditions are more likely to occur in the winter and spring as well because cooler water holds less oxygen and aquatic plant activity is minimal during these seasons (Figure 14). Also, denitrification of nitrate in streams has been found to be highest during low oxygen conditions (Rysgaard et al, 1994). This helps to explain the relatively lower nitrate concentrations recorded in the summer and autumn (see Figure 14), because very low dissolved oxygen levels are common and have been recorded in the Hellbranch during these warm seasons (Ohio EPA, 2004).

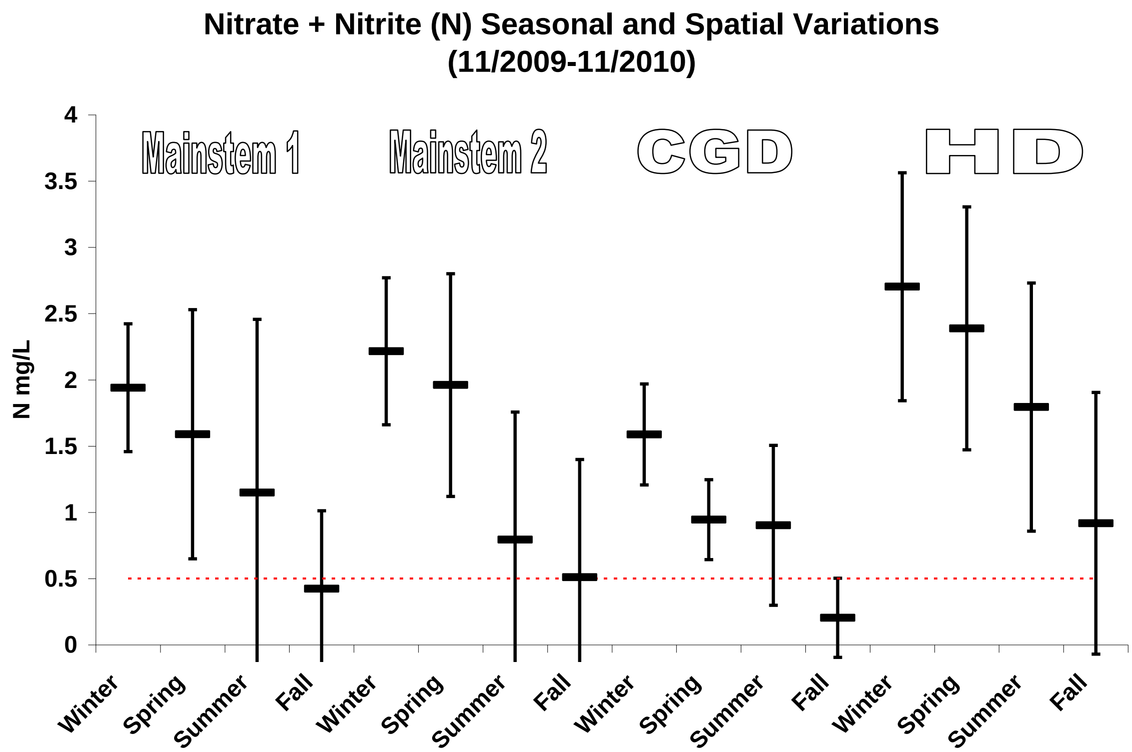

Figure 14 Box & whisker plots comparing each sampling location through each season for NO_3^- + NO_2^- -N in mg/L. The red dashed line at 0.5 mg/L represents the OEPA biological target concentration. Winter plots contain n=6 samples and all other seasons contain n=5. Error bars represent 95% confidence interval around each sample mean. Here winter is from December to March, Spring is April and May, Summer is June to early September and Fall is late September to early December.

Seasonal shifts do not show as distinctive of a control on TP when compared to nitrate. Figure 15 shows higher TP concentrations during the autumn months. The autumn has the most variability in TP concentrations as well (Figure 15). The highest TP concentration within all 4 locations was approximately 1.7 mg/L and recorded in HD in autumn. Higher levels of phosphate in autumn could be from mineral dissolution of phosphate from the underlying sediments. Iron oxide minerals such as goethite, hematite, lepidocrocite, and ferrihydrite are known to adsorb phosphate (Borggaard, 1983). They have also been found to deabsorb phosphate during low oxygen or reducing conditions, which could be expected during summer and fall months when stream temperature is high (Barber, 2002). Also, low dissolved oxygen concentrations have been recorded in the Hellbranch in the past, during summer and fall (Ohio EPA, 2004).

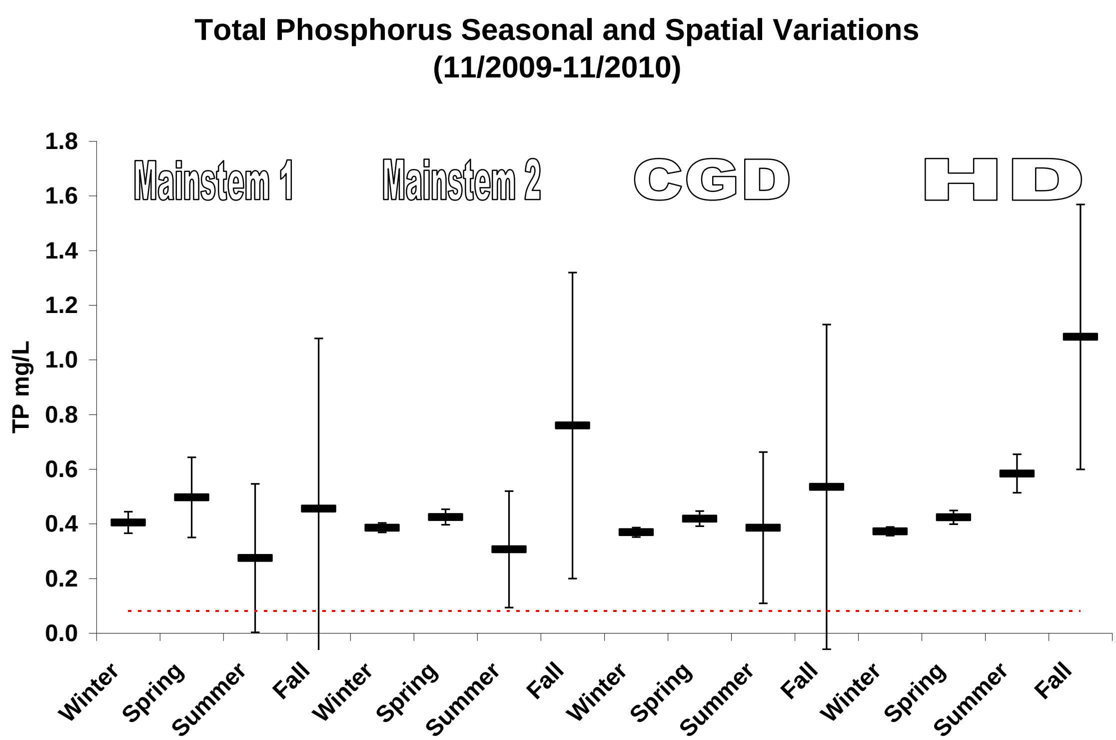

Figure 15 Box & whisker plots comparing each sampling location in each season for TP (as P) concentrations. Mainstream 1 is the location furthest downstream (at the USGS gage). Error bars represent 95% confidence interval around each sample mean. The red dashed line at 0.08 mg/L represents the OEPA biological target concentration. Similar to Fig. 6 winter is from December to March, Spring is April and May, Summer is June to early September and Fall is late September to early December. Winter plots contain n=6 samples and all other seasons contain n=5.

The mean values of TP in Figure 15 are always above the OEPA's biological target of 0.08 mg/L. Only one value of TP was recorded below 0.08 mg/L, at site M1 in mid October, during a month long dry spell. The majority of all P measured is present as DOP, on average in all samples 62% of P is DOP. There is not a large variation among sampling sites for DOP, yet most of the inorganic PO_4^{-3} is observed in the late summer and fall during the dry season.

Ammonium concentrations during the study year were found to be closer to safe levels as set forth by the OEPA, see Figure 16. Summer tends to have higher concentrations and HD has some anomalously high concentrations in the fall (Figure 16).

