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ASSESSING GROUND AND SURFACE WATER QUALITY AT REDOX INTERFACES ACROSS THE SHENANDOAH VALLEY, VIRGINIA

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INTRODUCTION

Emerging Groundwater Quality Issues

In the past decade, an ever increasing number of studies have found that Mn(II) in drinking water is a human health concern with wide ranging negative effects on IQ, infant mortality, and cancer rates, to name a few (Bjørklund et al., 2017; Bouchard et al., 2007, 2011; Hafeman et al., 2007; Khan et al., 2012; Langley et al., 2015; Sanders et al., 2014; Spangler and Spangler, 2009; Spangler and Reid, 2010; Williams et al., 2012). A recent study investigating Mn contamination in groundwater wells across the United States determined ~8% of groundwater wells in Virginia (out of 872 analyzed) have Mn concentrations ≥300 ppb (McMahon et al., 2018b, 2018a), the lifetime chronic exposure health advisory limit for Mn set by the Environmental Protection Agency (U.S. Environmental Protection Agency, 2004). It has been argued that this health advisory limit is set too high (Ljung and Vahter, 2007), with just ≥100 ppb Mn in drinking water leading to some health and developmental effects (Langley et al., 2015; Sanders et al., 2014). Approximately 21% of groundwater wells in Virginia analyzed by McMahon et al. (2018a, b) have Mn concentrations exceeding that threshold. With a majority of the population in the Shenandoah Valley relying on groundwater for their water supply (Virginia Department of Environmental Quality, 2015), Mn may negatively impact the health of tens of thousands of Virginians.

Mn contaminated groundwater wells have previously been identified in several locations throughout VA, including the upper portion of the Shenandoah Valley, VA. Potential sources of Mn and trace metal contamination in VA groundwater include: dissolution of the aquifer, soil-water or sediment-water interactions, Mn mobilization via desorption from mineral surfaces in the soil-water interface. Recent research on Mn contamination in the Roanoke River watershed points to mobilization of Mn associated with carbonate-rich rocks (Kiracofe et al., 2017). Two other recent studies investigating Mn groundwater contamination, one in the Piedmont region of North Carolina (Gillispie et al., 2016) and one surveying the entire United States (McMahon et al., 2018a) both found that soil geochemistry is strongly linked to Mn concentrations in groundwater. In order to predict the likelihood of Mn (or other trace metal) contamination in any drinking water source, identifying the major controls on their concentrations is critical.

Historical & Potential Future Impacts of Mill Pond Dams on Surface Water Quality

Increased aqueous Fe and Mn concentrations (and associated trace metals) in surface water is also linked with the stratification of impounded waters behind dams (Hess et al., 1989; Gordon, 1989; Dortch and Hamlin-Tillman, 1995; Ashby et al., 1999; Munger et al., 2017), negatively impacting surface water quality and surrounding ecosystems. In addition to these geochemical effects, another major consequence of dams includes reservoir infilling with sediments. These legacy sediments are stored behind dams that were constructed in the eastern United States from the earliest days of European settlement until the early 1900s (Walter and Merritts, 2008). Legacy sediments can potentially record evidence of land use changes, such as industrial and agricultural activities.

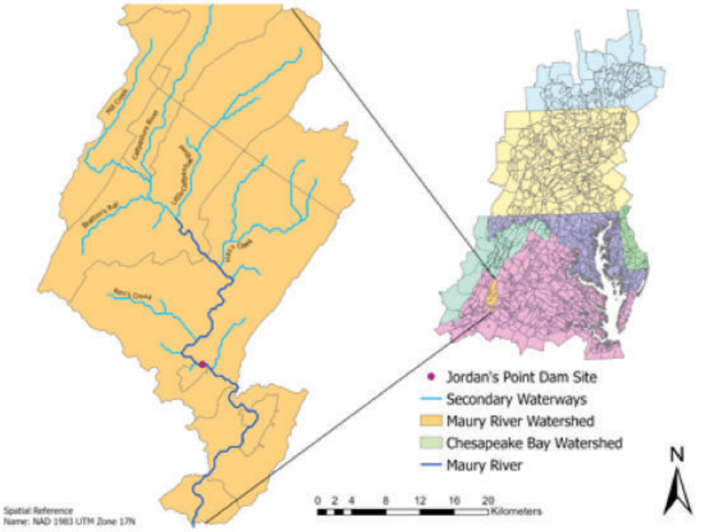

Figure 1. Map of Maury River watershed within the Chesapeake Bay Watershed. Includes the location of Jordan's Point dam in Lexington, VA, a recently removed milldam, and one of several sites sampled for legacy sediments in Rockbridge County. Map by Katie Larkin for her thesis.

