

ASSESSING LAND USE CHANGES USING THE LEGACY SEDIMENTS IN THE SHENANDOAH VALLEY OF VIRGINIA

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INTRODUCTION

Between the 17th and 19th centuries, thousands of dams were put in place in the state of Virginia to provide waterpower for agricultural and industrial purposes which caused an increased rate of sedimentation in the floodplains behind these dams (Walter and Merritts, 2008; Pizzuto and O'Neal, 2009; Balascio et al., 2019). These sediments are more formally known as legacy sediments because of the location and time frame in which they were deposited (Walter and Merritts, 2008; James, 2013; Balascio et al., 2019). These sediments are of interest because when dams are removed the legacy sediments are remobilized, and can release harmful pollutants that have built up in these sediments into the waterways (Walter and Merritts, 2008; Pizzuto and O'Neal, 2009; Kirwan et al., 2011, Palinkas et al., 2019; Balascio et al., 2019). This study hypothesizes that the changes in elemental and isotopic composition in these sediments reflect the changes in land use in the Maury River watershed in Virginia. The Maury is a tributary of the James River, which is part of the Chesapeake Bay Watershed (Fig. 1).

This project is part of a Keck Geology Consortium project focused on the historical and potential future impacts of millpond dams on surface water quality. This research will support the overall project by providing data regarding changes in land use since colonial times, the presence of geochemical pollutants in the sediments, and how those can affect the water quality in the Chesapeake Bay watershed.

Proxies

The proxies used in this study are as follows: total organic carbon (TOC), total nitrogen (TN), carbon

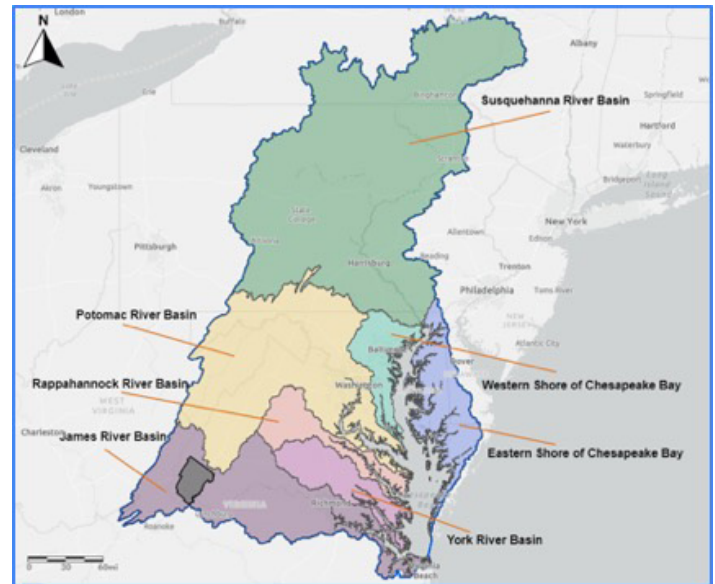


Figure 1. Chesapeake Bay Watershed. Rockbridge County is the gray polygon within the James River Basin. Map by Kallan Wilde.

to nitrogen ratio (C:N), nitrogen isotopes ($\delta^{15}\text{N}$), carbon isotopes ($\delta^{13}\text{C}$), and trace metals (Mn, Fe, Pb). The carbon to nitrogen ratio distinguishes between the amount of aquatic organic matter and terrestrial organic matter. TOC represents the fraction of organic matter that accumulated, while C:N values identify increases and decreases in the deposition of land organic matter from changes in land use (Meyers, 1997; Dean, 1999; Meyers, 2001). $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values can indicate trends relating to anthropogenic activities such as fossil fuel burning and atmospheric fallout (Holtgrieve et al., 2011; Dean et al., 2014). Changes in phytoplankton in lake matter can also cause an increase in nitrates, used to complement the C:N values to show an increase in land usage such as an increase in agriculture following deforestation (Hecky and Kilham, 1988; Meyers, 1997; Meyers, 2001; Balascio et al., 2019). The trace metals are proxies for different land uses such as mining, metal forging, and construction (Niemitz, et al., 2013;

Balascio et al., 2019).

METHODS

Sampling

Samples from the banks behind removed dams were collected at numerous locations, including Polecat Hollow and Jordan's Point (Fig. 2). In the vertical river banks, a sediment sample was taken every 5 to 10 centimeters from the top of the bank to the bottom (Fig. 3). We interpreted the bottom of the bank to be the present water level of the river, based on the presence of in situ tree stumps dated to the late 1700s, consistent with the onset of milling activity in the region (Iosso and Harbor, 2020).

