Managing Total Phosphorus Dynamic in a Small Rural/Urban Watershed using Geochemical Inference

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Abstract: Watershed fingerprinting or geochemical tracing of hydrologic pathways and processes involves the strategic spatial and temporal collection of water samples for chemical indicators. We used the stable isotopes of hydrogen and oxygen and major cations and anions found in fresh water systems to infer total phosphorus (TP) movement and storage in a small Midwestern rural/urban watershed.

Typically in Minnesota, water chemistry is dominated by calcium and magnesium charge balanced by bicarbonate alkalinity unless altered by human activity. Ion concentrations will vary in a landscape depending on the relative amounts of new precipitation added to the sampled water. Pre-event water found in lakes, wetlands and groundwater are influenced by biotic and abiotic factors such as organic carbon and soil/rock mineralogy.

Results of this study suggested that historically high concentrations of TP from years of wastewater treatment plant discharge were trapped in a down gradient wetland system. We inferred that new cleaner wastewater discharge may drive a change in equilibrium phosphorus concentration between sediment stored TP and event-based flow. Redirecting flow around TP wetland sinks will help prevent long-term down river water quality impairment.

Keywords: Phosphorus, wetland, geochemical, isotope, Midwest and TMDL.

1. INTRODUCTION

Jewitts Creek, a 10,620 hectare (ha) watershed located in west-central Minnesota, flows from Lake Ripley through Litchfield into the North Fork of the Crow River (NFCR) (Figure **1**). The Creek has a western tributary that originates in Stone Lake and flows through Schultz Lake before mixing in a large wetland complex with the main branch of Jewitts Creek. These lake/wetland systems in this region are linked with the subsurface flow and typically exchange surface water with ground water, suggesting the term fen could be used to describe portions of the wetlands found in this watershed. The headwaters of Jewitts Creek begin in loamy stagnation moraine of the Altamont association of the Des Moines Till, whereas much of the lower watershed is located primarily in outwash sands and gravels. Soils consist mostly of loams in the western ground moraine to loamy sands and organic soils in the eastern outwash. Most of the land use in the watershed is agricultural, primarily corn and soybeans; however, the creek flows through a large municipality and there are numerous wetlands located throughout the watershed. Total annual precipitation is 148cm; mean annual temp is 24.8°C with a growing season of 153 days. Upper Jewitts Creek is partially channelized but mostly a natural meandering channel until Litchfield where it is contained through the city. Below the City of Litchfield, the creek again becomes a meandering Rosgen "E" type channel until the creek becomes channelized as County Ditch#17 (section 25, Harvey Township, the eastern edge of the wetland system) through a large wetland between highway 34 and 300th street (Figure **1**). Before the creek crosses 300th street, outflow from Schultz Lake merges with CD#17. The area around the confluence of the east and west fork will be referred to as the Schultz Wetland System (SWS). Below 300th street the Madsen State Wildlife Management Area occurs along the western edge of CD#17 prior to entry into the NFCR.

In a Clean Water Partnership Phase I Diagnostic study conducted by the Crow River Organization of Water (CROW), Jewitts Creek was found to have impaired water quality. The Total Maximum Daily Load (TMDL) developed for the North Fork Crow River addressed several impairments in the reaches, among which Jewitts Creek was identified as being impaired by dissolved oxygen. Phosphorus concentrations in the creek are also high, exceeding 1,000µg/L occasionally [1].

The CROW study began in 2000 with 30 different sampling stations located throughout the 71 million ha Crow River basin; of the 30 water quality monitoring stations sampled over three years, Jewitts Creek contained the highest flow-weighted mean total phosphorus (TP) concentration (0.750mg/L) [2]. This relatively high load of TP from Jewitts Creek in turn influenced the downstream NFCR flow-weighted mean TP. The effects of the annual TP load were particularly important during the 2000 monitoring season, a low-