The Shenandoah Valley is home to many historical low head dams, primarily used for mills, iron forges, and other hydropower applications. Many of these dams have been breached over the years for a host of reasons.

When these dams are breached, streams can remobilize these legacy sediments, and any potential contaminants that accumulated with them (e.g., Walter and Merritts, 2008; Niemetz et al., 2013), negatively impacting downstream ecosystems via either geochemical contaminants or increased total suspended solids (TSS). We aim to characterize some of these legacy sediments at dams along the Maury River in Rockbridge County, Virginia (Fig. 1) to better assess their potential for erosion into and contamination of the waterway, and downstream water bodies like the Chesapeake Bay (e.g., Hupp et al., 2013; Niemetz et al., 2013). For example, sediment pollution negatively affects the benthic community through several ways, including low dissolved oxygen, sediment contamination, and nutrient loading (Dauer et al., 2000). In addition to the issues of sediment pollution, these sediments can also contain adsorbed trace metals like Cu and Pb (Lutgen et al., 2020), especially when associated with fertilizers and pesticides (Cu) or emissions due to combustion of leaded gasoline (Niemetz et al., 2013). By measuring such trace metals we can assess their potential contribution to the Maury River watershed.

Other geochemical indicators of interest include carbon and nitrogen and their stable isotopes, which we can use to discern land use changes. For example, the ratio of organic carbon to nitrogen in sediment is indicative of organic matter source, with higher values associated with terrestrial vegetation. We can thus use this ratio as an indicator of deforestation in the watershed. By measuring sediment and surface water trace metals, organic carbon content, and stable carbon isotopes, we aim to establish the history of post-colonial fluvial sedimentation in the Maury River watershed. Further, we can assess changes in channel geometry following the removal of dams to determine the potential for sediment pollution from legacy sediments.

Broadly Characterizing Water Geochemistry Across the Shenandoah Valley

With this research, we investigated the role of land use patterns, soil geochemistry, aquifer types, and dams on ground and surface water quality in the Shenandoah Valley region of Virginia. This region was selected because of the high concentrations of Mn in several wells in these areas (McMahon et al. 2018a), variable land use practices throughout the region, and presence of several historical mill pond dams. This work seeks to better understand the controls of Mn and other trace metals in redox active sites such as springs (in which sub/anoxic groundwater meets the oxygenated surface) and impounded waters (in which stratification can occur with depth), as Mn mobility is linked to its redox behavior.

METHODS

With this research we collected and analyzed spring waters to add to the already established well water databases [via the USGS National Water Information System (NWIS) and the Virginia Household Water Quality Program (VAHWQP; www.wellwater.bse.vt.edu)] (Fig. 2), as well as nearby surface waters and soil cores, and investigated the geochemistry and fluvial sedimentology of historical dams. Water samples were analyzed using field probes for in situ pH, dissolved oxygen (DO), temperature, and specific conductivity measurements, and samples were collected for further analysis of cation and anion

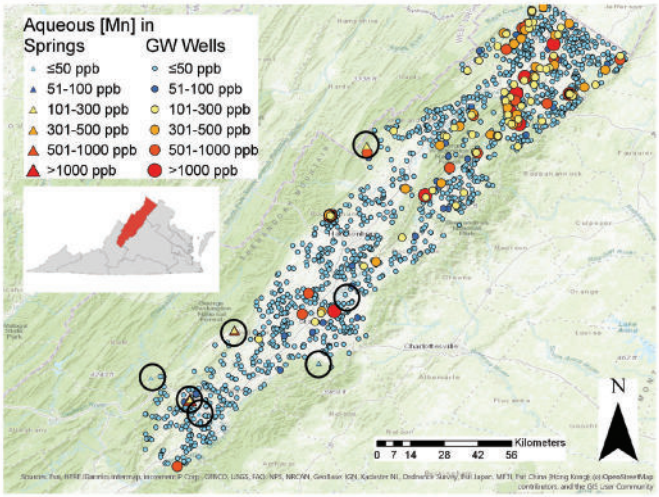

Figure 2. Map of aqueous Mn concentrations in springs (triangles) and groundwater wells (circles) in the Shenandoah Valley, VA, with increasing concentrations increasing the relative size of each data point based on demarcations from ≤50 ppb (light blue) to 51-100 ppb (dark blue) to 101-300 ppb (yellow; above which low level chronic exposure to Mn via drinking water may result in health effects), 301-500 ppb (orange), 501-1000 ppb (light red), to >1000 ppb (dark red). Field sites for springs and seeps are denoted with black circles.

concentrations by ion chromatography (IC) and major elements and trace metal concentrations by inductively coupled plasma-mass spectrometry. Soil samples were analyzed for total element concentrations by X-ray fluorescence and Mn speciation by Mn K-edge X-ray absorption near edge structure (XANES) spectroscopy.

