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THE GEOCHEMISTRY OF RELICT MILL POND WATERS AND STRATIFIED RESERVOIRS IN THE SHENANDOAH VALLEY, VA

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INTRODUCTION

An assessment of stratified reservoirs and their impact on aqueous geochemistry is imperative to mitigate the effects of Mn and N contamination. Seasonally stratified reservoirs allow metals, such as manganese (Mn) and iron (Fe), to accumulate in the water column due to reducing conditions, and be released to downstream rivers through dam discharge (Munger et al., 2017). Dam removal can remobilize and release soluble contaminants from impounded sediments to water systems, and transport them downstream along with the now remobilized sediments (Niemetz et al., 2013; Curran and Coveleski, 2021). Mn and N are of particular interest, due to their known impacts on human and environmental health. This study aims to better understand contaminants in water systems for the purpose of improving water quality.

Manganese is a naturally occurring metal that has been identified as a potential contaminant in Roanoke County groundwaters (Kiracofe et al., 2017) and dam impacted water (Munger et al., 2017). In oxic waters, insoluble Mn is trapped in benthic sediments as Mn (oxyhydr)oxide minerals or bound to stream sediments via sorption processes, as evidenced by changes in aqueous Mn concentrations downstream of dams (Gordon et al., 1984; Hess et al., 1989; Dortch & Hamlin-Tillman, 1995; Ashby et al., 1999). In anoxic conditions (such as those at depth within a lake or reservoir), Mn can be reduced to Mn^{2+} which is most stable in the aqueous phase, thereby allowing the metal to become heavily concentrated (Davison, 1993). If waters are released via a bottom sluice gate or dam tailrace, Mn^{2+} can be transported downstream, and may be present in the flowpath for months after leaving reducing conditions (Munger et al., 2017). When the tailrace transports anoxic impounded sediments and water, the contaminants accumulate further downstream, thereby impacting community and environmental health.

Elevated concentrations of Mn^{2+} and other contaminants in water have a negative impact on the quality of human life. When ingested over extended periods of time even in relatively low concentrations, Mn^{2+} presents symptoms of headaches, depression, and learning impairments in children (Spangler and Spangler, 2010). Consequently, the EPA has established an unenforceable Health Advisory (of 300 ppb Mn) in drinking water to decrease Mn^{2+} health effects (EPA, 2004).

The greatest threat to the Chesapeake Bay Watershed is eutrophication– the excessive nutrient enrichment as a result of phosphorus and nitrogen in water causes hypoxia, and a decrease in aquatic life (EPA, 2021). P and N are of particular interest as, when released from legacy sediments post-dam removal, they are difficult to control (Riggsbee et al., 2011). Phosphate is an anion that is naturally derived from phosphorus in phosphate minerals,which are mined for agricultural and industrial use (Florida Industrial and Phosphate Research Institute 2017). Phosphorus and nitrogen can enter watersheds as runoff from industrial, agricultural, and household cleaning products (European Environmental Agency, 2005). Increased P in water systems leads to eutrophication, creating anoxic water conditions ideal for Mn^{2+} solubility. Monitoring and identifying sources of excessive N and P enrichment is imperative to restoring watershed health. When a dam tailrace transports remobilized sediments, impounded waters, and soluble metals, the downstream water and ecosystems may be polluted with Mn^{2+}, N, and P.

The area of focus is the Maury River in Rockbridge County, Virginia (VA), located in the James Basin of the Chesapeake Bay Watershed. The Maury River contains many structures; our focus is a combination of six obsolete as well as operating dams. Most obsolete dams are along the river, with Lake Merriweather at its headwaters (Fig. 1). McCormick's Mill Dam is located outside of the Maury River watershed. Sites were selected to evaluate changes in water geochemistry as a function of stratification and location. In this assessment, we analyze aqueous geochemical characteristics to evaluate potential pollutants, with a focus on soluble aqueous manganese ([Mn^{2+}]), phosphorus and total nitrogen (TN).