Elemental Analysis

Sediments were dried overnight for 48 hours in an oven at 35°C and were ground using a mortar and pestle to homogenize the samples for total carbon and nitrogen analyses. A subset of samples was rinsed with HCl to remove inorganic carbon before pulverization and elemental analysis. Carbon and nitrogen elemental concentrations and stable isotope ratios for dried and powdered sediment samples were determined using a Costech ECS 4010 elemental analyzer coupled to a Thermo Electron Delta Plus stable isotope ratio mass spectrometer at Washington and Lee University. Carbon and nitrogen isotope data were calibrated using the USGS-40 standard. Elemental C and N were corrected based on an acetanilide standard. Duplicate measurements of unknowns were used to establish precision: standard deviations were better than 0.007 for %N, 0.08 for %C, 0.1 for $\delta^{15}\text{N}$, and 0.5 for $\delta^{13}\text{C}$.

PXRF

Samples were analyzed using a Thermo Fisher Scientific Niton XL3t GOLDD++ Handheld XRF using the Test All Geo analysis mode at Beloit College. The standards used were NIST 2709a (180-649) San Joaquin Soil, Thermo Fisher 180-647 SiO₂ blank, USGS SGR-1b Green River Shale, USGS SBV-1 Brush Creek Shale, AMIS 0547 Dolomite, Olifantsfontein, South Africa, AMIS 0461 Limestone, South Africa, and USGS W-2 Diabase. Mn, Fe, and Pb were calibrated based on these standards using the

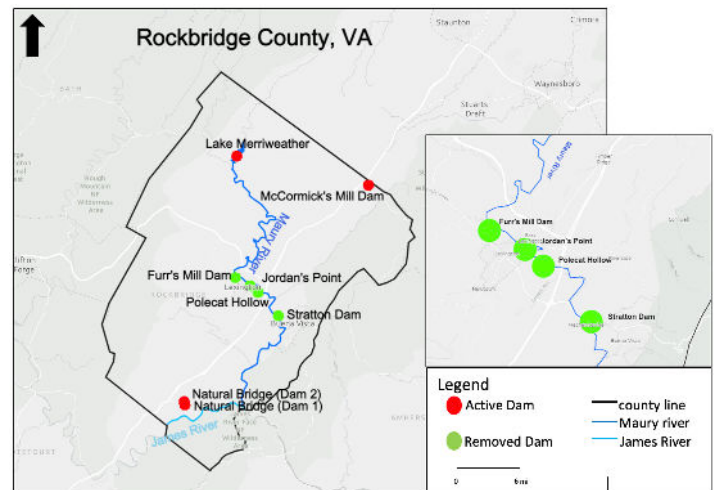


Figure 2. Legacy sediment and water sampling sites in Rockbridge County, VA. Red pins are sample collection sites at extant dams and green pins are sample collection sites where the dam has been removed. The inset map is a close-up map of the sites on the Maury River. The only sites reviewed in this study are Jordan's point and Polecat Hollow. Map by Kallan Wilde.

method of Rowe et al. (2012).

RESULTS

We assigned three broad temporal zones to the stratigraphy to contextualize changes through time at each site. These zones were based on trends in the proxies, some of which were consistent between sites.

Jordan's Point

The lowermost zone of interest is from 350 to 140 cm. In this zone, there are increases in C:N and $\delta^{13}\text{C}$ and they parallel one another throughout the column (Fig. 4). $\delta^{15}\text{N}$ steadily increases throughout this part of the column, and Fe and Mn increase until they decrease above 200 cm. Notably, the trace metals (Fe, Mn, Pb) are sampled at a coarser resolution in this zone, which limits our ability to compare their trends to the other proxies.

The middle zone of Jordan's Point chemostratigraphic column is from 140 to 60 cm. A major spike occurs in the C:N at 140 cm, and TC and TN steadily increase. $\delta^{15}\text{N}$ is invariable for the middle zone. There is a large spike in both Mn and Pb at the beginning of this zone after which they decrease. Fe decreases slightly over the course of this zone (Fig. 4).

The uppermost zone is between 60 and 0 cm and is



Figure 3. A photo of a student collecting samples from a bank at the Jordan's Point locality.

distinguished by the overall decrease in C:N, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and the trace metals. There is a slight increase in both the C:N and $\delta^{13}\text{C}$ followed by a decrease in both until 0 cm. At 60 cm a sharp decrease in the $\delta^{15}\text{N}$ is present, the same trend occurs with the Mn, Fe, and Pb. The TN and TC increase from 60 to 0 cm (Fig. 4).