Sediment samples were collected from banks behind breached dams at intervals of 5-10 cm. Samples were then dried and crushed before further analysis. Portable X-Ray Fluorescence (pXRF) measurements were taken to characterize heavy metal concentrations. Elemental abundances of C and N were measured on a Costech ECS 4010 elemental analyzer coupled to a Thermo Electron Delta Plus stable isotope ratio mass spectrometer. A Mastersizer 3000 was used to determine grain size distribution of sediments through time.

To characterize sediment mobilization potential, channel geometry was measured at the site of a recently removed dam site using a TopCon GTS-301 Total Station. Channel armor was measured for grain size using the Wolman pebble count method and a gravelometer.

Figure 3. Photo of the Keck 2022 Advanced team at Natural Bridge, VA. Left to right: Mia Groff, Haley Culbertson, Ani Croy, Maddie Holicky, Kallan Wilde, Margaret Anne Hinkle, Katie Larkin, Noah Willis, Martina Pulido, and Christopher Goldmann (absent: Eva Lyon).

RESEARCH

Our research team included nine students (eight supported by Keck) and two faculty members from five institutions (Fig. 3). We visited 31 sites, of which 24 were springs, seeps, or subsurface environments and seven were dams within the Shenandoah Valley. While all contributed to field work, sample collection, and laboratory analyses, each student took charge of a different component of the project, as follows:

Spring and Groundwater Geochemistry

Ani Croy (Washington and Lee University) examined the geochemistry of water samples collected at 24 springs and seeps visited by the Keck students. Combining the data from field probes with ion chromatography and ICP-MS data, Ani assessed correlations between aqueous Mn concentrations and other ions in solution, pH, DO, depth, most likely aquifer rock type, and more. While the data set taken as a whole indicates that few correlations

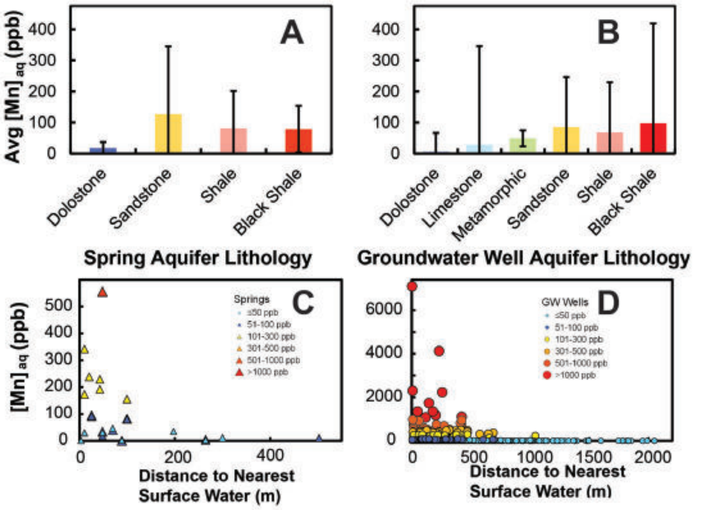

Figure 4. Aqueous Mn in groundwater wells (A,C) and springs (B,D) for average Mn in aquifers with different primary rock types (A,B) and actual aqueous Mn concentrations as a function of distance to nearest surface water bodies (C,D).

exist, when separated out by primary rock aquifer types (sandstone, black shale, and carbonate rocks, the three dominant aquifer types for our field sites), with carbonate aquifers exhibiting relatively low aqueous Mn concentrations, well below thresholds of concern for even low level chronic Mn exposure (Fig. 4A). Conversely, shale, black shale, and sandstone aquifers exhibit much higher average aqueous Mn concentrations (Fig. 4A). Meanwhile, distance to the nearest surface water appears to be correlated with Mn in springs and seeps, with those furthest away from surface water bodies exhibiting the lowest Mn concentrations (Fig. 4B). These results indicate that aquifer lithology serves an important control on spring water geochemistry, and that black shales and sandstones behave very differently than carbonate bearing aquifers.

