

ANALYSIS OF SOIL GEOCHEMISTRY TO BETTER UNDERSTAND GEOGENIC MANGANESE CONTAMINATION IN THE SHENANDOAH VALLEY

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INTRODUCTION

Manganese contamination in drinking water poses serious long-term health risks even at low concentrations if exposure is chronic. Children and infants are especially at risk, with the potential for neurodevelopmental defects, including problems with memory, attention, and motor skills (Williams et al., 2012). In the United States there is no legally binding standard for manganese in drinking water, only a secondary unenforceable aesthetic standard of 50 parts per billion (Spangler et al., 2010). However, recent studies have shown that exposure to as little as 100 ppb can pose a serious health risk (Williams et al., 2012). Manganese contamination can be anthropogenic and geogenic in nature. A recent study indicates that certain hydrogeologic provinces are more prone to having groundwater contaminated with manganese (Erickson et al., 2019). This current paper focuses on the Shenandoah Valley region of Virginia.

Because manganese contamination can be geogenic in nature, an understanding of an area's geology and hydrology is useful. Virginia's geology generally represents the products of advancing and retreating ocean shorelines, and the deformation resulting from the tectonic collisions that built the Appalachians in the Paleozoic Era (Torsvik, 2017). Our area of study lies in the Valley and Ridge province. The valleys are usually underlain by the Edinburg Formation, a limestone of Ordovician age. The ridges are usually composed of sandstones (Heller et al., 2018). The limestone has been preferentially weathered to create the valleys, leaving the sandstone in place as the ridges that generally run north-south.

One of these valleys, The Shenandoah Valley, lies mostly in north-central Virginia, with its northern terminus in Maryland. It is bounded by the Appalachian Plateau province to the west, and the Blue Ridge Mountains to the east. The Shenandoah River eventually runs into the Chesapeake Bay, flowing south to north for much of its course. Our study examines springs from six different sites throughout the Shenandoah Valley spanning from Shenandoah County to Natural Bridge, VA. This encompasses Rockbridge County in the south, through Augusta, Rockingham, and Shenandoah Counties. Whereas the southern end of our area of study may lie in the culturally defined Shenandoah Valley, hydrologically it does not. Our area of study can be broken into two different watersheds: the Shenandoah Watershed to the north and the James River Watershed to the south, which exits the Shenandoah Valley running from west to east through a gap in the Blue Ridge. Streams in this region are generally gaining streams, recharged with groundwater, responding quickly to precipitation events (Swain et al., 1991). Due to the tectonic history of the area the strata that compose the Valley and Ridge dip steeply in many places. Therefore, most wells will only penetrate the unit found on the surface, making surface lithology a good proxy for what unit a well will draw water from (Trapp et al., 1997).

Manganese is naturally found at around 600 ppm in upper continental rocks worldwide and 260 ppm in soils on average in the Eastern United States (see Cannon et al., 2017 for review). Manganese is a redox active element with +2, +3, +4, +5, +6, and +7 oxidation states (Railsback, 2003). The oxidation state of manganese controls whether or not manganese is

bio-available or not when consumed. Of the oxidation states most commonly found in natural systems (+2,+3, and +4), soluble manganese is most stable as Mn^{2+} , being found in anoxic conditions, while more oxic conditions, like a well mixed stream, oxidize manganese to Mn^{3+} or Mn^{4+} , precipitating out and forming minerals such as pyrolusite, todorokite, or buserite (Cannon et al., 2017).

In the Shenandoah Valley, Mn oxide ores are commonly found in fault breccias contained within the Antietam Sandstone (Carmichael et al., 2017). It is thought that this Mn originates from Mn dissolved in water percolating downward, into more reducing conditions, allowing it to remain as soluble Mn^{2+} . As water then upwelled and discharged through springs along faults, or directly into streams, the manganese was oxidized, forming the oxide ores that exist today (Carmichael et al., 2017). This model explains the occurrence of manganese oxides in fault breccia and ancient alluvium within the Shenandoah Valley. The goal of this project is to analyze the complex relationships that govern the redox state of manganese in groundwater in the Shenandoah Valley today. Through analyses of soil samples we hope to gain a better understanding of the redox chemistry that controls the oxidation state of manganese in groundwater.