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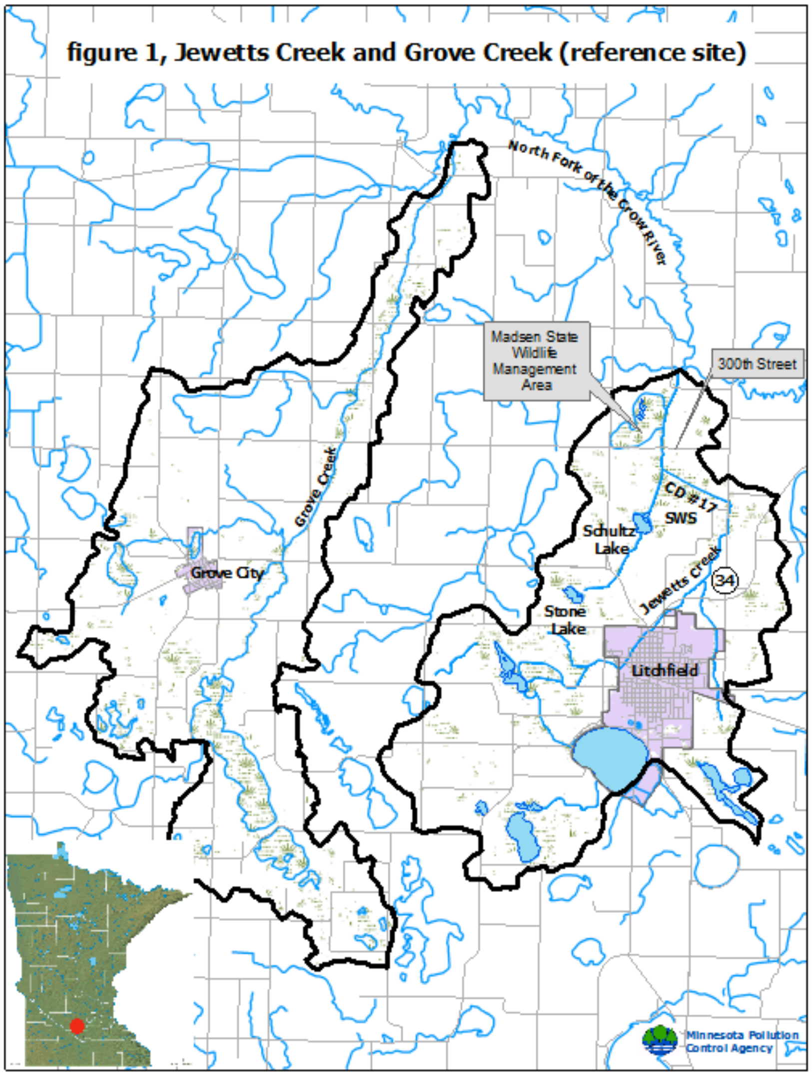


Figure 1: The location of Jewitts Creek in North Fork Crow River watershed.

flow year. These loads not only adversely drove algae blooms in the lower Crow River but also the Mississippi River. In addition to the excessive TP, low dissolved oxygen (DO) was found to occur in Jewitts Creek during the low-flow summer months. DO concentrations were typically below 5mg/L, the numeric criteria for Class 2B waters. Ambient water quality monitoring also found violations of the numeric criteria for ammonia (0.04mg/L for un-ionized ammonia in class 2B waters).

In addition to the poor chemistry, fish surveys in Jewitts Creek showed relatively poor results using the index of biotic integrity (IBI). As a result of this data and ambient water quality monitoring, Jewitts Creek was listed on the Section 303(d) list of the federal Clean Water Act [Title 40 of the Code of Federal Regulations (CRF), part 130] for low DO, Ammonia, and Impaired Biota.

Phosphorus is one of the most important nutrients in the freshwater systems as it affects primary production. Studies have looked at phosphorus loading dynamics being affected by various conditions, such as seasons [3], vegetation [4, 5], as well as spatial and temporal change of phosphorus concentrations [6, 7]. This study primarily looked at spatial and temporal variability of phosphorus concentrations within the watershed.

One of the methods with emerging interest is isotope analysis. The method is useful in studying hydrologic characteristics [8, 9] and sources of mixing [10]. By analyzing oxygen 18 ($\delta^{18}O$), and deuterium (δD), content in the water samples, a rough mixing source of water can be inferred. However, study of the more precise mixing mechanism will require use of other anions such as bromide and chloride. In this study, isotope data was used to explain the regional groundwater lake and snowmelt contributions.

2. METHODS

The primary objective of this study was the identification of stressors associated with municipal wastewater and stormwater runoff and agricultural non-point sources of pollution using concepts put forth by Mitch and Jørgensen (2004) [11]. Geochemical tools used by the authors in previous Minnesota watershed studies [12, 13] were applied to define end-member source water mixing in Jewitts Creek. Before describing the details associated with geochemical water tracing the ecological concept of buffer capacity needs to be defined. Jørgensen (2002) in his approach to ecological engineering has defined buffer capacity (β) as:

β = Δ(forcing functions)/ Δ(state variables)

Forcing functions are the external variables that are driving an ecosystem; in this study the primary forcing function is hypothesized to be wastewater discharge into Jewitts Creek. Yet, stormwater runoff and agriculture influences such as manure application may provide important clues during the data analysis. State variables are internal variables intrinsic to the definition of the described ecosystem, such as lake, wetland or stream. Because there is concern about TP accumulation below the wastewater outfall, we will focus our efforts on the Jewitts Creek channel and the Shultz Wetland System (SWS). The data will require interpretation with respect to natural background phenomenon [14] by using reference watersheds. In Figure **1**, a somewhat similar, but smaller creek than Jewitts Creek with no name (hereafter called "reference") is located just west of Jewitts Creek and Grove Creek, a stream with a nearly identical watershed, minus a major municipal wastewater treatment plant. It is just west of Litchfield and served a reference controls in this study. Both the reference and Grove systems have wetland interactions, yet lack large municipal wastewater effluent input. Nutrient and geochemical tracing data are presented by time and location. Additionally, data are grouped by season with implied hydrologic pathways. For example, "baseflow", as used in the graphics below, implies a winter baseflow condition (<0.3 cubic meters/second) in which municipal wastewater treatment plant (WWTP) effluent comprises a relatively large proportion of the water in Jewitts Creek; these are sites below the WWTP outfall. To contrast concentrations of ions in the baseflow, "winter" refers to winter baseflow conditions above the WWTP, at the mouth of the reference stream, in the NFCR, and Grove Creek. Data labeled "spring" refers to samples collected in May of 2004, when flow conditions were elevated (>0.3 cubic meters/second) yet below bankfull; whereas data labeled "summer" refers to samples collected in June of 2004, when flow conditions were slightly above baseflow.