Chris Goldmann (Trinity University) focused on the aqueous geochemistry and spatial distributions of >1,900 groundwater wells across the Shenandoah Valley, combining data from the VAHWQP and the USGS NWIS database. Mapping the data in ArcGIS, alongside aquifer type, surface lithology, relict Mn ore mines, orchards, surface water maps, and geologic features like faults, dikes, and sills, allowed Chris to determine if correlations exist between such aspects and elevated Mn in groundwater. Chris found that elevated Mn in groundwater in the Shenandoah Valley is most likely geogenic in origin rather than from anthropogenic activities. Chris identified aquifer lithology (Fig. 4B) and distance to surface waters (Fig. 4D) as well as the overall groundwater redox state (determined via principal component analysis) as exerting the strongest controls on Mn concentrations in groundwater wells, consistent with Ani's findings for our field spring and seep sites. Aquifer lithology shows a distinct distribution, indicating that aquifers in karst terrain are more oxic and therefore less likely to have elevated Mn, while those in shales and sandstones are more reducing and therefore at higher risk of elevated Mn.

Noah Willis (Whitman College) researched the interplay between aqueous Mn in our spring and seep water samples and soils by analyzing soils with X-ray fluorescence to determine if there is a correlation between elevated Mn in soils and elevated Mn in the springs and seeps. Noah, like Chris and Ani investigating the geochemistry of waters, identified distinct trends in soil geochemical makeup based on aquifer lithology, with Fe and Mn most correlated in soils from shale and sandstone parent rocks. Soils in regions with sandstone surface lithology were found to have the highest Mn soil content, while those in black shale and carbonate lithologies have similar average Mn soil concentrations (1200 and 1900 ppm Mn, respectively).

Haley Culbertson (Washington and Lee University) investigated soil Mn redox states, general soil properties, and how they relate to aqueous Mn concentrations in our spring and seep field sites. Haley analyzed samples first with SEM-EDS to identify samples of particular interest, and then prepared those select samples for Mn K-edge XANES spectroscopic analyses and analyzed the data by performing linear combination fits on our sample spectra using a suite of Mn oxidation state standards. Haley found soils containing higher Mn(IV) fractions are closest to springs and seeps with low aqueous Mn (and also tend to have higher soil pH), while soils with higher Mn(II) fractions are near springs and seeps with elevated aqueous Mn (and tend to have more acidic soil pH). Haley's work suggests that while lithology does by and large control aqueous Mn concentrations in groundwater and springs, that soils and waters are intimately connected with one another.

Surface Water Impacts by Mill Dams

Martina Pulido (Beloit) measured and analyzed water properties and aqueous geochemistry behind both active and removed dams. She found that waters behind active dams are stratified, fostering low-oxygen conditions in which Mn2+ can accumulate at levels exceeding EPA standards. This finding is concerning, as at least one of these sites is upstream of drinking water intake for Lexington, VA.

Kallan Wilde (St. Norbert College) utilized land use data like historic maps, census data, and aerial photography to identify potential sources of pollution in the Maury River watershed. This involved creating GIS maps corresponding to different periods of time and their associated pollution sources. For example, in a map representing all identified sources prior to 1860, dozens of sources, including mines, forges, mills, and farms, were identified. These maps may be particularly useful in interpreting sedimentological data through time.

Mia Groff (Whitman College) and **Maddie Holicky** (Beloit College) studied the legacy sediment package that accumulated behind dams on the Maury River. Maddie analyzed organic carbon and nitrogen values, and measured heavy metal concentrations to track land use changes through time. She noted three general phases of land use that can be interpreted in the context of activities like deforestation, mining, and metal forging (Fig. 5). Mia measured sediment grain sizes and compared measurements to heavy metal concentrations, noting a negative relationship between Mn and Fe concentrations and grain size. This relationship suggests that these metals are more likely to adsorb onto finer grain sizes like clay.

Katie Larkin (Washington and Lee University) studied the changes in channel morphology following the removal of a low head dam on the Maury River in 2019 (Fig. 1). Katie repeated several channel cross section measurements at areas that were flagged as susceptible to bank erosion following an initial study in 2019. Results show that the channel upstream of the dam has deepened, and nearly 4000 m3 of sediment has been removed in the surveyed reach. These findings support the importance of tracking channel response to dam removal, especially considering the elevated concentrations of heavy metals in some legacy sediment horizons.