METHODS

Data collected included GPS coordinates, water at varying depths, and field data. To collect in situ water chemistry field data (pH, dissolved oxygen, temperature, and specific conductivity), a YSI 556 Multi-Probe System (MPS) was lowered to the desired depth. All bottled samples were immediately sealed and promptly refrigerated upon return to the lab. One aliquot of each sample was filtered; another aliquot was filtered and acidified. A phenolphthalein titration with a bromocresol green-methyl red titration test was used to collect alkalinity measurements. Filtered but unacidified samples were analyzed for major cation (e.g., Ca^{2+} , Mg^{2+}, Na^+, K^+, NH_4^+) and anion (e.g., Cl^-, SO_4^{2-}, NO^{3-}, NO^{2-}) concentrations by ion chromatography (IC) analysis. TN was calculated as the sum of ammonia (NH_4^+), nitrate (NO^{3-}), and nitrite (NO^{2-}). To perform the inductively coupled mass spectroscopy (ICP-MS) analysis (P, Cl, K Al, Fe, Mn), the filtered and acidified samples were diluted with a 1:1 ratio with 2% nitric acid solution (trace metal grade).

Sites of interest included reservoirs behind extant dams, and former dam localities where pockets of stagnant water remained (Fig. 1). Extant dams were found at Lake Merriweather (LM), McCormick's Mill Dam (MMD), and Natural Bridge Dam (NBD). Obsolete dams include Polecat Hollow (PH), Stratton's Dam (SD), Furr's Mill Dam (FMD), and Jordan's Point (JP).

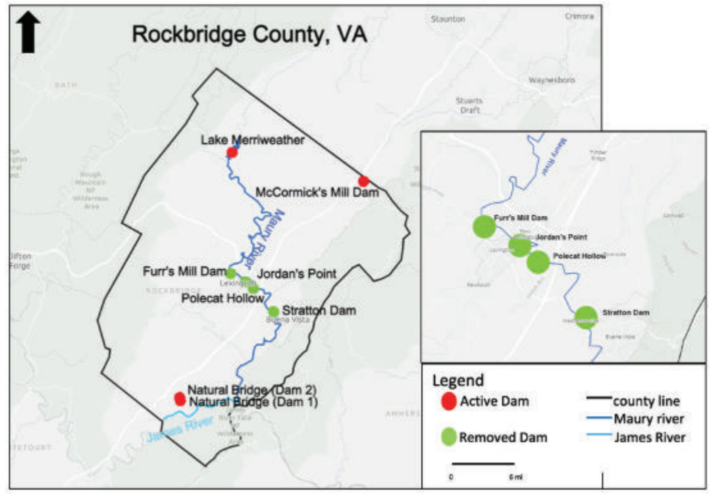

Figure 1. Sample sites in Rockbridge County, VA. Red points show operating dams. Green points show demolished dams. Figure by Kallan Wilde.

RESULTS

As expected, DO and temperature change as a factor of depth. At McCormick's Mill, where sampling was repeated every 3-4 months, DO increases from summer to winter as expected due to the temperature dependence of gas solubility (Fig. 2A). Temperature decreases with depth, as expected. The aqueous Mn concentration generally increases from shallow waters to deep waters (Fig. 2B). Total nitrogen varies with depth, initially decreasing, before increasing towards the bottom of the reservoir (Fig. 2C).

Lake Merriweather has the largest range of Mn^{2+} concentrations, and the greatest TN concentration of all sample sites (Fig. 3A). Over 25% of data collected at LM lies above the EPA human health advisory benchmark of 300 ppb (HA). The upper quartile is $\log(Mn^{2+})=1.93$. The lower quartile is $\log(Mn^{2+})=0.55$. McCormick's Mill Dam contains the second highest concentration of Mn^{2+}. All other obsolete dams contained Mn^{2+} concentrations that did not exceed EPA standards, but show a medium-large distribution (Fig. 3). In comparison, NBD has negligible Mn^{2+} concentrations, and the smallest distribution of data. Mn^{2+} concentrations that exceed EPA standards are at LM and MMD.