Beginning on March 26th 2002, water samples were collected from the western edge of Litchfield, above the WWTP, just below the WWTP, just above the mouth of Jewitts Creek and the reference stream just west of Jewitts Creek (Figure **1**). These same sites were re-sampled on August 20th and 22nd 2002, before and after a bankfull storm-event. Initial interpretation of the data suggested that winter baseflow conditions were perhaps the most important flow conditions related to buffer capacity exceedance and impaired water quality in lower Jewitts Creek. Additional data was then collected from the same sites described above along with new sites located at 300th street (below the SWS), Lake Ripley outlet, NFCR at highway 34 and near the mouth of Grove Creek.

Prior to sample collection, field parameters of temperature, pH, specific conductance, Eh, and DO were made using a multi-parameter instrument. Samples for cation and anion analyses were chilled and transported to the Hydrogeochemistry Lab, University of Minnesota, Minneapolis, Minnesota. Cations and silica were measured in acidified samples by Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS). Anions were measured by Ion Chromatography (IC) analysis [15]. Analyses of the stable isotopes of hydrogen (δD) and oxygen ($\delta^{18}O$) were performed by mass spectrometry at the University of Waterloo, Waterloo, Canada [16].

In addition to the water geochemistry, sediment and soil-water samples were collected at locations shown in Figure **2**. Sediment and soil-water samples were collected on Feb 9th, 2004 and May 11th, 2004 and analyzed by the Department of Soil, Water, and Climate, University of Minnesota for ortho-Phosphorus (P) and total-P using the water extractable Bray-P method [17]. Locations shown in Figure **2** are from channel bed sediments and SWS locations labeled near-ditch and 61-m from the ditch at depths of 5-cm and 15-cm. Channel sediment was also collected 255-m, 120-m and 2-m above the confluence of the west fork and CD#17 (Figure **2**). These data were collected to better understand the spatial extent of phosphorus in the SWS, given the past likelihood of phosphorus loading from the WWTP.

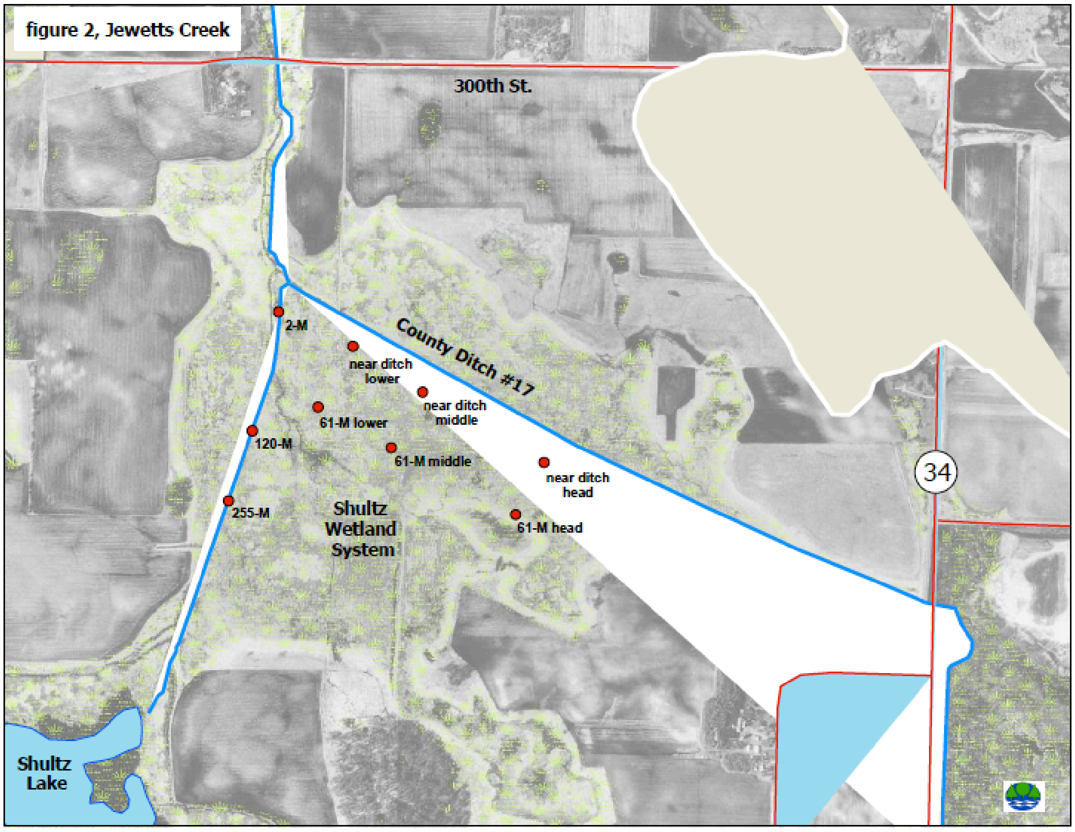


Figure 2: Jewitts Creek (Figure **1**). Sampling dates included 12-30-03, 1-20-04 (winter), 5-10-04 (spring), 6-10-04 (summer), and 2-14-05.

