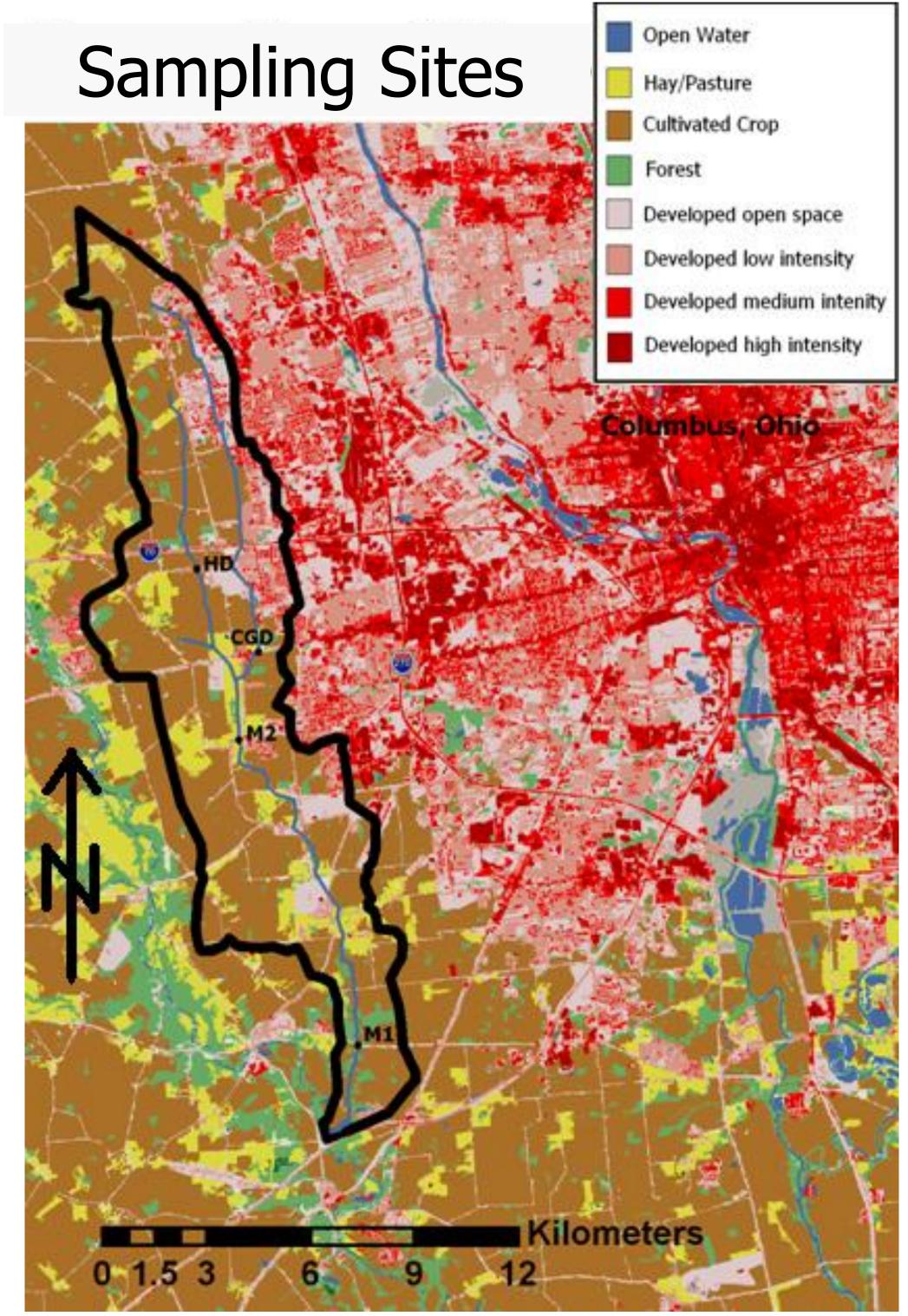
Spatial and Temporal Variations of Water Quality in a Recently Urbanized Watershed in Central Ohio