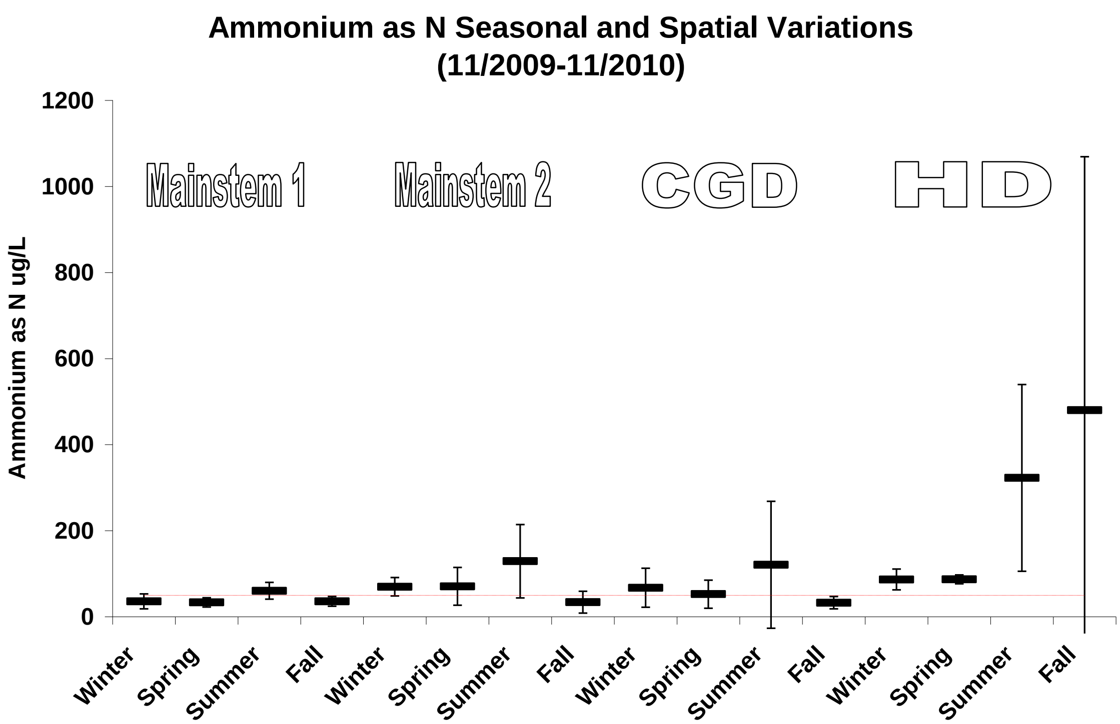

Figure 16 Box & whisker plots comparing each sampling location in each season for NH_4^+-N concentrations. Mainstream 1 is the location furthest downstream (at the USGS gage). Error bars represent 95% confidence interval around each sample mean. The red dashed line at 0.05 mg/L represents the OEPA biological target concentration (note y axis is in ug/L). Winter plots contain n=6 samples and all other seasons contain n=5.

The higher concentrations of ammonium in the summer and fall may represent an increase of organic detritus from flushes of dying vegetation and insects. Notice, however, the retention of ammonium to the mainstem of the Hellbranch is low.

Suspended sediment concentrations do not show a common seasonal trend along the stream. Instead, it appears to be more variable, maybe due to local differences and adjacent erosion (Figure 17). Hamilton Ditch has lower amounts of TSS than the mainstem, during winter, summer and fall, whereas CGD has the highest value of TSS. The values of TSS in the HD and several other locations are significantly below the OEPA's target (Figure 17).

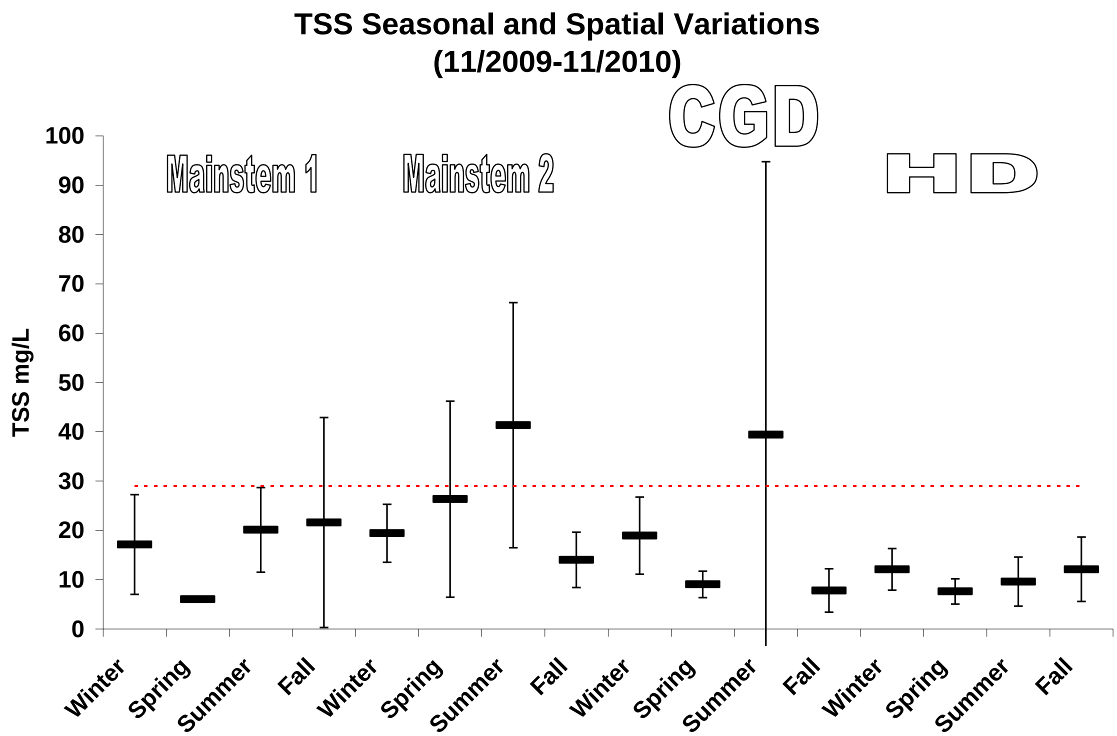

Figure 17 Box & whisker plots comparing each sampling location in each season for TSS concentrations. Mainstream 1 is the location furthest downstream (at the USGS gage). Error bars represent 95% confidence interval around each sample mean. The red dashed line at 29 mg/L represents the OEPA biological target concentration. Winter plots contain n=6, summer n = 4, spring and fall contain n=5 samples.

Hamilton Ditch tends to have much higher levels of N and P compared to the urban catchment CGD and downstream (Figure 18 and Figure 19). Results show that the urban catchment, CGD, has significantly lower nitrate than HD, based on a t-test with α=0.05, see Figure 18. Additionally, CGD, which drains approximately 65% urban land, has the lowest mean concentrations of TP and nitrate of all four sampling sites (Figure 18 and Figure 19). One explanation is, because HD, M2 and M1 drain primarily cultivated crop land- tilled land containing large areas of non-compacted soil that is exposed for much of the year and also undergoes fertilizer application. Cultivated crop land has been found to input more nutrients into surface water systems than urban land (Paul and Meyer, 2001). Hamilton Ditch drains a larger total percentage of cultivated crop lands, whereas CGD has had most of its agricultural land converted to urban use.

Similar results showing higher nitrate and TP IN HD were found by the Ohio EPA study in 2001/02. Additionally, Riker-Coleman, 2000, found nitrate to be higher in HD as compared to CGD. However, the differences between HD and CGD in these two studies were not as dramatic as what is observed currently. This could be due to land-use changes, and the addition of riparian buffers that has taken place since 2000. Also, slightly different sampling locations and local variations in stream morphology/biology could have also played a role.

Shields et al (2008) found a similar result; the two most heavily developed catchments in their study did not have the highest N export, and in general they found no strong correlation between development magnitude and N export. However, increased impervious surfaces- commonly associated with development, was strongly correlated with N Export (Shields et al, 2008). There is a possibility that recent stream restoration projects focused on CGD may have effectively lowered nutrient yields from the CGD catchment (Figure 18 and Figure 19). The two stream restoration projects restored a total of around 7137 linear ft of previously channelized stream reaches along CGD, including additions of riparian buffers with thousands of native plants and trees and the restoration of a natural flood plain for a predicted 100 year storm (Seger, 2008).