3. RESULTS

Figure **3** is a plot of TP concentrations (mg/L) by location from above the WWTP to the mouth, including the reference stream and the NFCR. The highest concentrations occurred just below the WWTP into and through the wetlands to the mouth. The NFCR, downstream of the confluence with Jewitts Creek at highway 34, showed a small TP increase above the reference stream during January of 2004.

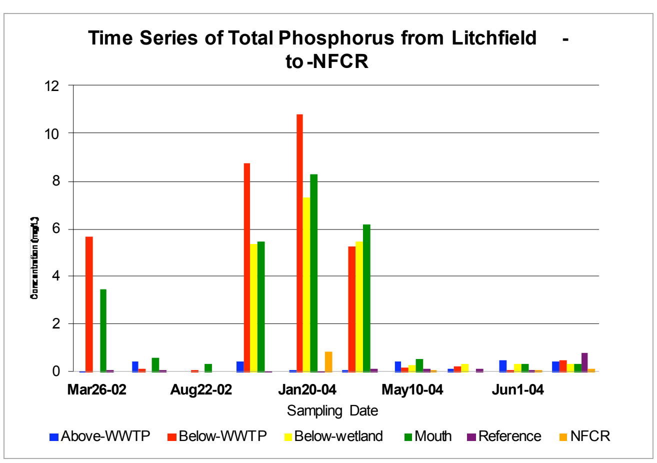


Figure 3: Time series plot of TP by location from March 2002 to February 2005.

Figure **4**, similar to Figure **3** also highlights the relatively high TP concentrations in January of 2004. Overall the graph illustrates the relatively high TP from WWTP during winter baseflow conditions.

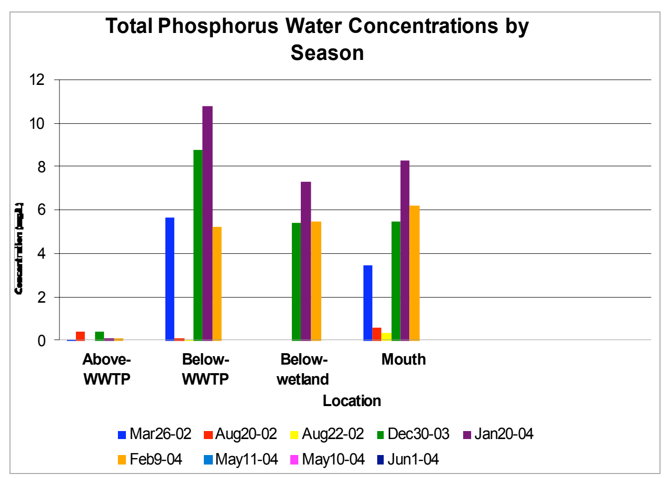
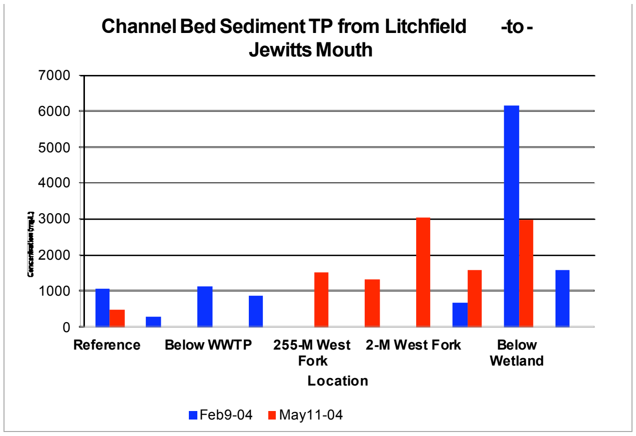
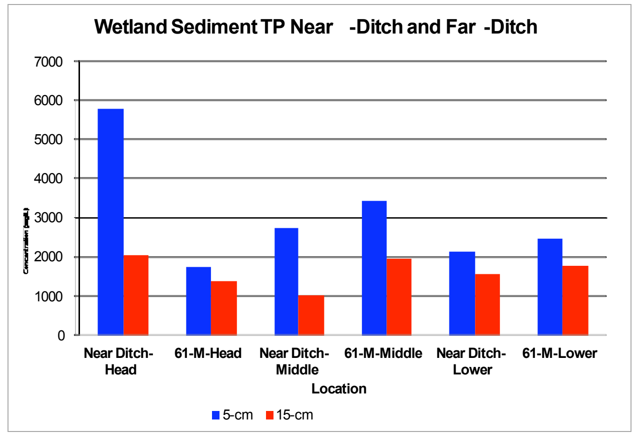


Figure 4: Repositioning of Figure **3** that illustrates the TP concentration by date.

Figure **5** shows the relative channel bed sediment TP from the reference stream and Jewitts channel locations shown in Figures **1** and **2**; note the highest concentrations were found in the SWS. Figure **6**





Figures 5 and 6: Illustration of the concentration and location of sediment TP.

presents a focused view of wetland TP near CD#17 and at three sediment sampling sites located 61-m south of the ditch; note the highest concentrations were found in the upper 5-cm near the ditch as Jewitts creek water enters SWS.