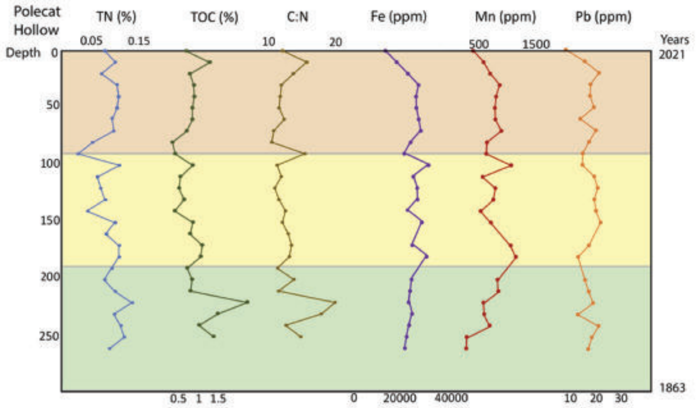

Figure 5. Chemostratigraphic profile for one of the legacy sediment sites (Polecat Hollow). Horizontal color bands represent different phases of land use in the region: Widespread deforestation and mining in the post-colonial era (green), Declining mining and shift to agriculture (yellow) and recent changes, including further reduction in mining activities (orange). Plot by Maddie Holicky for her thesis.

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REFERENCES

Ashby, S. L., Myers, J. L., Laney, E., Honnell, D., & Owens, C. 1999. The effects of hydropower releases from Lake Texoma on downstream water quality. Journal of Freshwater Ecology, 14, 103–112.

Bjørklund, G., Chartrand, M.S., Aaseth, J., 2017. Manganese exposure and neurotoxic effects in children. Environmental Research 155, 380–384. https://doi.org/10.1016/j.envres.2017.03.003

Bouchard, M., Laforest, F., Vandelac, L., Bellinger, D., Mergler, D., 2007. Hair Manganese and Hyperactive Behaviors: Pilot Study of School-Age Children Exposed through Tap Water. Environmental Health Perspectives 115, 122–127. https://doi.org/10.1289/ehp.9504

Bouchard, M.F., Sauvé, S., Barbeau, B., Legrand, M., Brodeur, M.-È., Bouffard, T., Limoges, E., Bellinger, D.C., Mergler, D., 2011. Intellectual Impairment in School-Age Children Exposed to Manganese from Drinking Water. Environmental Health Perspectives 119, 138–143. https://doi.org/10.1289/ehp.1002321

Dauer, D. M., Ranasinghe, J. A., & Weisberg, S. B. 2000. Relationships between benthic community condition, water quality, sediment quality, nutrient loads, and land use patterns in Chesapeake Bay. Estuaries, 23, 80-96. https://doi.org/10.2307/1353227

Dortch, M. S., & Hamlin-Tillman, D. E. 1995. Disappearance of reduced manganese in reservoir tailwaters. Journal of Environmental Engineering, 121, 287–297.

Gillispie, E.C., Austin, R.E., Rivera, N.A., Bolich, R., Duckworth, O.W., Bradley, P., Amoozegar, A., Hesterberg, D., Polizzotto, M.L., 2016. Soil Weathering as an Engine for Manganese Contamination of Well Water. Environmental Science & Technology 50, 9963–9971. https://doi.org/10.1021/acs.est.6b01686

Gordon, J. A. 1989. Manganese oxidation related to the releases from reservoirs. Journal of the American Water Resources Association, 25, 187–192.

Hafeman, D., Factor-Litvak, P., Cheng, Z., van Geen, A., Ahsan, H., 2007. Association between Manganese Exposure through Drinking Water and Infant Mortality in Bangladesh. Environmental Health Perspectives 115, 1107–1112. https://doi.org/10.1289/ehp.10051

Hess, G. W., Kim, B. R., & Roberts, P. J. W. (1989). A manganese oxidation model for rivers. Journal of the American Water Resources Association, 25, 359–365. doi:10.1111/j.1752-1688.1989.tb03072.x

Hue, N.V., Vega, S., Silva, J.A., 2001. Manganese Toxicity in a Hawaiian Oxisol Affected by Soil pH and Organic Amendments. Soil Sci. Soc. Am. J. 65, 153–160. https://doi.org/10.2136/sssaj2001.651153x

Hupp, Cliff R., Noe, G. B., Schenk, E. R., & Benthem, A. J. 2013. Recent and historic sediment dynamics along Difficult Run, a suburban Virginia Piedmont stream. Geomorphology, 180–181, 156–169. https://doi.org/10.1016/j.geomorph.2012.10.00

Khan, K., Wasserman, G.A., Liu, X., Ahmed, E., Parvez, F., Slavkovich, V., Levy, D., Mey, J., van Geen, A., Graziano, J.H., Factor-Litvak, P., 2012. Manganese exposure from drinking water and children’s academic achievement. NeuroToxicology 33, 91–97. https://doi.org/10.1016/j.neuro.2011.12.002

Kiracofe, Z.A., Henika, W.S., Schreiber, M.E., 2017. Assessing the Geological Sources of Manganese in the Roanoke River Watershed, Virginia. Environmental Engineering Science 23, 43–64.