Introduction

The Big Darby Creek, just west of Columbus, Ohio is declared a National Scenic River and is home to several endangered species of aquatic life. Recent threats to its water quality have gained national attention. A major tributary, Hellbranch Run, drains land (95.8 km²) in western Franklin County that has recently seen conversion of agricultural land to urban and commercial. Urbanization is known to cause pulses of fine sediments to be flushed into streams when storm water meets large impervious surfaces (e.g. roads, roofs and parking lots). The Hellbranch watershed drains row cropland mainly which supplies large amounts of inorganic nutrients derived from fertilizers. Also much of the headwaters of Hellbranch Run are channelized ditches with oversized cross sectional area, once built to drain farmland. Due to a very low gradient they are stagnant and show little ability to naturally recover.

Objective

Knowing current spatial and temporal trends of water chemistry is important for those working to protect the stream and to evaluate the success of restoration projects. Due to a major increase in impervious surfaces in the watershed over the last 15 years and subsequent changes to its hydrology, water quality is expected to be further degraded.



2006 Land-use, land-cover data from the national land cover database (NLCD), and has 30m spatial resolution.

Methods

Water samples are being taken at four locations on the Hellbranch (see map) and takes place every two weeks over the course of one year starting in Nov. 2009. Sampling involves taking a liter of water from the stream and using the Thermo Scientific Orion 5 Star Meter to measure temperature, pH and TDS in the field. Samples are also filtered through a 0.45 micron glass fiber filter at the sampling site and then frozen (to prevent biologic nutrient breakdown). Pre-weighed filters are dried and reweighed to the nearest .0000g to find total suspended solids (TSS). The samples are taken to Dr. W. B. Lyons' lab in the School of Earth Sciences to be analyzed for major nutrients, including nitrate, nitrite, phosphate, ammonium and silica concentrations using the Skalar SAN++ analyzer, an automated wet chemistry analyzer. Using ion chromatography we determined major cations Na⁺, K⁺, Mg²⁺, Ca²⁺ and major anions Cl⁻, Nitrate and Sulfate. Daily average loads were estimated using a time series of historic data of time, flow and concentrations and LOADEST software which performs log linear regression models. The web

application "WHAT" created at Purdue University was used for hydrograph analysis and baseflow separation; the recursive digitial filtering method was used for hydropgraph separation.