To better understand the pattern and nature of the nutrient concentrations in Jewitts Creek and the SWS, Figures **7-15** attempt to elucidate hydrologic source waters and pathways using geochemical characteristics of natural and anthropogenic waters associated with seasonal processes e.g., temperature. Figure **7** presents a plot of ionic strength verse TP by flow and season. Flow, as used in the figures, is defined by winter baseflow in Jewitts Creek (<0.3cms) and the Jewitts Creek August 2002 stormflow (>2cms). Season, as used in the figures, is defined by samples collected from May 2004, and June 2004. The winter category represents non-Jewitts Creek samples except above the WWTP, the reference stream, NFCR, and Grove Creek. The stormflow waters show the lowest ionic strength because of rainwater dilution, whereas the highest TP concentrations are found in association with the highest ionic strength waters. A relatively high R^2 (>0.91) is shown for the baseflow data in contrast to the weak relationship for winter R^2 (>0.017).

Figure **8**, similar to Figure **7** also shows a strong R^2 (>0.78) for baseflow waters when compared to sodium, a cation typically found in municipal wastewater; winter condition shows a weak relationship R^2 (>0.013). Because most of the water that entered the WWTP was derived from ground water *via* municipal wells, Figure **9** presents the relationship between sodium and silica, an ion that occurs in relatively high concentrations in sand and gravel outwash aquifers. A moderate linear relationship (R^2 0.47) is shown for the baseflow water compared to the winter linear line (R^2 0.004). Several additional data points from regional ground water were added to the winter data set to illustrate the very poor linear trend between sodium and silica in natural waters.

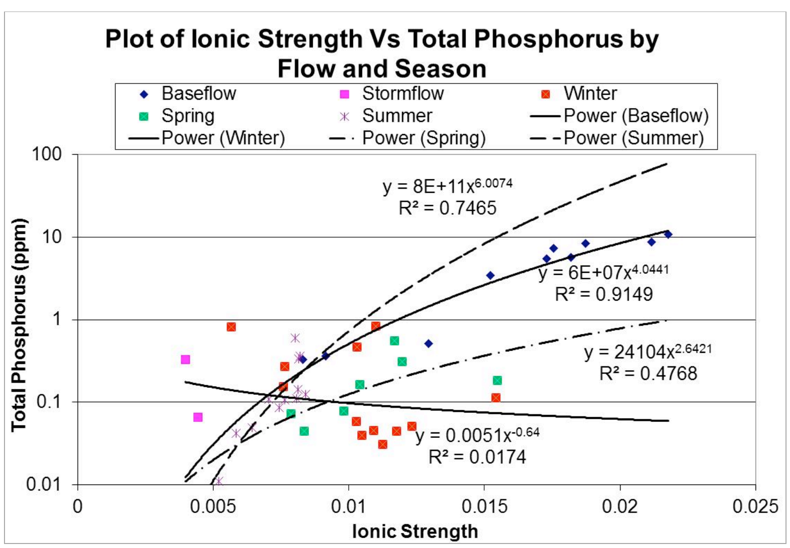
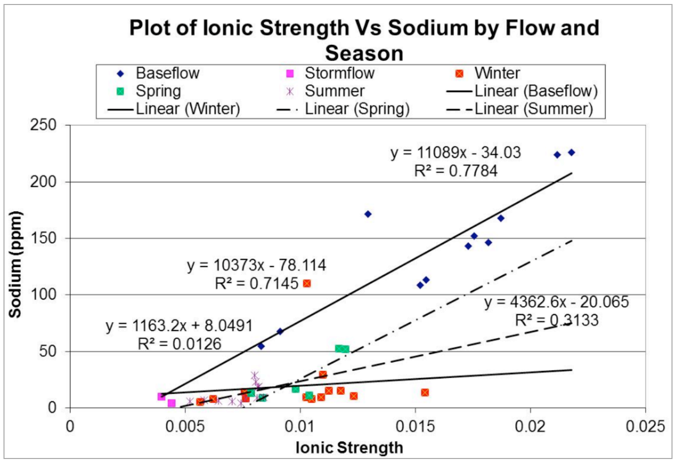
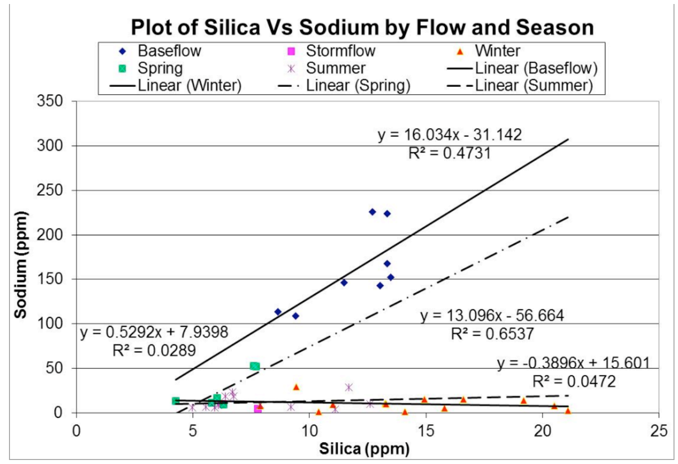
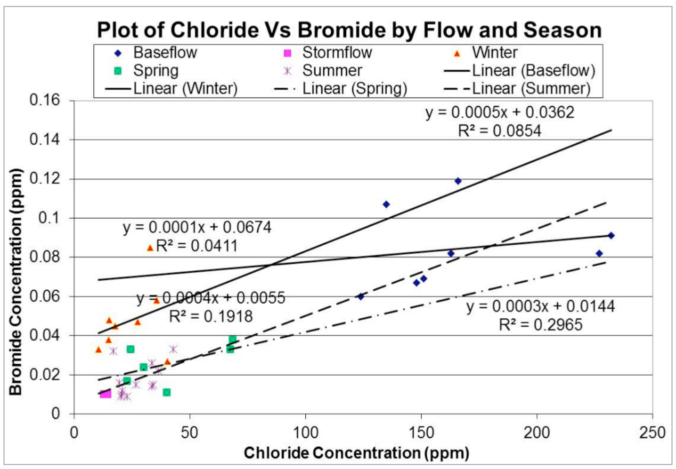


