Exploring Water Quality Transformation in Ridgetop Wetland Systems of the Daniel Boone National Forest

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Introduction

Natural ridgetop wetlands in the Daniel Boone National Forest of Eastern Kentucky are systems of groundwater and surface water exchange which provide crucial ecosystem services such as groundwater storage and drought support to local vegetation (Malzone 2019). In efforts to mitigate the loss of natural wetlands in Kentucky, several constructed wetlands have been built on ridgetops in the Daniel Boone National Forest. However, the constructed wetlands do not function properly because they have limited groundwater storage systems and a perennial hydroperiod. Their differences in physical hydrology suggest that constructed wetlands will also have different chemical hydrology than natural wetlands. This study conducts a first order water quality assessment of constructed wetland sites in the Daniel Boone National Forest, including samples from natural wetlands, local wetlands, and local streams. The preliminary water quality data collected in this study is used to identify biological processes that impact wetland water chemistry and to track evidence for road disturbance in natural waters. The major ion and nutrient analysis conducted in this study provides evidence for limestone weathering, atmospheric deposition, and subsurface redox reactions facilitated by bacteria in the wetland sites. Comparative differences in the water quality of natural and constructed wetlands were observed, particularly in higher bicarbonate levels at constructed wetlands due to stagnant water, high respiration, and road disturbance. Differences in the water quality of individual constructed wetlands suggest both natural variation and road disturbance influence water quality.

Methods

Acidified, non acidified, and bulk samples of surface water and groundwater (when accessible) were collected at each site twice across a five week period from June 1, 2021 to July 7, 2021. Baylors, syringes, and a hydraulic pump were used to extract the water from various wetland and stream sites. All samples were filtered with a 0.45 micron filter and refrigerated to preserve nutrients for lab analysis (Buskirk 2020). YSI Pro DDS was also used in the field to measure temperature, specific conductance, pH, nitrate, and chloride levels at each site. Acidified samples were measured for phosphate, ammonium, and nitrate absorbance through UV-Vis spectroscopy. An ion chromatograph was used to measure anion concentration of Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-} Br^-, and F^- , and cation concentration of K^+ , Li^+, Na^+ , NH_4^+, Ca^{2+}, Mg^{2+}. Alkalinity titrations were performed on 100 mL of the filtered bulk samples in order to quantify the bicarbonate ion (Buskirk 2020). These titrations used 0.16 sulfuric acid and a 0.1 multiplier for a pH gran titration. 25 mL filtered samples with a 0.4 multiplier and 1.6 sulfuric acid were used for titrating samples of notable high bicarbonate or very cloudy water. Piper diagrams were generated to show the percentage of dominant ions in water samples by independent variables including constructed wetlands, natural wetlands, and reference waters.

Results and Discussion

Natural wetland sites generally had higher nutrient values than constructed wetlands. **Figure 1** plots nitrate in surface water across all wetland sites, demonstrating comparatively higher nitrate in all natural wetland surface water. Nitrate values at the DC2 natural wetland suggest denitrification occurring down a gradient, with high nitrate levels in the surface water that decrease as water moves into the ground and out of the wetland system (**Figure 2**). Potassium ion concentration increased systematically amongst constructed wetlands in the Daniel Boone National Forest (**Figure 3**). Wetlands with high potassium ion concentration were shaded, deeper into the forest, and had lots of hardwood debris, indicating an environment of high respiration and less disturbance. Impact of road disturbance can be tracked to most constructed wetlands sampled, despite the absence of limestone bedrock. Soils in the Daniel Boone National Forest are mostly composed of sandstones and silicate rocks, which suggests a prevalence of silicate weathering at all wetland sites (Kentucky Geological Survey 2021). **Figure 4** shows that most natural wetlands are influenced by silicate weathering but many constructed wetlands are influenced by carbonate weathering, despite the similar silica dominant soils at both sites. This plot suggests that carbonate weathering is coming from limestone dissolution from road dust rather than carbonate weathering in local soil. Four distinguishable water types occurring in the sampled natural waters can be identified from a Piper diagram which plots their percent distribution of dominant cations and anions (**Figure 5**). In area A, magnesium rich waters influenced by silicate weathering are observed, mainly in reference water samples. In area B, high sulfate, high sodium, and low bicarbonate waters are observed in natural wetland samples. These samples are dominated by rainwater and likely influenced by atmospheric deposition of nitrogen and sulfur. In area C, areas of high potassium and high bicarbonate are observed in waters of constructed wetlands that experience more shade and more hardwood decay. In area D, waters with extremely high bicarbonate are observed, indicating wetlands and reference waters either built on limestone bedrock or heavily influenced by road disturbance.

Conclusions

Constructed wetlands in the Daniel Boone National Forest are showing both natural variation in their water chemistry and disturbance from dust impacts of limestone roads. Natural wetlands generally had higher nutrient concentrations than constructed wetlands because they are rainwater dominant. Constructed wetlands were much more likely to have their water quality altered due to high respiration and hardwood decay environments, conditions which increase the bicarbonate and potassium ion. Constructed wetlands vary chemically from both one another and from natural wetlands, suggesting that their ability to function as bioreactors and provide nutrient cycling services to local ecosystems is limited.