Langley, R., Kao, Y., Mort, S., Bateman, A., Simpson, B., Reich, B., 2015. Adverse neurodevelopmental effects and hearing loss in children associated with manganese in well water, North Carolina, USA. J Environ Occup Sci 4, 62. https://doi.org/10.5455/jeos.20150403060427

Li, M.S., Luo, Y.P., Su, Z.Y., 2007. Heavy metal concentrations in soils and plant accumulation in a restored manganese mineland in Guangxi, South China. Environmental Pollution 147, 168–175. https://doi.org/10.1016/j.envpol.2006.08.006

Ljung, K., Vahter, M., 2007. Time to Re-evaluate the Guideline Value for Manganese in Drinking Water? Environmental Health Perspectives 115, 1533–1538. https://doi.org/10.1289/ehp.10316

Lutgen, A., Jiang, G., Sienkiewicz, N., Mattern, K., Kan, J., & Inamdar, S. 2020. Nutrients and Heavy Metals in Legacy Sediments: Concentrations, Comparisons with Upland Soils, and Implications for Water Quality. Journal of the American Water Resources Association. 56, 669-691.

McMahon, P.B., Belitz, K., Reddy, J.E., Johnson, T.D., 2018a. Elevated Manganese Concentrations in United States Groundwater, Role of Land Surface–Soil–Aquifer Connections. Environmental Science & Technology 53, 29–38.

McMahon, P.B., Reddy, J.E., Johnson, T.D., 2018b. Data for Elevated Manganese Concentrations in United States Groundwater, Role of Land Surface-Soil-Aquifer Connections. U.S. Geological Survey Data Release. https://doi.org/10.5066/P9Y4GOFQ

Munger, Z. W., Shahady, T. D., Schreiber M.E. 2017. Effects of reservoir stratification and watershed hydrology on manganese and iron in a dam-regulated river. Hydrological Processes, 31, 1622-1635.

Niemitz, J., Haynes, C., & Lasher, G., 2013. Legacy sediments and historic land use: Chemostratigraphic evidence for excess nutrient and heavy metal sources and remobilization. Geology, 41, 47-50. https://doi.org/10.1130/G33547.1

Sanders, A.P., Desrosiers, T.A., Warren, J.L., Herring, A.H., Enright, D., Olshan, A.F., Meyer, R.E., Fry, R.C., 2014. Association between arsenic, cadmium, manganese, and lead levels in private wells and birth defects prevalence in North Carolina: a semi-ecologic study. BMC Public Health 14, 955. https://doi.org/10.1186/1471-2458-14-955

Semu, E., Singh, B.R., 1995. Accumulation of heavy metals in soils and plants after long-term use of fertilizers and fungicides in Tanzania. Fertilizer research 44, 241–248. https://doi.org/10.1007/BF00750931

Spangler, A.H., Spangler, J.G., 2009. Groundwater Manganese and Infant Mortality Rate by County in North Carolina: An Ecological Analysis. EcoHealth 6, 596–600. https://doi.org/10.1007/s10393-010-0291-4

Spangler, J.G., Reid, J.C., 2010. Environmental Manganese and Cancer Mortality Rates by County in North Carolina: An Ecological Study. Biol Trace Elem Res 133, 128–135. https://doi.org/10.1007/s12011-009-8415-9

U.S. Environmental Protection Agency, 2004. Drinking Water Health Advisory for Manganese.

Virginia Department of Environmental Quality, 2015. Commonwealth of Virginia State Water Resources Plan.

Walter, R. C., & Merritts, D. J. 2008. Natural streams and the legacy of water-powered mills. Science, 319, 299-304.

Williams, M., Todd, G.D., Roney, N., Crawford, J., Coles, C., McClure, P.R., Garey, J.D., Zaccaria, K., Citra, M., 2012. Toxicological Profile for Manganese.