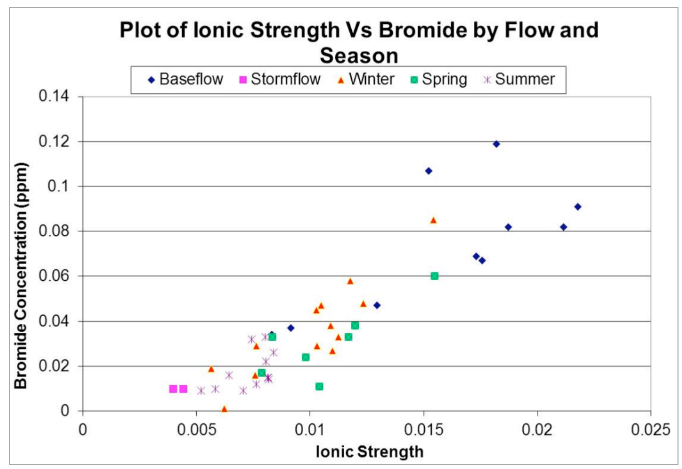
Figure 7: Plot of ionic strength vs TP for the designated source waters.





Figures 8 and 9: Plots of ionic strength vs sodium and silica vs sodium for the designated source waters.





Figures 10 and 11: Plots of chloride vs bromide and ionic strength vs bromide for the designated source waters.

Another indicator of water pollution is chloride. Figure **10** shows a chloride-to-bromide ratio of ~1000:1 for the baseflow waters compared to Cl:Br ratios of ~300:1 for the other data groups. This data affirms the higher un-natural salts associated with the WWTP baseflow during the winter months [18].

Using Bromide, Figure **11** shows a relatively clear breakout of the 5 different source water groups. These data appear to suggest incremental dilution based on the relative amount of seasonal runoff. Figure **12**, similar to Figure **11** uses molar calcium + magnesium (typically the largest driver of ionic strength in natural Minnesota waters) verses strontium (a relatively mobile trace element found in Minnesota till derived soils) to evaluate differences between polluted and natural waters found in Minnesota. The highly correlated waters occurred in the winter flow of the reference stream (R^2=0.99) with relatively high concentrations of strontium and in the summer data set (R^2=0.97) with relatively low concentrations of strontium. These waters were derived from the wetland complex west of the SWS shown in Figure **1**. These data suggest that non-wastewater influenced wetlands discharge more strontium as cation exchange occurs with the till derived soil material.

Figure **13**, similar to Figure **11** shows 4 different source water groups based on ammonia-N (ammonia-N was not measured in the stormflow samples). Baseflow samples tend to cluster with the higher ionic strength water, yet in this example the ammonia-N concentrations are only moderately high compared to data primarily from above the WWTP and the reference stream; these areas are likely more influenced by agriculture. To put into perspective the amount of available-P verse the TP, Figure **14** shows strong correlations for both the summer and winter data (R^2=0.99). The spring data represents the mix between baseflow and winter (R^2=0.83), whereas the baseflow clusters in the upper right corner.