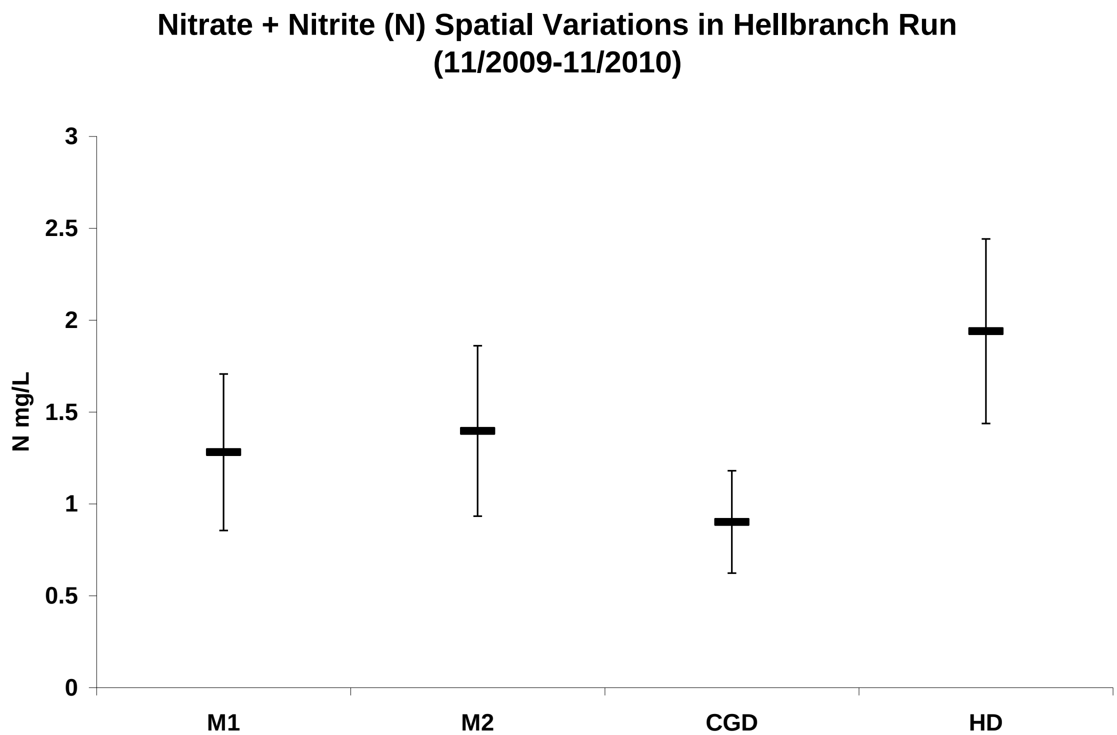

Figure 18 Box & whisker plots comparing nitrate-nitrite as N for each sampling location using all data collected in the yearlong study. Error bars represent 95% confidence interval around each sample mean. For each location n=23.

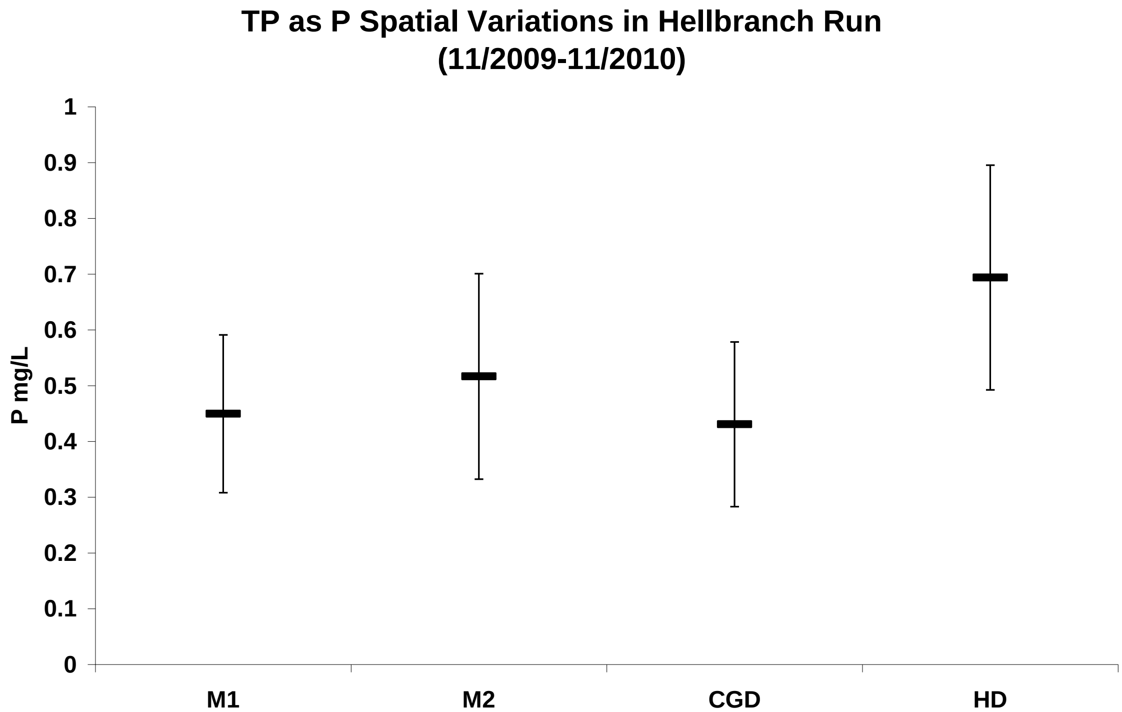

Figure 19 Box & whisker plots comparing TP as P for each sampling location using all data collected in the yearlong study. Error bars represent 95% confidence interval around each sample mean. For each location n=23.

An explanation for higher nutrient loads upstream is the fact that streams play a large role in nutrient retention and transformation, e.g. around 30% on N in streams is removed by either burial or denitrification (Caraco and Cole, 1999). Peterson et al (2001) found that headwaters are capable of retaining 50% of inorganic N inputs. It is reasonable to assume that some portion of N and P that is input upstream is being retained or transformed biologically in the headwaters of Hellbranch Run before making it downstream (Butturini and Sabater, 1998; Peterson et al, 2001). This is magnified during low flows, warmer seasons, and in streams which have long water residence times (i.e. low gradients) such as the Hellbranch (Butturini and Sabater, 1998; Valett et al, 1996). Upstream, in HD, stream temperature was typically the lowest of all four sites followed by CGD, M2 and M1 (Table 3).

Stream Temperatures (ºC) for Each Sampling Site for Each Day in the Study Period				
	M1 (ºC)	**M2 (ºC)**	**CGD (ºC)**	**HD (ºC)**
11/26/09	8.4	8	7.5	7.5
12/14/09	11.6	11.2	11.2	10.6
12/27/09	5.2	6.6	5.6	4.6
1/16/10	0.9	1	0.9	1.5
1/29/10	-0.1	-0.1	-0.1	-0.2
2/21/10	2	1.3	1.5	1.2
3/6/10	3.9	5.5	5.6	4.5
3/21/10	12.5	11.3	12.6	11.2
4/2/10	16.7	16.1	17.8	16.5
4/16/10	18.1	18.1	18.3	17.1
4/30/10	19.1	19.8	19.9	18.8
5/9/10	13.4	12.3	11.6	10.9
5/28/10	21.9	22.3	22.4	20.3
6/9/10	20	21.2	21.3	20
7/31/10	22.7	23.4	22.4	20.9
8/15/10	24.2	24.9	25.3	23.9
8/27/10	17.6	19	17.2	16.9
9/16/10	20.2	20.1	21.5	19.3
9/26/10	16.6	16.7	15.9	15.5
10/14/10	13.8	13.6	13	12.7
11/5/10	7.4	7.1	6.7	7.2
mean	13.14	13.30	13.24	12.42
median	13.8	13.6	13	12.7
Std. Dev.	7.57	7.75	7.84	7.30
Max	24.2	24.9	25.3	23.9
Min	-0.1	-0.1	-0.1	-0.2

Table 3 Stream Temperature for each sampling location and each day sampled during the study.

Suspended sediment shows a different trend, with higher levels downstream on average, this is because sediment load scales with the drainage area, i.e. the further downstream the more land that is being drained by the stream (Figure 20). Because fine grained sediment can stay suspended even in very low flows, it tends to accumulate downstream. Notice the mean concentration of TSS at M1 is above the OEPA's target of 29 mg/L (Figure 20). The highest mean concentration is at site M2, just below the confluence of HD and CGD, a similar finding was found by (Ohio EPA, 2004). Phosphate has been found to relate to TSS, because it tends to adsorb to fine-grain sediments and then is released to the stream upon dissolution, thus showing higher concentrations downstream (Butturini and Sabater, 1998). However, in the Hellbranch there may be more retention/removal of P physically in sediments or biologically, because the highest values are found upstream (Figure 19).