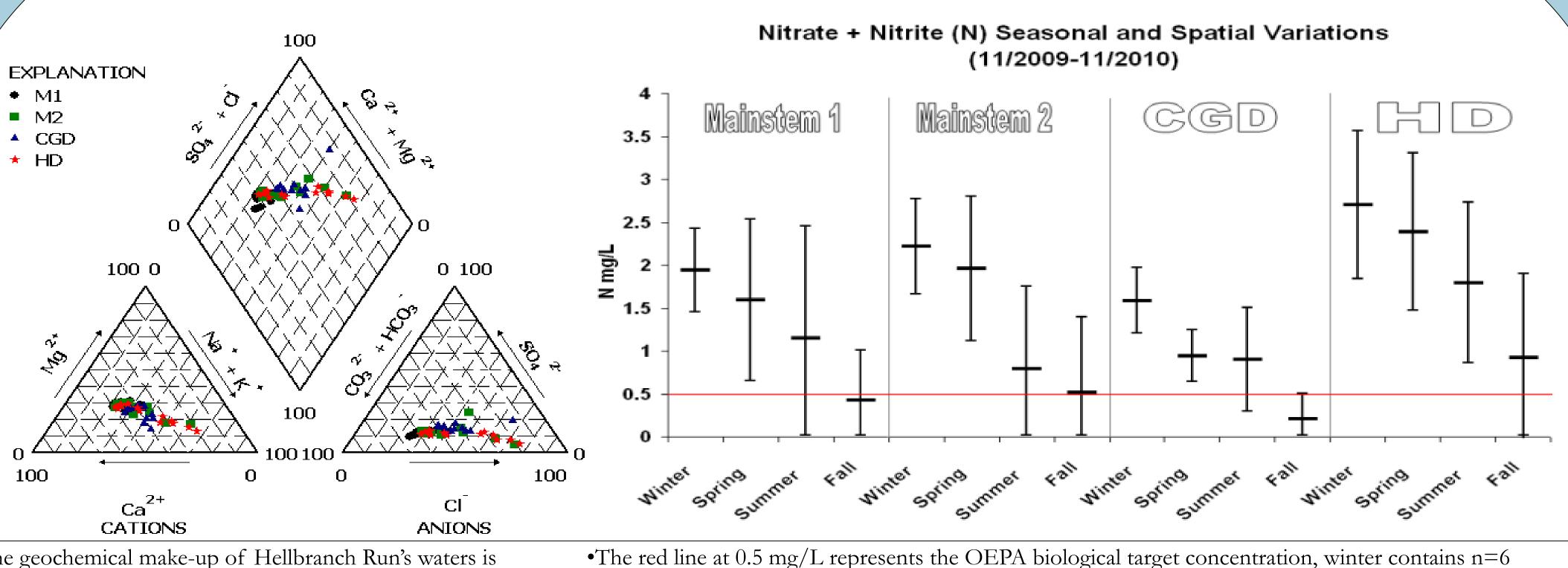
John M. Volk

School of Earth Sciences, The Ohio State University



Schoeller Plot for Baseflow Chemistry

Results and Discussion



Inorganic N:P Spatial Variations

Total Inorganic P (eq)

•The geochemical make-up of Hellbranch Run's waters is mostly Ca-Na-Cl and Ca-Mg-HCO₃, some are Na-Cl waters. •Total dissolved solids range from 224-2018, median 587 mg/L. Highest values of TDS are found in HD (mean 851 mg/L while lowest found in the CGD (mean 558 mg/L) target levels. HD has the highest levels of most solutes and inorganic nutrients likely from agricultural fertilizers. •The mean TIN:TIP molar ratios for the Hellbranch is ~56:1, suggesting that P is limiting.

•Na-Cl water is found upstream near urban areas, and highest in HD. HD site is near a major U.S. interstate highway which receives large deicing salt applications

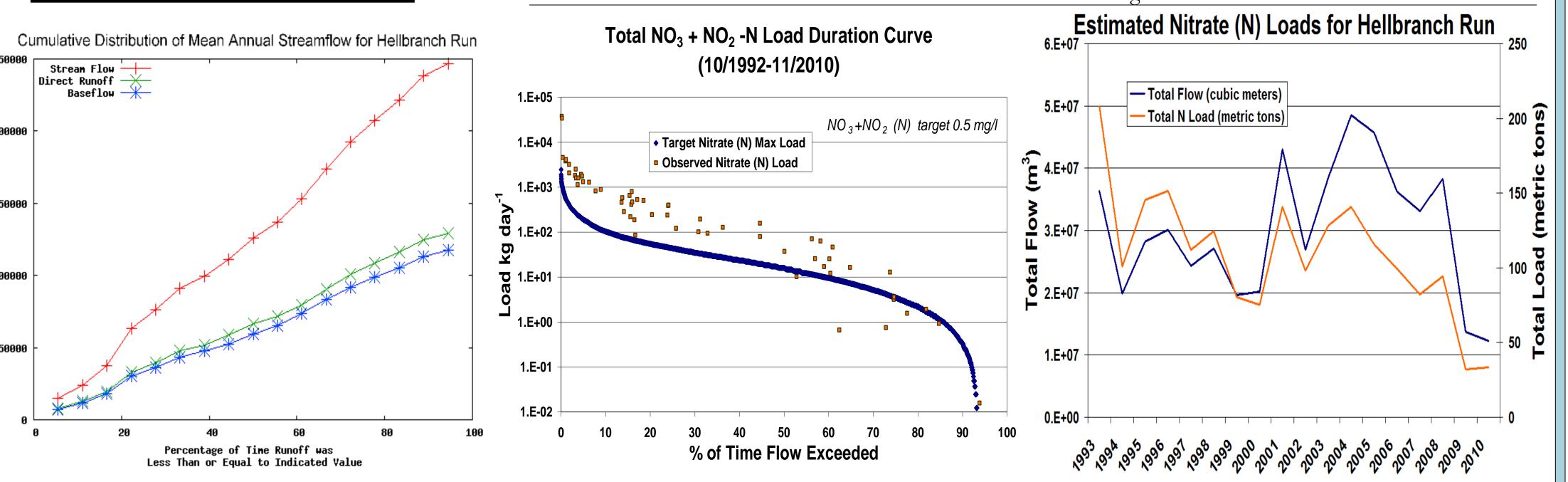
> Statewide EPA Biological **Toxicity Target Criteria** Nitrate-N: 0.5 mg/L Phosphorus: 0.08 mg/L **TSS: 29 mg/L** Chloride: 230 mg/L