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Appendix A

This appendix contains figures relevant to the results of the study which are referenced in the Results and Discussion sessions of this write up.

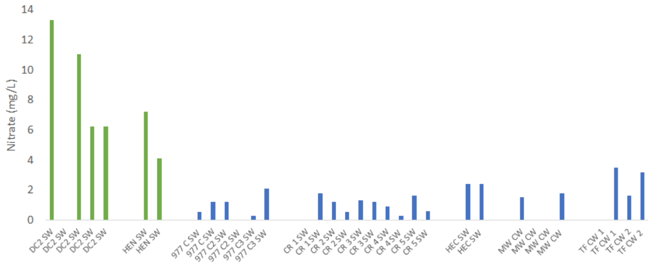

Figure 1. *Graph of Nitrate concentration (mg/L) by wetland site. Green bars represent natural wetland sites and blue bars represent constructed wetland sites.*

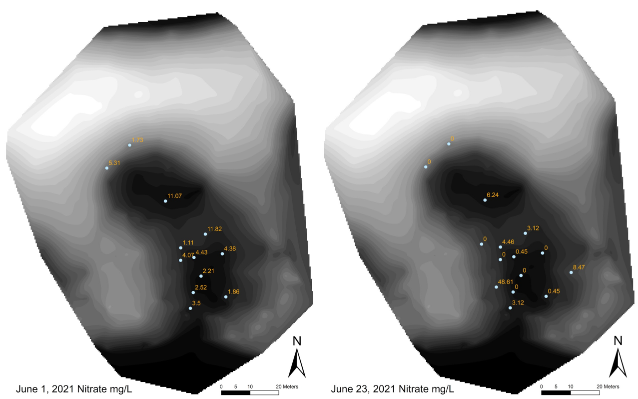

Figure 2. *Map of DC2 natural wetland wellfield nitrate levels in mg/L from sampling on June 1, 2021 and June 23, 2021.*

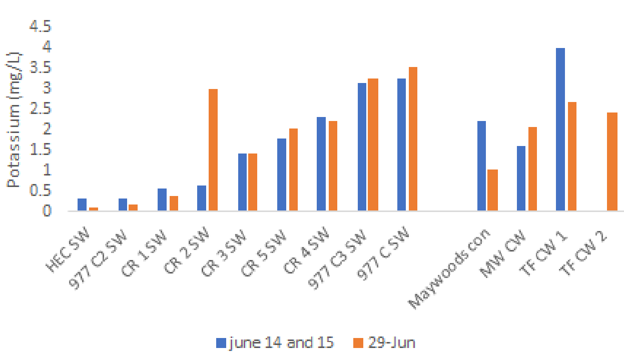

Figure 3. *Graph of Potassium ion concentration (mg/L) by wetland site and sampling date for constructed wetland sites. The sites are grouped by constructed wetlands in the Daniel Boone National Forest (left group) and local constructed wetlands (right group).*

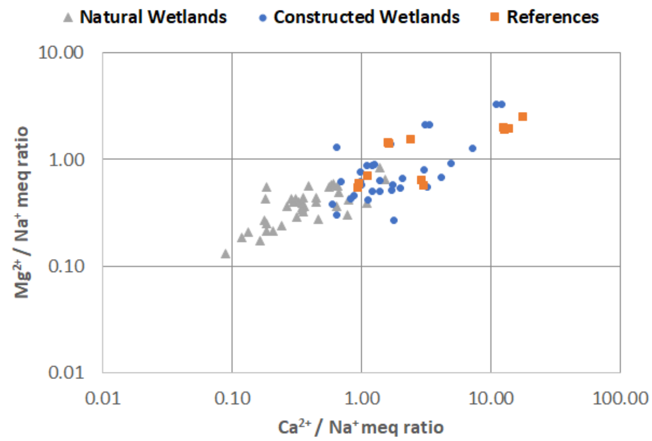

Figure 4. *Graph of Ca^{2+} and Mg^{2+} concentration (mg/L) normalized to Na^{+} by site. Ratios of Ca^{2+} ,Mg^{2+}, and Na^{+} less than or equal to 1 indicate waters impacted by silicate weathering. Ratios of Ca^{2+}, Mg^{2+}, and Na^{+} greater than 1 indicate waters impacted by carbonate weathering.*

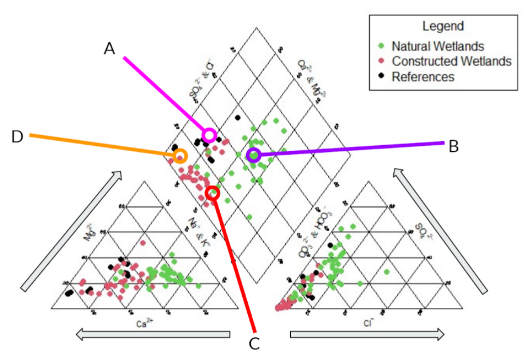

Figure 5. *Piper Diagram plotting percentage of dominant ions in each water sample. A, B, C, and D, correspond to identifiable water types expanded upon in the Results and Discussion section.*

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