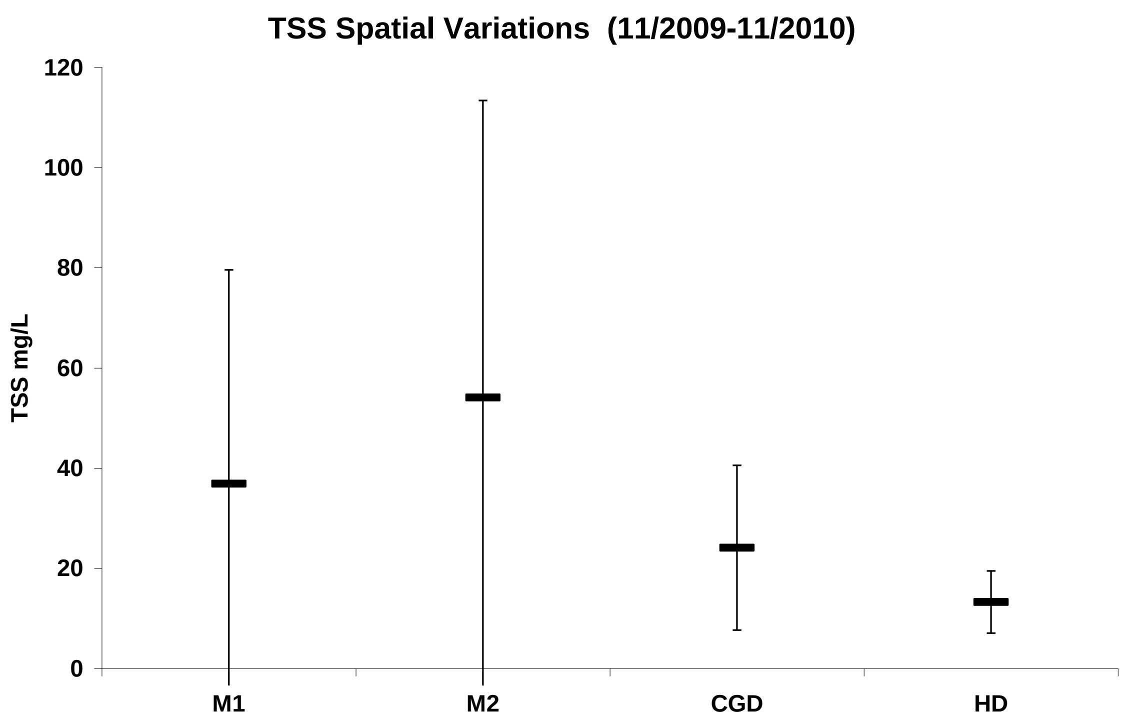

Figure 20 Box & whisker plots comparing TSS for each sampling location using all data collected concentrations. Error bars represent 95% confidence interval around each sample mean. For each location n=22, notice the general increase as you move downstream.

The CGD, shows an interesting variation when looking at major N species. Figure 21 shows all four sampling locations and their mean proportions of different N species including DON, and the relative mean amounts of TN (the size of the pies). Clover Groff Ditch has the lowest mean amount of TN and has slightly higher proportion of DON. The higher proportion of organic N is likely due to the lack of nitrate fertilizers in the stream, or from urban input in the form of organic yard waste. Usually, large amounts of DON is characteristic of forested catchments containing leaf litter and organic detritus, first growth forests tend to have the most DON (Inamdar and Mitchell, 2007). There is a possibility the small increase in DON at CGD is from the new forested areas being placed around the CGD. All four locations show that nearly 75% of N in all stream reaches is inorganic nitrate.

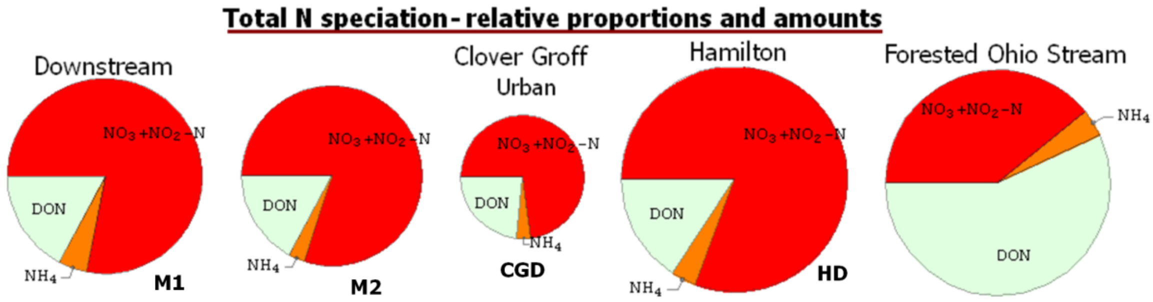

Figure 21 Proportions of average values for three different N species (all as N) from each station from 11/2009 to 11/2010, n=23. The size of the pies represent the relative amounts of TN from site to site. The forested stream is Grand River near Painsville, OH from 1994 to 1996 n=6, size is not to scale for the forested stream; it is about 8 times larger.

The C:N:P molar ratio in aquatic environments was found to represent the needs of marine phytoplankton and is called Redfield's ratio, numerically the Redfield ratio is 106:16:1 (Redfield, 1958). The ratio represents the proportion of each nutrient needed for growth of marine phytoplankton. It has been documented that if a system has more than 1 mole of P but less then 16 moles of N for example, the phytoplankton will not be able to grow. Redfield's ratio can be used as a comparison tool as to which nutrient may be limiting in an aquatic environment; however Hellbranch Run is not a marine system. To classify N:P ratios in freshwater streams we can use cutoff ratios: if N:P is less than 10:1, then N is limiting and if it is above 20:1, P is limiting. From Figure 22, it seems that the Hellbranch Run has excess P, and N is the limiting nutrient, the average TN:TP ratio is approximately 9:1.

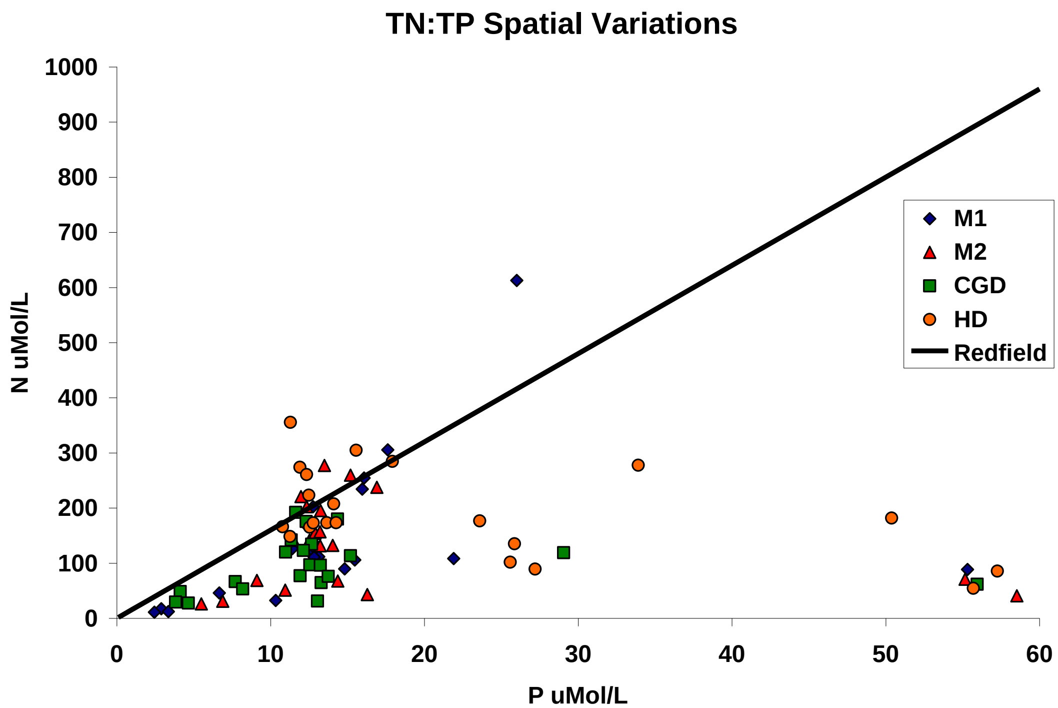

Figure 22 TN and TP in uMol/L for each four locations on the Hellbranch. The outliers with high amounts of P represent fall samples, with most of their TP consisting of inorganic P.