▲ Site 2 Site 3 • Site 4
— Redfield Ratio

samples while other seasons contain n=5. Error bars represent 95% confidence interval around each

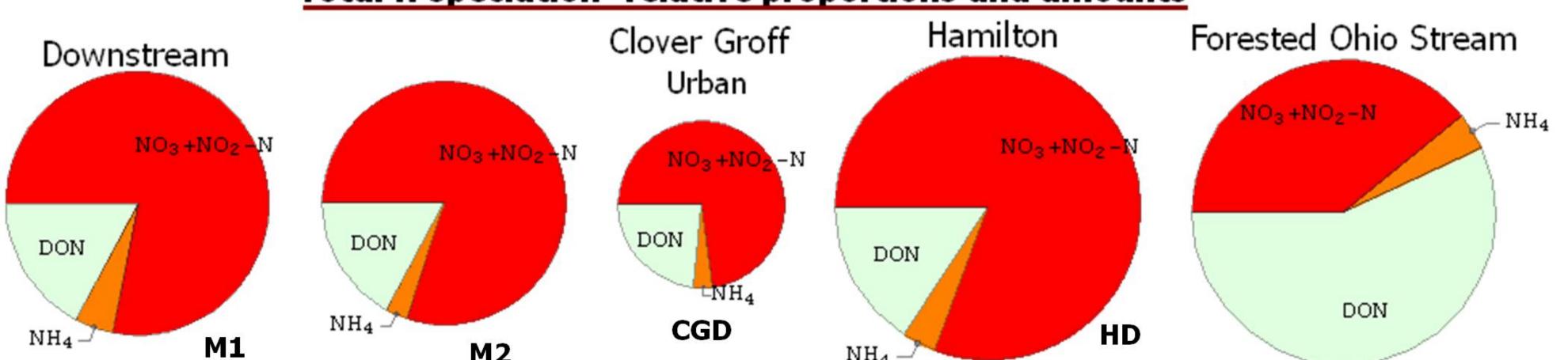
sample mean. Note the strong season control on nitrate, and lower concentrations in CGD.

•TSS, TP, and silica have moderate (0.6 < R < 0.8) positive relationships with streamflow; NO_3^- is related to baseflow. •TDS, Sulfate, Cl⁻, Na⁺, Ca²⁺, and Mg²⁺ have a moderate-strong negative linear relationship with streamflow. •Nitrate and TP concentrations decrease downstream while TSS is highest at the confluence of HD and CGD.



- •The base flow index (BFI) for the 18 year period is 0.48 and daily mean baseflow was found to be 0.53 m³ s⁻¹ and median 0.26 m³ s⁻¹, recorded at location M1. •Instantaneous discharge data from 1993 to 2009 was provided by the USGS, LOADEST input data included n=303 for TP, n=261 for Cl⁻, n=81 for Nitrate (N).
- •The LOADEST model which includes decimal-time as an explanatory variable estimates slight increase or no change in TP and Cl⁻, but a decrease in NO₃⁻.