The highest concentration and distribution of TN is at Lake Merriweather. TN exceeds HA EPA guidelines at all sites (Fig. 3B) (EPA, 2009). Phosphorus does not exceed SMCL EPA limits at any site on the Maury

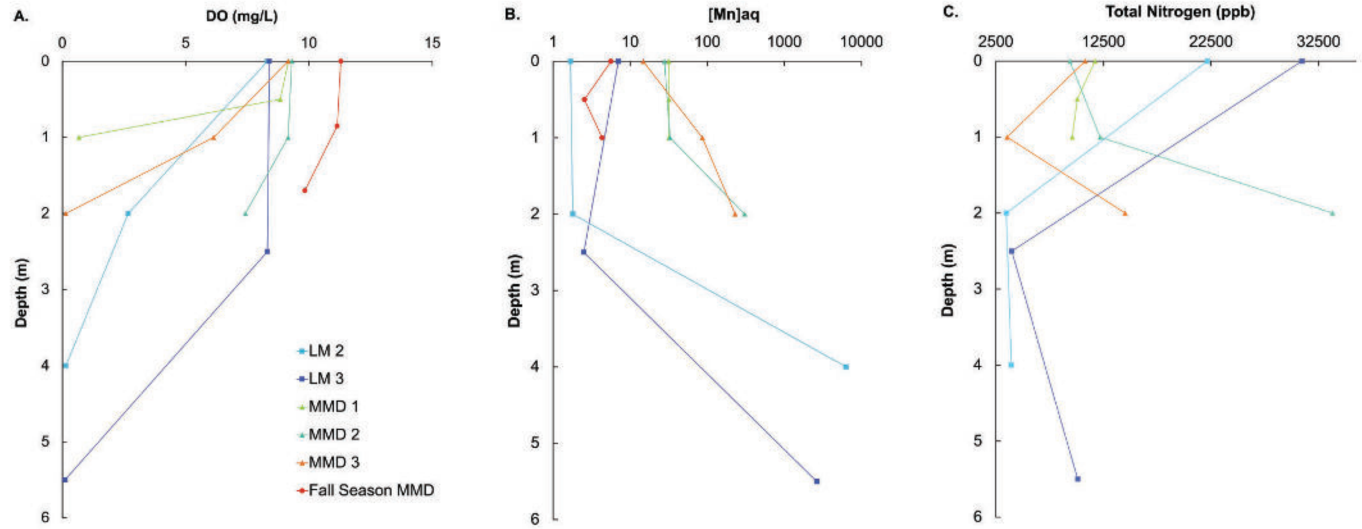

Figure 2. A) Relationship between dissolved oxygen (mg/L) and depth. DO decreases with depth for samples from Lake Merriweather (LM) and McCormick's Mill Dam (MMD). Chemoclines for (B) Mn(II) and (C) total nitrogen. Mn(II) increases with depth for both samples from LM and all samples from MMD collected in summer. Only the water sampled in fall from MMD had no clear relationship between Mn(II) and depth.

River (Figure 3D). Iron exceeds SMCL only at Lake Merriweather (Fig. 3C). The highest concentrations for aqueous Mn^{2+}, TN, and Fe are found at Lake Merriweather. The largest concentration of P can be found in the non-stratified reservoirs.

All non-stratified sites and Lake Merriweather have similar hydrochemical facies (Fig. 4). These samples present a calcium cation type, and a bicarbonate anion type, which corresponds to a calcium bicarbonate type. The samples demonstrate that weak acids exceed strong acids. Finally, we can determine that alkaline earths exceed alkalis in these samples.

With some minor differences in anion and cation concentrations, MMD exhibits similar hydrochemical facies to other sites (Fig. 4). The sample demonstrates that weak acids exceed strong acids and that alkaline earths exceed alkalis. Furthermore, MMD has higher total dissolved solid (TDS) than all other sites.

IMPLICATIONS OF THIS WORK

Are waters behind dams stratified?