However the inorganic forms of N and P: mainly ammonium, nitrate and phosphates are first to be taken up biologically and assimilated, thus total inorganic N (TIN) and total inorganic P (TIP) are more of a concern for eutrophication and algal blooms. The TIN:TIP molar ratios for the Hellbranch are very different from the TN:TP ratios. When viewing TIN:TIP, P is the limiting nutrient, see Figure 23. The average TIN:TIP ratio is about 56:1, suggesting that inorganic P is the limiting nutrient.

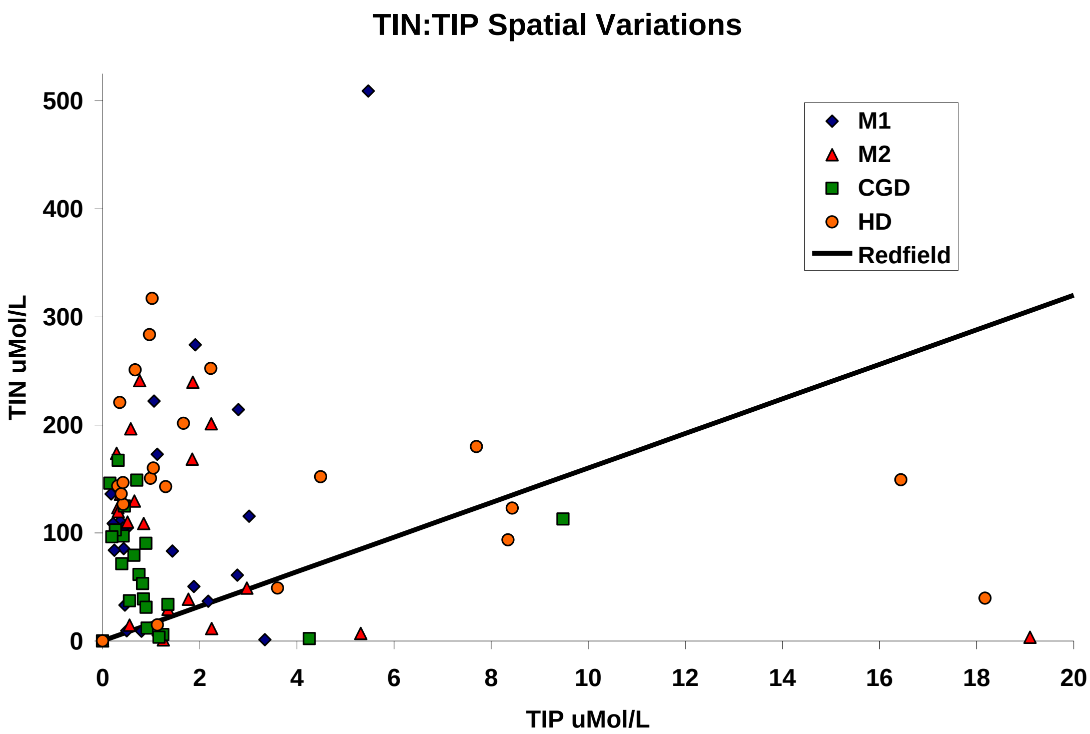

Figure 23 TIN and TIP in uMol/L for each four locations on the Hellbranch.

The high proportions of DOP relative to phosphate also suggest P is the limiting nutrient for plant growth in the Hellbranch. Phosphate could also be retained by adsorption to minerals especially those containing iron oxides or hydroxides, such as goethite, hematite lepidocrocite, and ferrihydrite (Borggaard, 1983). The proportion of DOP to inorganic phosphate also shows a seasonal variation, in late summer and fall there is very high proportions of phosphate relative to TP. This could be due to phosphate deadsorption from iron oxides and hydroxides in fluvial sediments. This dissolution of phosphate occurs especially during anaerobic or reducing stream conditions, which has been documented in the summer and fall in Hellbranch (Ohio EPA, 2004; Barber, 2002).

Although the N:P ratio gives insight to nutrient limitation, it is important to note that in the case of the Hellbranch the levels of N and P are very high, and eutrophication is probably common. In other words, most of the time, neither N nor P are likely to be in limiting amounts for algal growth.

Time Series for nitrate, TP and TSS

Using the program LOADEST, historical streamflow data, and nutrient data, along with those from this study, estimated loads were calculated for the period of 01/01/1993 to 12/31/2010. Total P, nitrate+nitrite (N) and TSS daily loads were estimated for each day in the period. The resulting data were combined into total yearly loads; see Figure 24, Figure 25 and Figure 26. There was more TP and TSS historical data available and it was collected over longer stretches of time compared to nitrate. The majority of the nitrate historical data were collected in 1996. The program LOADEST can do a better job at estimating loads with more data, spread over the entire time period and thus the regression model used to estimate nitrate loads was not the same as used for TP and TSS. To determine which model to use, the regression model's residuals are plotted vs. its output z-scores to test if they are normally distributed, if not then the R^2 from this plot will be <0.95. If this occurs, then another regression models' data are chosen as output data, namely the least absolute deviation (LAD) data from LOADEST (Runkel, Crawford and Cohn, 2004). This was the case for nitrate load estimates, and the LAD model was used to compensate for this. The major results from the time series are: 1) an estimated drop in nitrate loads in general between 1993 and 2010 and 2) TP and TSS loads appear to not have changed noticeably during the study period. By observing the total yearly loads, the control that total flow has on estimated loads is very strong; to see the general change overtime estimated loads were normalized. Estimated loads in g d^{-1} were normalized by dividing them by the daily flows in m^3 d^{-1} to get mean concentrations in mg/L per day. The resulting values show the peak winter concentrations of nitrate-Nitrite (N) are estimated to have dropped by about 65% from near 7 mg/L in winter 1993 to 2.4 mg/L in winter 2010 (see Figure 27).

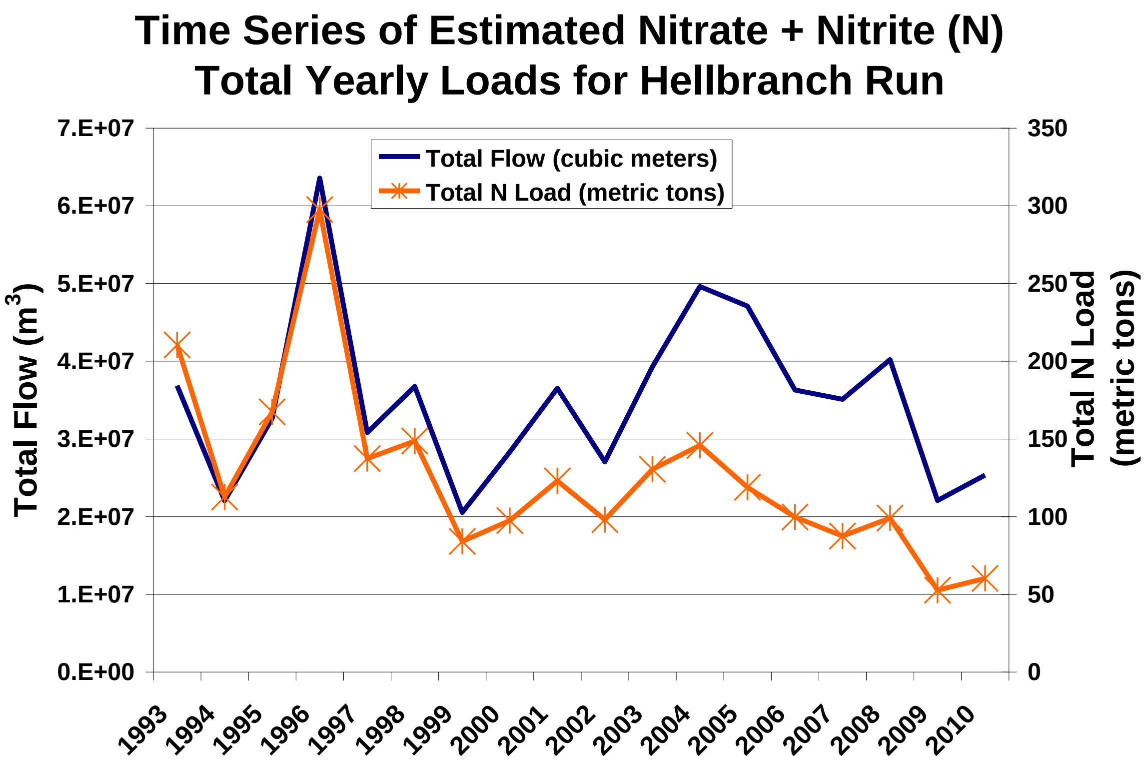

Figure 24 Total nitrate-nitrite (N) yearly loads and yearly flow for Hellbranch Run at the USGS gage (site M1) using historical USGS flow data and nutrient data, including this studies nutrient data. There were n=88 observations used in the estimation model. Notice the general decrease overtime in N loads.