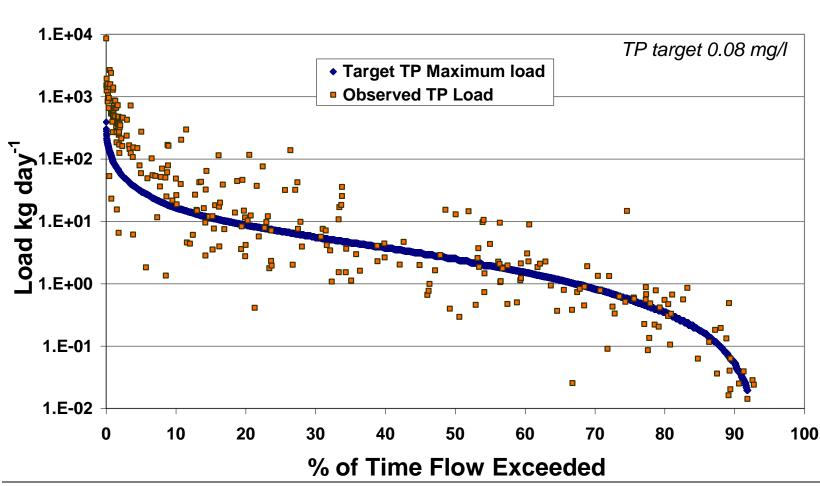
Total N speciation - relative proportions and amounts Hamilton Clover Groff



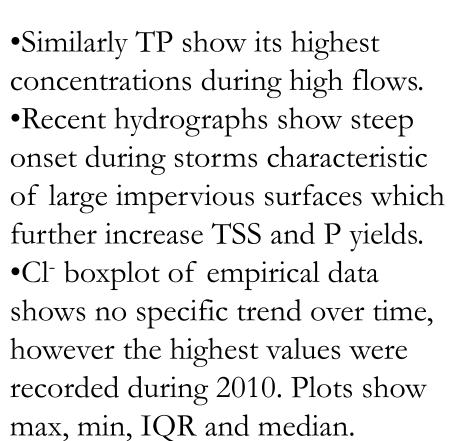
Proportions of average values for three different N species from each station from 11/2009 to 8/2010, n=16. The forested stream is Grand River near Painsville, OH from 1994 to 1996 n=6, size is not to scale for the forested stream; it is about 8 times larger.

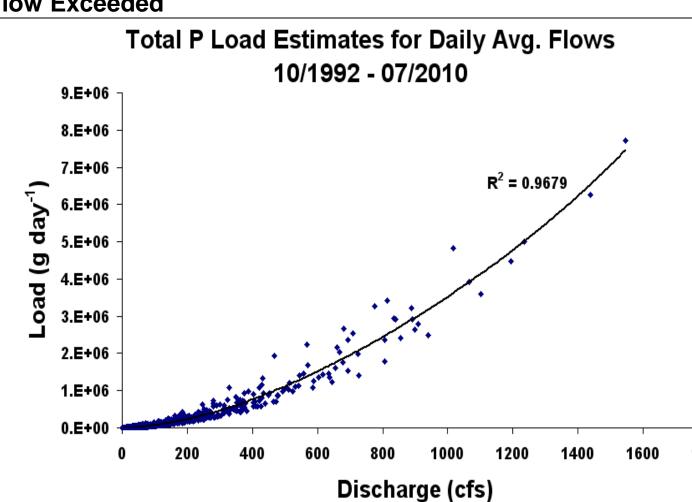
Results and Conclusions

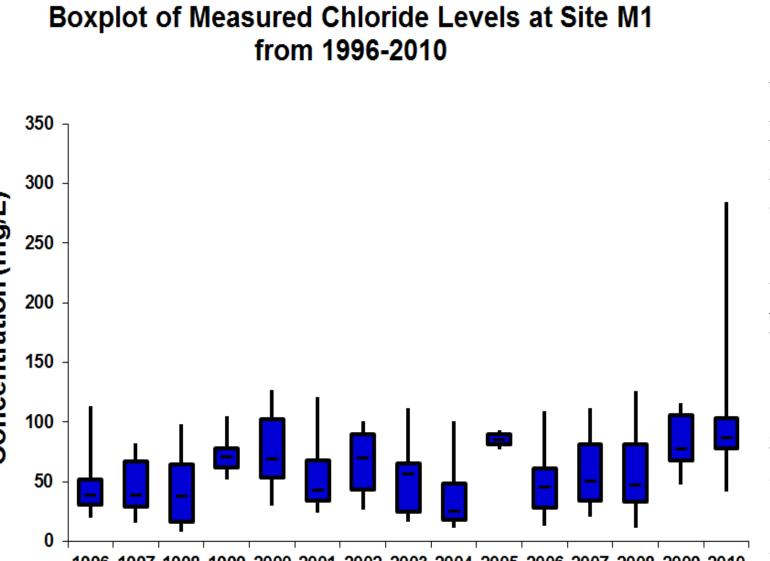
Total P Load Duration Curve (10/1992-11/2010)