Polecat Hollow

The lowermost zone of interest is from depths of 260 to 190 cm. In this zone the TOC and C:N trends both increase at 230 cm after which they decrease. TN also spikes at 220 cm, but in less magnitude than C:N and TOC. The Mn and Fe trends increase steadily until a depth of 190 cm, which marks the end of the zone. Throughout the zone Pb ranges from 8 to 21 ppm (Fig. 5).

The middle zone of interest is from 190 to 90 cm. TN, TOC, C:N, Fe, and Mn do not vary often throughout this part of the column, except for their increases at 100 cm. The Pb concentrations are relatively invariant (Fig. 5).

The uppermost zone begins at a depth of 90 cm where a few of the trends change. There is a large increase in C:N and a slight increase in TOC at a depth of 20 cm, after which both trend to lower values. TN increases at the beginning of this zone and then stays fairly

consistent. Fe and Mn decrease at 30 cm until depth of 0 cm while Pb starts to decrease at 20 cm until 0 cm (Fig. 5).

DISCUSSION

Both Jordan's Point and Polecat Hollow localities show trends that relate to the hypothesis. These trends are divided into zones of interest, which represent three broad intervals of time: 1. post-colonial forest clearing activities and early agriculture and mining in the Shenandoah Valley region, 2. the stabilization and continuation of agriculture in the area and the decrease in mining, and 3. an overall increase in the effects of anthropogenic activities like farming and burning of fossil fuels as discussed below. Both sites show these three broad zones, albeit at different levels in the bank stratigraphy (Fig. 4, 5).

The zones are referred to by depth from the bottom of the column to the top. The dates for the top and bottom of the column were assigned based on when the dam was put into place (bottom) and the present (top) assuming the sedimentation rate was constant. A constant sedimentation rate is unlikely, but there is not currently an established age model that would more accurately represent changes in sedimentation rate through time. The river is still capable of overtopping its banks and depositing sediments after dam removal (Kirwan et al., 2011; Palinkas et al., 2019, Iosso and Harbor, 2020), hence the date of 2021 at the top of the bank.

The assigned zones for Polecat Hollow and Jordan's Point somewhat align. While the zones and some of the trends in both represent the same three changes in land use, there are differences in the lengths of the zones along with differences in the trends overall (Fig. 4, 5). Because sedimentation rate changes while the dams are in place due to the removal of trees in the surrounding landscape, along with intense weathering events, and then changes significantly after the dams are removed due to changes in mean water level, (Iosso and Harbor, 2020), it is very difficult to cross-compare the localities' chemostratigraphy by layer.

The geochemical analysis of sediments at Jordan's Point reveal land use changes based on elemental changes seen in the chemostratigraphy. The lowermost

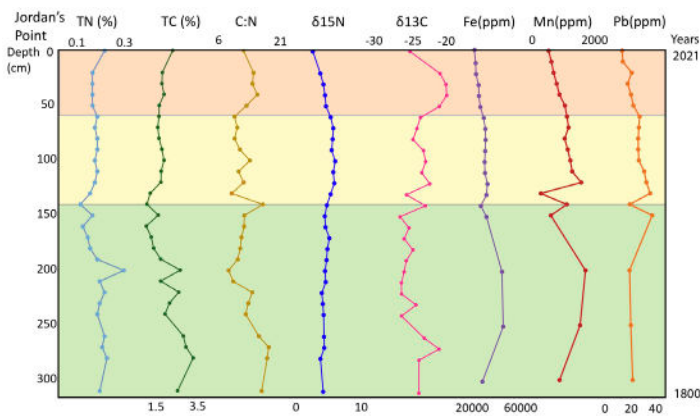


Figure 4. Chemostratigraphic profile for Jordan's Point. Zones of interest are as follows: lowermost (green), middle (yellow) and uppermost (orange).

zone is characterized by an increase in C:N and TC in the lower depths of the column, which suggests an increase in deforestation. Likewise, the concentrations of Fe and Mn increase over this zone. These trends are likely related due to the burning of trees to power metal forges during the late 1800s into the early 1900s. (Miller, 1996; Wilkinson and McElroy, 2007; Pavlowsky et al. 2017; Niemietz et al. 2013; Balascio et al. 2019). These same trends in C:N, TOC, Fe, and Mn occur in the lowermost zone of Polecat Hollow (Fig. 5). Thus, it appears that deforestation can be correlated with the increase in heavy metals related to mining and forging of these elements in the region as (Miller, 1996; Wilkinson and McElroy, 2007; Pavlowsky et al., 2017; Niemietz et al., 2013; Balascio et al., 2019).