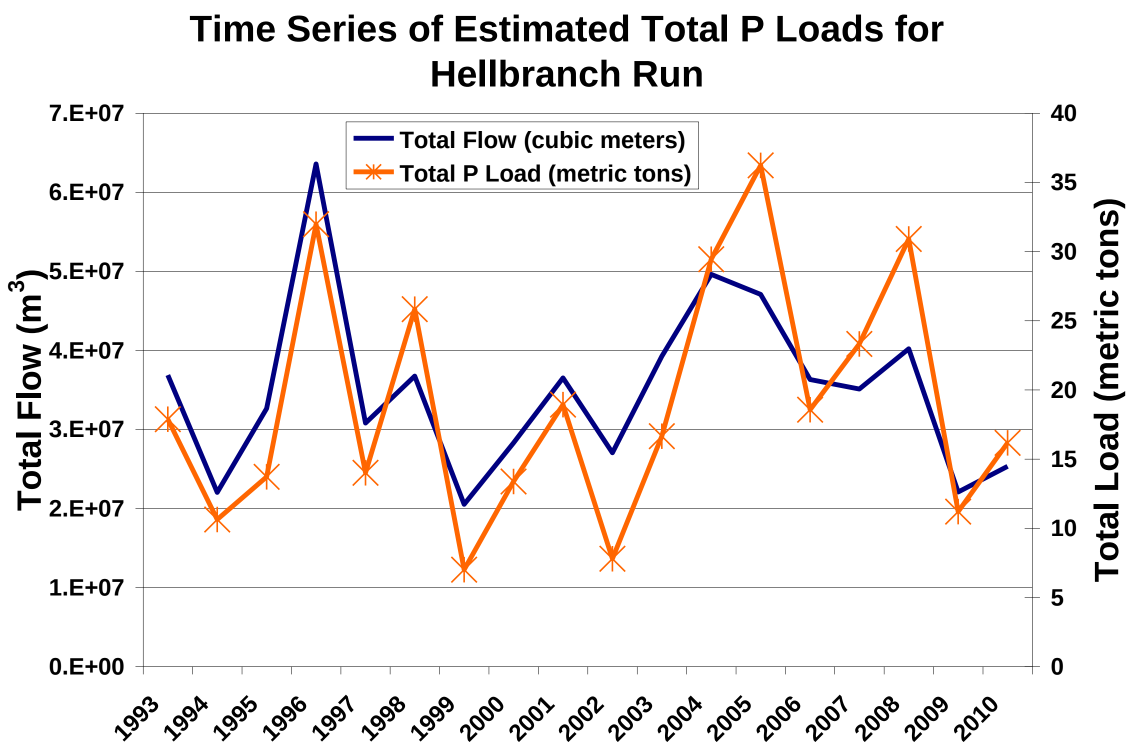

Figure 25 Total yearly TP loads and yearly flow for Hellbranch Run at the USGS gage (site M1) using historical USGS flow data and nutrient data, including this studies nutrient data. There were n=308 observations used in the estimation model. Notice the estimated load was highest in 2005, and exceeds the flow line in 2004, 2005, 2007, 2008 and 2010.

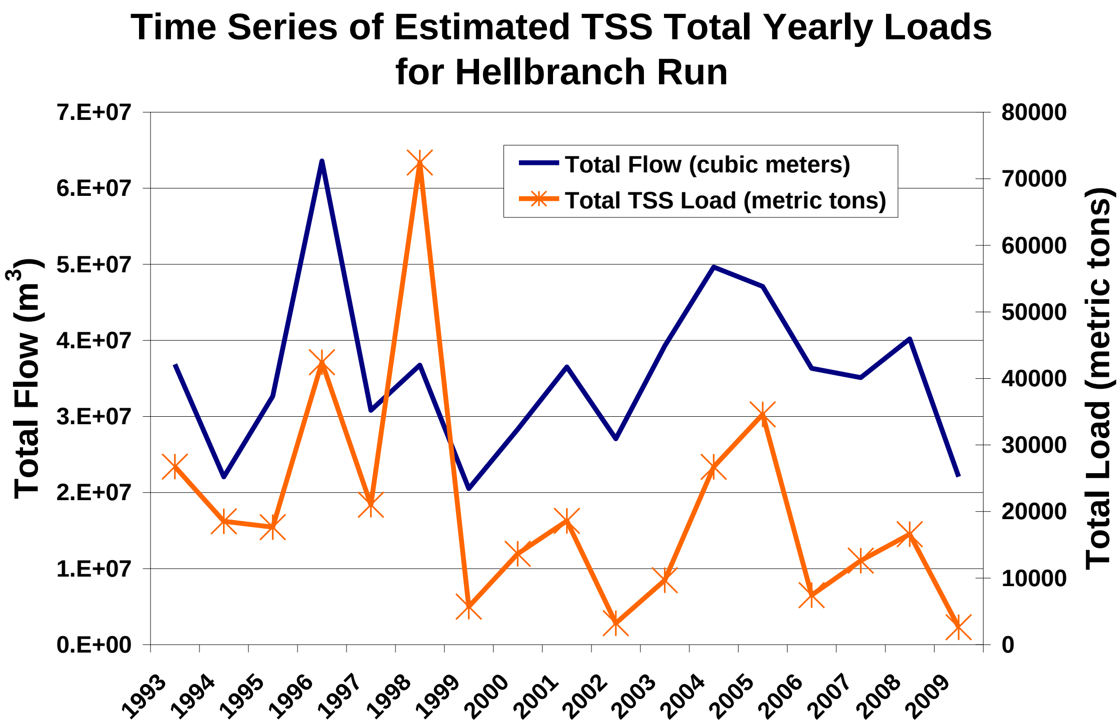

Figure 26 Total yearly TSS loads and yearly flow for Hellbranch Run at the USGS gage (site M1) using historical USGS flow data and nutrient data, including this studies nutrient data. There were n=269 observations used in the estimation model. Notice the estimated load was highest in 1998.

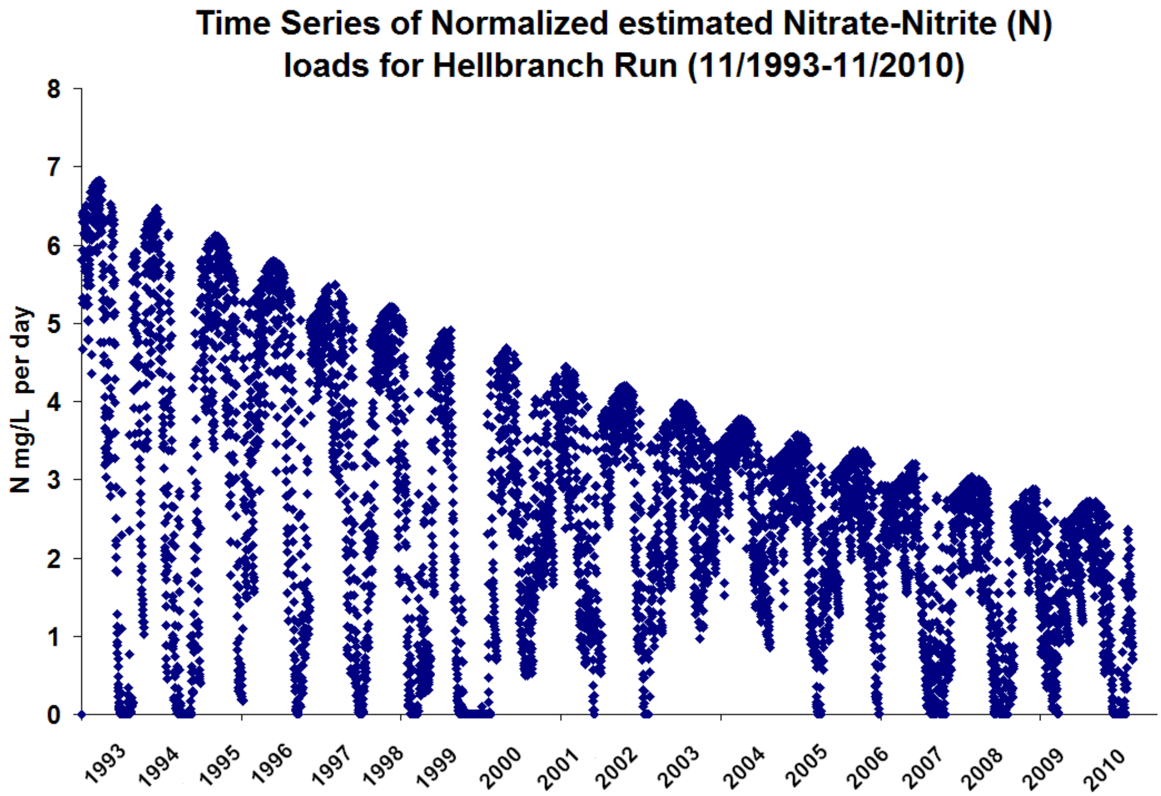

Figure 27 Normalized daily estimates for nitrate-nitrite (N) loads, for the time period 1993-2010. The regression model clearly estimates near a 65% reduction in average nitrate loads over the 18 year period.