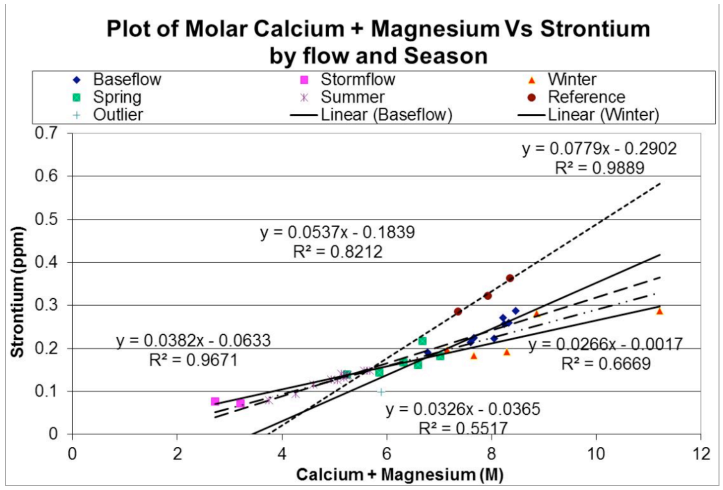
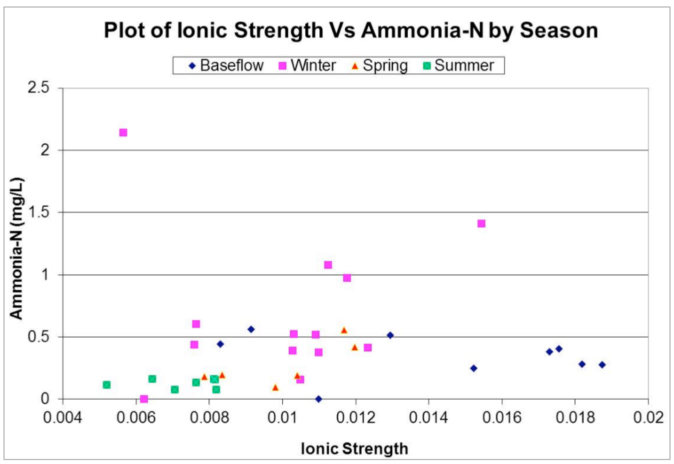
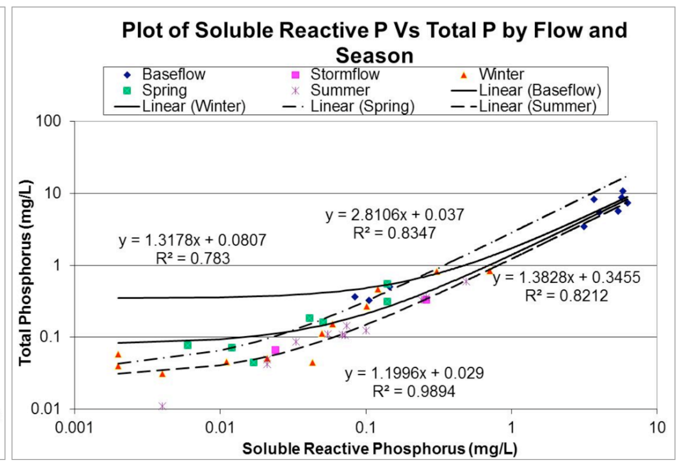


Figure 12: Pot of calcium + magnesium vs strontium illustrates the geochemical influence of native glacial soils.





Figures 13 and 14: Relationship between source waters and nutrients.

The stable isotopes of δD and $\delta^{18}O$ (Figure **15**) illustrate a range of source water type with season. Winter data tend to plot toward the lower right whereas the summer data tend to plot off the meteoric water line in the upper left corner. The spring source waters show the largest variation whereas the baseflow data show a relatively tight cluster similar to values found in the regional ground water.

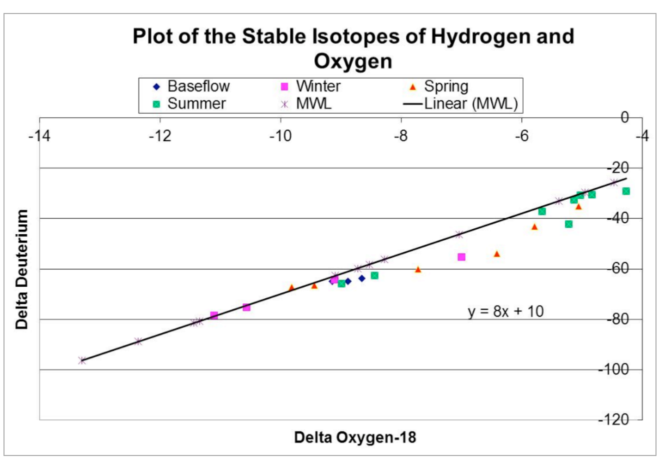


Figure 15: Plot of the stable isotopes hydrogen and oxygen along a Minnesota meteoric water line.

Seasonal data show a decrease in DO concentrations from cold winter conditions into warm summer conditions. DO concentrations typically remain above 5mg/L in Jewitts Creek except when available oxygen is consumed by increased biological activity during August. DO in Jewitts Creek never fell below 4mg/L during the study, whereas the reference stream showed the lowest measured DO during the August 20th, 2002 sampling event.

4. DISCUSSION

Applying Jorgensen's (2002) *β* to Jewitts Creek suggests that the concentration of Litchfield WWTP effluent during winter baseflow exceeds both channel and wetland assimilation capacity. (Total Maximum

Daily Loads (TMDL) are defined by the waste load allocation + load allocation + a margin of safety = the streams assimilative capacity.) Further, WWTP effluent appears to enter the NFCR; however β may not necessarily be exceeded in the larger riverine system. Detailed monitoring has not occurred in the NFCR between Jewitts mouth and highway 34. Mitch and Jørgensen (2004) indicate that β should be considered multidimensional; implying that for one type of change there may be many buffer capacities corresponding to each of the state variables. Further, because state variables are non-linear, buffer capacities will not be constant. Therefore, Mitch and Jørgensen (2004) indicate that restoration efforts should be considered in light of the relationship between forcing functions and state variables [19]. Consideration must be given to specific stressors at defined scales.