The increasing trends for trace metals Fe and Mn correlate with changes seen in C:N and may be attributed to increases in mining and smelting in the area (Balascio et al., 2019; Pavlowsky et al., 2017, Scott 2015). Scott (2015) describes the fourteen furnaces that operated between 1820 and 1920 and the large number of iron ore deposits present in the area. The furnaces needed a great amount of iron ore to operate; on average it took 10 tons of ore to make one ton of pig iron (Scott, 2015). The increases in Fe and Mn in the lowermost zone at Jordan's Point may be related to this increase in mining and forging activity (Fig. 4).

The middle zone of Jordan's Point likely represents the decline in mining in the area and the stabilization of agricultural practices. There are increases in TOC, C:N, Fe and Mn in Polecat Hollow's middle zone

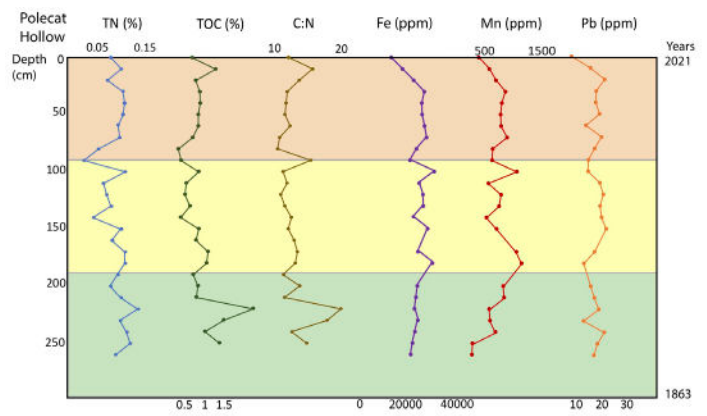


Figure 5. Chemostratigraphic Profile for Polecat Hollow. Zones of interest are as follows: lowermost (green), middle (yellow) and uppermost (orange).

which can also be attributed to these land changes. Balascio et al. (2019), describes how Lake Matoaka showed significant fluctuations in TOC and C:N due to the terrestrial-derived organic matter due to early agricultural practices in the area. In this zone, there is also a slight increase in Pb followed by Mn, and which may all be related to the increase in agricultural activity in the early 1900s (Niemietz et al., 2013, Balascio et al., 2019). Niemietz et al. (2013) relates the presence of heavy metals in agricultural soils and sediments surrounding farms to fertilizer usage. The increases in both Fe, Mn and Pb could be a reflection of the increase in fertilizer usage, such increases are also seen in the middle zone of Polecat Hollow in the Fe and Mn (Niemietz et al., 2013; Balascio et al., 2019) (Figure 4, 5)

The uppermost zone for both sites is characterized by a decrease in C:N and all of the trace metals. At Jordan's Point, where isotopic values were measured, there are declines in $\delta^{15}\text{N}$, and $\delta^{13}\text{C}$. The decrease in $\delta^{15}\text{N}$ is consistent with the atmospheric fallout of isotopically depleted nitrogen seen by Holtgrieve et al. (2011), which is due to the increased, widespread industrial N production in the past half-century. This change in $\delta^{15}\text{N}$ is also related to $\delta^{13}\text{C}$. A shift to lower $\delta^{13}\text{C}$ after ~1950 CE may be attributed to the increased consumption of fossil fuels and increased use of fertilizers (Dean et al., 2014).

Throughout most of this zone at both sites Fe and Mn decrease gradually until the end of the column, which could be attributed to the shift away from the Fe and Mn mining and smelting operations (Figure 4, 5). According to Scott (2015), the mining of iron ore and

the iron industry in general, decreased significantly after the 1920s (Miller, 1996). This could explain the general decrease of C:N and TOC throughout this zone in Polecat Hollow's chemostratigraphy because if less mining was happening, then less deforestation to power forges would occur (Meyers, 1997; Dean, 1999; Meyers, 2001; Balascio et al., 2019).

CONCLUSION

Based on the trends in the chemostratigraphic data, the hypothesis of this research can be supported. Although the age control of that data is lacking, there are general trends whose order is consistent with the overall history. Because of the trends relating to the mining of iron ore, and agriculture, it is reasonable to conclude that the sediments deposited behind 19th century milldams preserve a record of human activities in the Maury River watershed.

There were some limitations to the study, including the lack of absolute time constraints for the data, which made interpreting the timing of changes in land use difficult. Another consideration is the effect of fluvial processes on these sediments. This study was conducted on Maury River bank sediments, whereas many of the studies that apply similar methodologies are based on lake sediment archives. Thus, there could be influences on these geochemical data that are not accounted for in our interpretations.

With more research on the legacy sediments, there will be a greater understanding of the intensity that human activities long term and short term have on fluvial sediments and how those sediments impact the environment overall.

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