The predicted decrease in nitrate loads could be attributed to the increase in urban land-use in the watershed, because urban land provides a smaller input of fertilizer and thus less major nutrients to the stream when compared to cultivated crop land (Paul and Meyer, 2001). Additionally, recent stream remediation projects and creation of stream buffers along the Hellbranch could have also played a role. Normalized data for TP and TSS did not show any noticeable change over the 18 year period, instead most variations are mostly related to variations in daily streamflow.

Conclusions

Total phosphorus and nitrate, show current concentrations and loads frequently above the OEPA's target. Ammonia and TSS, however, are not in violation nearly as often. Nitrate loads are especially high in the winter and spring whereas TP is highest in the fall. Both TP and nitrate concentrations are found to be highest in Hamilton Ditch. The recent efforts to protect the stream and restore the CGD headwater may have been a meaningful factor in the lower nutrient concentrations from this streamreach. However the lower concentrations of N and P in this streamreach are most likely due to less agricultural input of N and P in the catchment. There is considerable nutrient removal or retention along the Hellbranch Run, which is evident by lower concentrations downstream. This is positive news because the effort by many local and national organizations is to lessen the loads of major nutrients to the Big Darby Creek. Interestingly, there is very little correlation between runoff and major nutrients in the Hellbranch. Instead nitrate is related to baseflow and TP and TSS have higher correlations with total streamflow. Using modeling software, LOADEST, there is a 65% predicted decrease in nitrate loads through the Hellbranch mainstem from 1993 to 2010, whereas TP and TSS do not show a predicted change. Lowered nitrate during this time period may be due to the near 15% increase in urban land-use in the watershed during this period, which means less agricultural land-use. There has also been significant effort to protect the entire Hellbranch Run, much of which has been completed well before this study took place. Overall, there is good news and bad news; CGD shows significantly lower N and P concentrations compared to other reaches of the stream, and ammonium is often found below the EPA's target. However, TP and nitrate loads are still very high, often exceeding the OEPA's target loads.

Future Research

Due to the shear amount, much of the data collected in this study was not put into this manuscript. The data for major ion water chemistry are very interesting and should be published in a later manuscript.

The CGD showed unusually low nutrient and TSS concentrations; it would be a worthwhile investigation to focus on the CGD and to analyze local variations and retention of nutrients. At the CGD, research can be done to quantify the effectiveness of stream remediation by measuring stream chemistry or insect counts above, within and below the remediated stream lengths, or within and below the newly connected wetlands.

Another project could look at groundwater along the Hellbranch, the USGS and ODNR have both investigated groundwater, but no one has looked at groundwater quality.

Additionally, a mathematical model could be created from the shear amount of data that has been collected in this study along with the historical data to predict nutrient loads. For example, a simple model for nitrate flux at the stream gage could be modeled using a first order differential equation of the form: $\partial N/\partial t=C_1f(t)-C_2g(t)$. Where C_1 and C_2 are arbitrary positive constants and f(t) is a function representing the input rate of N and g(t) is a function representing the output rate of N, both as a function of time. Temperature could be used as an output function and precipitation or a combination of precipitation, amount of agricultural land in the drainage area and baseflow could be used as the input function. Solve the differential equation for N(t), or amount of N at time t, then use portions of the collected data for comparison when solving for the coefficients C_1 and C_2.

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Appendix

	NO_3^-+NO_2^- (N) ug/L				NH_4^+ (N) ug/L			
Site:	**M1**	**M2**	**CGD**	**HD**	**M1**	**M2**	**CGD**	**HD**
11/26/09	432	187	136	146	33	18	30	61
12/14/09	1581	2319	808	2747	36	39	53	75
12/27/09	2955	3304	1306	4343	45	51	54	100
1/16/10	1530	1620	964	1901	21	106	37	106
1/29/10	2343	2662	2256	3448	76	88	85	68
2/21/10	1498	1595	1573	1652	24	83	174	121
3/6/10	1880	2395	2021	3005	26	37	24	87
3/21/10	1433	1720	1409	1870	23	52	29	37
4/2/10	1436	1854	1314	1986	28	50	35	68
4/16/10	1170	1696	1026	2009	27	119	84	99
4/30/10	1152	1507	494	2141	24	33	26	102
5/9/10	1121	1480	711	1920	45	41	31	80
5/28/10	3067	3266	1179	3886	43	110	88	86
6/9/10	3772	2739	2002	3463	68	78	81	70
7/31/10	634	328	511	1675	73	81	31	454
8/15/10	822	465	406	645	31	76	29	40
8/27/10	429	52	430	2024	86	108	43	496
9/16/10	88	385	1161	1168	43	302	419	554
9/26/10	25	15	37	2	47	82	45	553
10/14/10	79	31	8	466	47	18	22	1623
11/5/10	1	2	33	1224	16	12	14	86

Table 4 Nitrate+nitrite (N) and ammonium data table

	DON (N) ug/L				TN (N) ug/L			
Site:	**M1**	**M2**	**CGD**	**HD**	**M1**	**M2**	**CGD**	**HD**
11/26/09	772	787	698	989	1237	992	864	1196
12/14/09	402	377	217	306	2019	2735	1078	3128
12/27/09	563	530	320	534	3563	3885	1680	4977
1/16/10	193	261	355	306	1744	1987	1357	2314
1/29/10	414	339	349	322	2833	3089	2690	3838
2/21/10	244	302	243	303	1767	1980	1990	2076
3/6/10	423	403	412	561	2329	2835	2458	3653
3/21/10	342	383	443	516	1798	2155	1882	2422
4/2/10	325	270	375	271	1790	2174	1724	2325
4/16/10	367	381	35	317	1565	2195	1144	2425
4/30/10	375	303	830	661	1551	1843	1350	2904
5/9/10	313	331	320	429	1479	1852	1062	2430
5/28/10	172	258	324	297	1237	992	864	1196
6/9/10	437	509	436	455	3282	3634	1590	4268
7/31/10	548	307	389	1762	4277	3326	2520	3987
8/15/10	662	406	313	566	1255	716	932	3890
8/27/10	128	270	207	42	1516	947	748	1250
9/16/10	110	277	88	170	643	430	680	2563
9/26/10	96	503	330	208	241	964	1668	1892
10/14/10	27	523	408	455	169	600	412	763
11/5/10	435	353	338	115	153	572	437	2545

Table 5 DON and TN data table

	PO_4^{-3} (P) ug/L				TP (P) ug/L			
Site:	**M1**	**M2**	**CGD**	**HD**	**M1**	**M2**	**CGD**	**HD**
11/26/09	44	52	87	107	1713	1708	1733	1773
12/14/09	286	175	71	158	386	411	369	387
12/27/09	266	176	40	97	498	418	340	350
1/16/10	34	29	38	30	393	388	389	389
1/29/10	107	55	30	64	395	371	360	369
2/21/10	20	30	43	40	354	356	351	349
3/6/10	17	27	14	34	384	382	382	382
3/21/10	47	42	25	36	406	398	393	396
4/2/10	39	35	18	40	398	400	376	334
4/16/10	41	62	61	94	407	409	412	423
4/30/10	23	49	52	99	397	410	410	437
5/9/10	136	80	78	123	479	435	426	442
5/28/10	100	72	84	92	494	471	471	482
6/9/10	181	212	67	211	546	524	445	555
7/31/10	178	128	80	426	459	339	239	1050
8/15/10	263	168	85	342	678	445	254	843
8/27/10	206	213	128	731	206	213	128	731
9/16/10	47	282	900	801	90	282	900	801
9/26/10	108	505	118	1725	108	505	118	1725
10/14/10	76	1813	404	1560	76	1813	404	1560
11/5/10	317	119	110	792	320	170	144	792