Three dams were tested for stratification: LM, MMD, and NBD. LM and MMD are stratified, with temperature and DO decreasing with increasing depth. NBD is not stratified; its reservoir is not large enough to allow for significant changes in temperature and DO with depth. Similarly, all other sites (obsolete dams) are not stratified.

Stratified reservoirs are characterized by changes in temperature and DO with depth. Furthermore, this study investigated the stratified characteristics of specific conductivity; conductivity increases with depth. Greater conductance reflects an increase in total dissolved solids. Lastly, LM can be categorized as 'more stratified' than MMD – its lower temperature and DO correspond with a low specific conductivity and higher concentrations of Mn^{2+}.

Are contaminants, including Mn, present behind dams?

All sites contain aqueous Mn^{2+} (Fig. 2A) with variable concentrations. Mn^{2+} exceeds the Environmental Protection Agency (EPA) human health benchmark at LM and MMD (Fig. 3A), the only two stratified reservoirs. At these two sites, Mn^{2+} increases with depth, where low oxygen conditions exist. Lake Merriweather performs regular flushes; water mixing as a result of water mobilization oxidizes the reservoir. Under such conditions, soluble Mn may be mobilized, but eventually decreases in concentration downstream via oxidative precipitation or sorption processes (Gordon et al., 1984; Hess et al., 1989; Dortch & Hamlin-Tillman, 1995; Ashby et al., 1999; Munger et al., 2017). This scenario can serve as a model for 'dam removal' and the resulting impacts on water chemistry. If a dam is removed, then the reservoir no

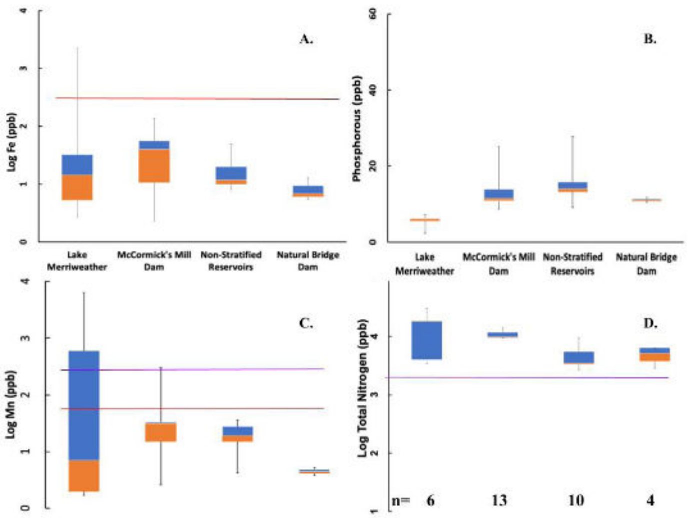

Figure 3. Box plot showing log(Mn^{2+}) distribution between LM, MMD, and the non-stratified reservoirs of the Maury River. Non-stratified reservoirs contain Polecat Hollow, Stratton's Dam, Jordan's Point, and Furr's Mill Dam. Lower boundary has Natural Bridge Dam. Blue boxes are the upper quartile of data; orange boxes are the lower quartile. Red line marks EPA Secondary Maximum Contaminant Level (SMCL) log(50 ppb), purple line marks EPA Health Advisory (HA) log(300 ppb).

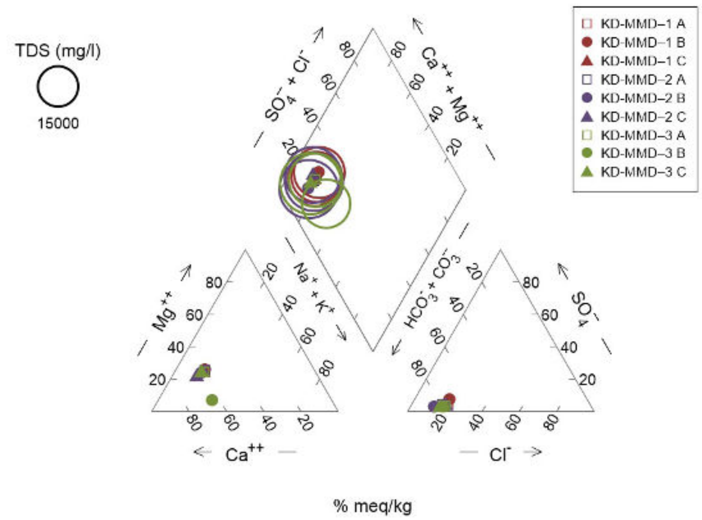

Figure 4. Piper diagram showing hydrochemical facies for waters from behind McCormick's Mill Dam (MMD). Different colored markers represent three sampled sites within the reservoir.