The city of Litchfield has discharged WWTP effluent with a range of TP concentrations (8-15mg/L) into Jewitts Creek for decades; years of effluent deposited TP near the headwaters of CD#17 (Figure **6**). The extent of the anthropogenic TP in the SWS is not entirely clear; Figures **5** and **6** show a build-up of sediment TP near the confluence of CD#17 and the Schultz Lake tributary. This is likely a function of decreased stream power and increased hydraulic residence at the confluence. Nevertheless, it is not clear whether β has been exceeded for TP in the SWS. There may be portions of the wetland that would respond differently given a different pattern of flow distribution. However, below 300th street, the bed sediment TP was double that found in the SWS in the Feb 9th, 2004 sampling event. This data suggests that perhaps soluble forms of P and or TP bound with sediment from the SWS may be transported and retained below 300th street. Data from Jewitts mouth is considerably lower suggesting that the high TP sediment is being trapped between 300th street and the mouth. The Madsen State Wildlife Management Area wetland β may have been exceeded for TP.

Richardson and Marshall (1986) have developed a conceptual model that explains biotic and abiotic components controlling P in a fen receiving municipal wastewater effluent. They suggest that unfertilized fens will have limited P-availability; and P movement will be controlled by plant uptake and soil exchange. With the addition of WWTP effluent, P-movement and storage will be initially influenced by microorganisms. Algal populations become important, yet they are only a temporary P-sink. In less than a year of effluent additions the biotic components became P-saturated in the Michigan study fen [20]. Further, biotic storage in algae, microbes and vegetation is returned to the wetland surface at the end of the growing season; autumn stormflow can flush this available-P downstream. Long-term P-storage occurs in the soil and is directly related to the exchange capacity. P-loading greater than 15kg/ha will likely exceed soil-P sorption capacity over time and result in P-export [20]. Soil pH and mineralogy also influence long-term P-storage; Calcium in higher pH systems, and iron and aluminum in lower pH systems will bind P and limit mobility. However, depending on changes in the wetland water oxidation state, iron will be less reliable than aluminum. The data indicate that reduced conditions occurred during May 2004. The presence of minerals such as hydroxylapatite or variscite provides reliable long-term retention of soil bound-P. Additional work is needed to identify the type of minerals in the SWS and along the channel bed of Jewitts Creek below 300th street. Should this portion of Jewitts Creek along with the Madsen State Wildlife Management Area wetland be isolated from future surface water flow into the NFCR?

Historically, the Litchfield WWTP delivered TP concentrations of 8-15mg/L during winter baseflow conditions, which amounts to a load of ~5800-to-11000kg/day for 3-4 months. Because the pattern of baseflow distribution in the SWS was limited to the channel, most of the TP was likely exported downstream to the wildlife management area and the NFCR. The SWS probably has not received TP loadings greater than 15kg/ha except during out-of-bank flows and then only within close proximity to CD#17.

Ammonia-N results suggest that either WWTP effects have been removed or minimized in Jewitts Creek relative to data collected above the WWTP, the reference stream and Grove Creek. Though the WWTP would appear to be the likely causal candidate for ammonia-N impairment in Jewitts Creek, other factors will require further investigation. The release of relatively high concentrations of strontium and ammonia in the reference stream during the winter suggests that system wetlands are possibly being flushed by ground water discharge. Water tables in the region have risen over the last decade driving more ground water exchange with wetland systems [21].

The DO results were somewhat typical for other streams measured across Minnesota. Though exceedance of water quality standards occurred in both

Jewitts Creek and the reference stream, the data can be explained by the presence of wetlands in the watershed [22]. Low DO in-part may explain the poor IBI scores for fish in both Jewitts Creek and the reference stream. Applying Jørgensens (2002) β to the DO conditions in both Jewitts Creek and the reference stream suggests that either natural forcing functions are at work or perhaps some other additional anthropogenic forcing functions such as agriculture must be further investigated. One of the primary observations of this study is that other factors beyond the effects of the municipal WWTP effluent are likely present not only in Jewitts Creek but the reference stream as well. The stressor identification process [23] now has enough information to exclude causal candidates and build a stressor story.

5. ECOSYSTEM RESTORATION OPTIONS

A new Jewitts Creek channel from below the WWTP to the NFCR could be considered based on the results of this study. The data indicate that TP has accumulated in the SWS and the Madsen State Wildlife Management Area wetland. Recent daily monitoring reports from the Litchfield WWTP indicated the TP concentrations have dropped to less than 1mg/L (MPCA, Delta Data System). The recent Litchfield WWTP upgrade may have resolved the WLA portions of the Jewitts Creek TMDLs. However, the residual effect of high TP remains downstream and could be mobilized by the cleaner WWTP effluent. Equilibrium phosphorus concentration will require some desorption of phosphorus from the downstream areas as cleaner Jewitts Creek water passes over sediment with higher TP concentrations. This could result in continued TP loading into the NFCR for the next decade or longer. Limiting the amount of flow from the SWS and the Madsen State Wildlife Management Area wetland might benefit the NFCR. One option for limiting the flow from the high TP areas is the construction of a new Jewitts Creek channel which bypasses the TP contaminated areas.

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