Table 6 Phosphate and TP data table

	DOP (P) ug/L			
Site:	M1	M2	CGD	HD
11/26/09	1670	1656	1645	1666
12/14/09	100	235	298	229
12/27/09	233	242	300	253
1/16/10	358	359	351	359
1/29/10	289	316	330	305
2/21/10	333	325	309	309
3/6/10	367	355	367	349
3/21/10	359	356	368	359
4/2/10	358	365	358	294
4/16/10	366	347	351	329
4/30/10	374	361	358	338
5/9/10	343	354	348	318
5/28/10	394	398	386	391
6/9/10	364	311	378	343
7/31/10	281	211	159	624
8/15/10	415	277	169	501
8/27/10	0	0	0	0
9/16/10	42	0	0	0
9/26/10	0	0	1	0
10/14/10	0	0	0	0
11/5/10	3	52	34	0

Table 7 DOP data table

Site M1	F mg/L	Cl mg/L	SO4 mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L
11/26/09	0.28	112.0	58.2	60.9	2.47	27.5	86.8
12/14/09	0.20	58.2	33.8	28.3	3.08	20.7	59.6
12/27/09	0.20	47.9	35.3	22.7	3.28	23.2	61.7
1/16/10	0.18	132.0	62.7	65.8	1.92	29.0	76.6
1/29/10	0.20	81.5	48.6	40.4	2.53	27.2	81.5
2/21/10	0.21	284.7	69.4	146.0	2.45	33.5	89.7
3/6/10	0.19	106.2	54.0	54.4	1.77	24.0	82.2
3/21/10	0.20	77.4	46.0	40.1	2.33	27.1	76.0
4/2/10	0.20	72.1	45.6	37.9	1.97	28.2	75.0
4/16/10	ND	83.6	48.0	47.33	2.18	32.7	79.7
4/30/10	ND	96.7	50.5	53.53	1.94	31.2	67.9
5/9/10	ND	99.8	46.9	55.41	2.08	30.3	73.4
5/28/10	0.34	73.0	38.56	35.94	1.83	26.17	70.24
6/9/10	0.32	50.1	26.11	25.25	2.82	18.56	51.72
7/31/10	0.35	80.7	38.92	45.73	2.33	21.24	45.46
8/15/10	0.32	77.3	33.98	43.27	2.66	17.66	46.55
8/27/10	0.39	87.04	37.97	50.70	2.62	24.03	64.16
9/16/10	0.346	72.40	38.15	47.42	2.655	29.35	71.22
9/26/10	0.249	78.03	40.03	49.90	2.95	29.62	80.23
10/14/10	0.313	87.26	44.68	55.21	3.05	29.36	81.17
11/5/10	0.35	146.50	55.57	103.70	6.144	29.17	67.55

Table 8 Major ions data table for site M1

Site M2	F mg/L	Cl mg/L	SO4 mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L
11/26/09	0.26	128.0	47.8	70.1	2.79	26.1	80.9
12/14/09	0.21	62.7	40.7	31.0	2.37	23.3	67.3
12/27/09	0.21	58.1	42.3	28.1	2.83	25.2	68.2
1/16/10	0.18	185.4	59.8	103.9	2.18	26.5	74.6
1/29/10	0.20	86.7	49.2	43.1	2.41	27.2	81.6
2/21/10	0.21	416.7	70.0	208.0	2.67	32.6	94.9
3/6/10	0.19	126.8	56.5	68.0	1.88	25.9	90.3
3/21/10	0.20	86.6	49.4	45.0	2.19	27.4	76.2
4/2/10	0.20	81.9	49.4	42.9	1.92	28.7	77.5
4/16/10	ND	96.7	47.4	52.42	1.94	32.7	79.6
4/30/10	ND	103.7	49.6	57.03	1.89	31.7	73.5
5/9/10	ND	125.0	47.4	68.20	2.20	30.4	73.4
5/28/10	0.36	78.2	38.91	38.44	1.74	25.51	68.54
6/9/10	0.28	40.3	18.88	22.18	2.88	13.05	35.96
7/31/10	0.35	98.2	43.54	51.64	2.55	20.80	42.88
8/15/10	0.31	58.4	40.32	33.79	2.45	15.57	42.27
8/27/10	0.38	127.37	41.97	68.35	3.02	21.52	53.26
9/16/10	0.314	443.66	36.44	238.05	4.098	34.14	71.68
9/26/10	0.381	173.64	126.09	99.12	7.55	31.50	80.20
10/14/10	0.330	309.56	53.31	153.86	8.34	29.56	87.48
11/5/10	0.47	48.66	77.98	53.25	3.736	16.90	52.74

Table 9 Major ions data table for site M2

CGD	F mg/L	Cl mg/L	SO4 mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L
11/26/09	0.32	152.1	65.2	84.5	3.40	23.2	73.9
12/14/09	0.22	56.4	48.7	30.3	2.28	18.1	57.2
12/27/09	0.23	60.6	58.2	32.6	2.29	23.3	66.9
1/16/10	0.19	239.8	67.2	114.2	2.63	22.8	68.7
1/29/10	0.22	107.5	61.9	57.1	2.65	25.7	82.3
2/21/10	0.23	406.2	77.8	211.6	3.05	29.6	85.5
3/6/10	0.20	168.5	71.7	85.8	2.10	25.2	88.2
3/21/10	0.18	99.3	60.2	53.9	2.51	25.5	72.7
4/2/10	0.21	95.2	61.1	51.5	2.24	26.9	69.3
4/16/10	ND	131.0	64.2	71.94	2.47	31.1	79.0
4/30/10	ND	110.6	63.3	61.96	2.36	29.1	64.8
5/9/10	ND	141.6	64.8	78.02	2.55	30.2	71.7
5/28/10	0.33	94.3	49.16	47.42	2.10	22.76	61.08
6/9/10	0.27	48.6	29.57	27.17	2.35	13.95	40.02
7/31/10	0.33	83.7	46.86	45.04	2.45	19.52	41.15
8/15/10	0.28	49.2	28.01	25.96	1.92	13.52	36.04
8/27/10	0.43	148.00	51.63	78.22	2.82	23.29	58.80
9/16/10	0.11	46.12	19.10	30.26	5.713	5.40	25.94
9/26/10	0.57	327.17	127.89	125.99	7.99	30.14	115.69
10/14/10	0.50	188.04	66.27	106.13	7.97	27.26	78.68
11/5/10	0.50	58.01	80.53	60.80	3.678	16.80	50.66

Table 10 Major ions data table for site CGD

HD	F mg/L	Cl mg/L	SO4 mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L
11/26/09	0.33	253.3	69.1	137.8	4.62	28.6	87.3
12/14/09	0.24	78.2	51.6	41.7	2.38	25.4	74.6
12/27/09	0.21	65.1	45.1	30.5	2.58	27.1	74.6
1/16/10	0.00	361.4	70.6	169.8	2.60	30.6	90.4
1/29/10	0.22	99.8	56.3	51.5	1.99	29.1	89.4
2/21/10	0.15	619.2	74.9	310.6	2.99	36.7	118.2
3/6/10	0.19	126.3	57.9	67.2	1.89	27.1	91.5
3/21/10	0.20	92.4	49.6	47.9	1.93	28.3	77.4
4/2/10	0.20	88.2	48.1	46.0	1.83	29.2	77.5
4/16/10	ND	109.2	47.9	59.55	1.82	33.2	80.8
4/30/10	ND	142.9	57.2	78.61	1.95	34.0	82.4
5/9/10	ND	159.8	56.0	89.02	2.21	34.1	89.4
5/28/10	0.35	80.6	41.38	41.70	1.79	26.83	78.14
6/9/10	0.30	48.8	20.69	28.75	2.88	15.44	46.50
7/31/10	0.48	191.7	55.57	101.60	3.30	25.45	60.47
8/15/10	0.45	101.1	44.24	56.98	3.44	22.30	64.19
8/27/10	0.66	434.73	68.34	229.64	4.19	43.08	109.88
9/16/10	0.52	438.68	60.92	245.99	5.62	32.12	79.53
9/26/10	0.94	516.90	116.90	285.82	6.73	50.89	136.05
10/14/10	0.76	873.68	82.25	492.18	10.81	50.15	134.63
11/5/10	1.17	272.62	132.39	184.26	4.86	40.94	113.83

Table 11 Major ions data table for site HD