longer stratifies, and soluble materials are remobilized in an oxidized environment, eventually changing to insoluble forms. Less aqueous Mn^{2+} results in less Mn contamination.

Three other aqueous elements of interest (Fe, N, and P) were studied, though only one was not found at high concentrations. Iron is not the focus of this study, but it was found to increase in concentration as a factor of depth at LM and MMD similar to Mn. Concentrations of phosphorus do not exceed EPA standards at any sites. There are elevated concentrations of TN throughout all sites tested on the Maury River (Fig. 3D). Future impacts suggest that high TN concentrations in water will acidify and aggravate eutrophication downstream.

How do stratified reservoirs compare to non-stratified reservoirs?

All sites can be categorized as a calcium and magnesium bicarbonate type (Fig. 4), according to their hydrochemical facies (Piper, 1944). However, three sites deviate from this trend: LM, MMD, and NBD. These three sites vary in their chemical composition, but there is one link between them: active dams. Two of the three sampling sites at LM have calcium magnesium sulfate type waters; MMD has a high TDS, and greater ionic concentrations; NBD has a calcium magnesium sulfate type at depth. At these stratified reservoirs, specific conductivity and alkalinity increase with depth. LM is found in a shale bedrock, while MMD is within a limestone bedrock. The surrounding karst terrain increases alkalinity, the buffering capacity of the solution, and conductivity. High alkalinity and high conductivity are consistent with high TDS observed at MMD.

CONCLUSION

Contaminant solubility of the Maury River is dependent on stratified conditions, impacting the aqueous chemistry downstream, and influences in-situ chemical characteristics as well. The stratification of reservoir dams like LM and MMD, at the head of the Maury River, promotes ideal conditions for the solubility of aqueous Mn^{2+} and Fe^{2+}. Impounded water at depth creates oxygen-reducing conditions ideal for aqueous Mn^{2+} solubility and high conductivity. Lake Merriweather and McCormick's Mill Dam contain the highest aqueous Mn^{2+} concentrations. These sites are stratified reservoirs, but other chemical characteristics vary. Lake Merriweather is overall less conductive, less oxygenated, and colder than McCormick's Mill Dam.

Some elements are not influenced by the stratification, such as silicon and phosphorus. Sources of silicon, phosphorus, and total nitrogen can be derived from surrounding bedrock or land use. LM source material is derived from the surrounding shale bedrock, and all other sites lie within a limestone bedrock. The bedrock runoff can be accumulated at both stratified and non-stratified sites. TN is potentially present as a result of surrounding agricultural land use and wastewater runoff. Future investigations could involve an analysis of the aqueous chemistry of high TN waters in comparison to Maury River reservoirs. Similarly, silicon inputs and elevated concentrations are dependent on location and proximity to the river, as opposed to stratified conditions. Phosphorus does not show significant impacts in the Maury River, perhaps due to lower input of P.

The findings of this study are indicative of the Maury River's susceptibility to some water contaminants from active impoundments. Elevated Mn^{2+} concentrations found at the stratified reservoirs pose a potential health risk in the case of dam failure or reopening the bottom drain sluice gate, closed since 2012 per Virginia Department of Environmental Quality orders (Stuart, 2012). While there are low P concentrations throughout the sites here analyzed in the Maury River, high TN behind these impoundments may increase the risk of eutrophication downstream. Contaminant conditions are influenced by reservoir size and stratified conditions, and are reflected by changes in TDS.

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