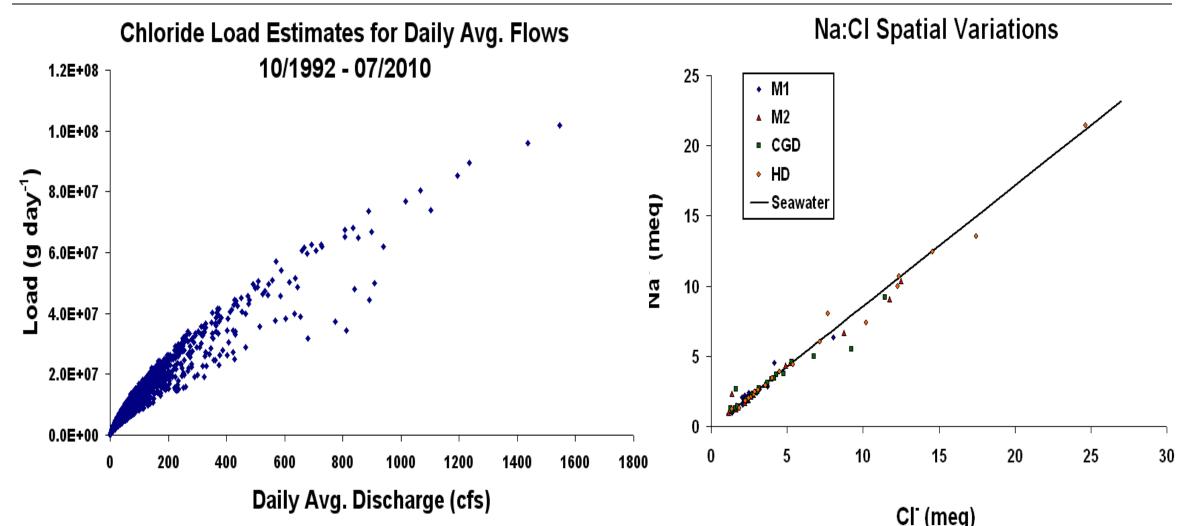
•TSS and PO_4^{3-} are flushed into the stream during storms, PO₄³dissolution from fine sediments increases downstream. This graph shows TSS loads have exceeded the EPA target during the highest flow condtions (top 20% where all flows were ranked 0-100%).







•The Na:Cl molar ratio varies between 0.72 and 1.69 however, most samples lie near the ratio of seawater: 0.858. Lower ratios (below 1:1) could also represent NaCl transport through soils, where Na+ will exchange with major cations and H+ ions, whereas Cl- is more mobile. Ratios near 1:1 or slightly above were observed in autumn suggesting dissolution of residual halite near the stream.



•Total phosphorus and nitrate, show current concentrations and loads frequently above the OEPA's target while ammonia and TSS are not in violation nearly as often.

•Higher phosphate concentrations in autumn may be the result of desorption from iron oxide minerals such as goethite, hematite, lepidocrocite, and ferrihydrite during reducing conditions. •Lower concentrations of N, P and conservative ions in CGD is likely due to less agricultural input in the catchment, or a dilution to to less groundwater input. There is nutrient removal or retention along the Hellbranch Run, which is evident by lower concentrations downstream. •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. •Clover Groff Run's water quality appears to have improved-possibly a result of recent restoration projects; Latham and Frank Parks which include morphologic changes to restore flood plains, meandering, riffles, buffers and wetlands.

•Future research includes a mathematical model using the data collected in this study and historical data to predict nitrate loads, using temperature, flow, and time as variables.

Acknowledgements

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