METHODS

Field Methods and Sample Treatment

Water samples were collected from a series of springs and seeps across the Shenandoah Valley (Fig. 1) as close as possible to the point where water emerged from the subsurface. 250 mL polypropylene bottles were primed three times with spring water before sampling. An aliquot of each sample was filtered in the field with 0.22 μm filters, discarding the first 1 mL of filtrate and saving the filter paper for microscopic analysis of the filtered solids. Two aliquots of filtered water were collected, one simply taken back to the lab and refrigerated at 4°C for ion chromatography analyses (to determine major anion and cation concentrations). The other aliquot was acidified to 1% nitric acid (trace metal grade) upon returning to the lab and then refrigerated for major element and trace

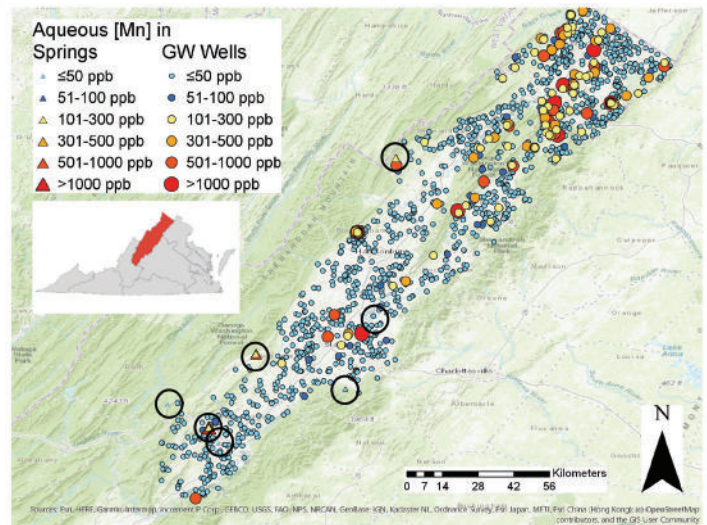


Figure 1. Map of aqueous Mn concentrations in springs (triangles) and groundwater wells (circles) in the Shenandoah Valley, VA, with increasing concentrations increasing the relative size of each data point based on demarcations from ≤ 50 ppb (light blue) to 51-100 ppb (dark blue) to 101-300 ppb (yellow; 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.

metal analyses via inductively coupled plasma-mass spectrometry. In the field, a YSI probe was used to measure dissolved oxygen (DO), specific conductivity, temperature, and pH.

Soil cores were collected as close as possible to the spring or pond itself. Additional cores were also taken up- and down-gradient of each spring and seep. Cores were sealed in polyethylene bags and then refrigerated upon return to the lab.

The Munsell soil classification is a system used to sort samples of damp soil into different discrete color categories. We used this system to separate soil cores into different color-based horizons. A subsample was collected from each Munsell defined horizon, and dried at 105°C overnight. Samples were then ground in an agate mortar and pestle for 8 minutes to create a fine powder. An aliquot of sample was used to make slides for X-Ray Diffraction (XRD) and the rest was set aside for total elemental analyses by X-ray fluorescence (XRF) and later soil sequential extractions to assess the mobility of elements of interest.

XRF Analyses

Samples were dried and ground following the protocols outlined above were then packaged in pXRF cups. A Thermo Scientific Niton XL3t pXRF was set to analyze samples with the “test all geo” program for 120 seconds. The instrument was calibrated for Mn with USGS standards SGR-1b, AGV-2, and BCR-2. At the start of each run, an initial calibration was performed with the three standards, five samples were analyzed, and then a second calibration was performed with the same three standards. No systematic drift associated with a drop in battery voltage was noticed upon analysis. A calibration curve was created with the standards and used to determine the concentrations of Mn and Fe in each soil subsample.

RESULTS

When plotted, data from pXRF analysis of soil samples visually shows a positive correlation between total Fe concentration in soil and total Mn concentration in soil, however owing to the wide range of Fe concentrations, only has an R^2 of 0.074 (Fig. 2). A breakdown of total Fe concentration in soil and total Mn concentration in soil by aquifer lithology reveals no real trends in any of the aquifer lithologies. (Fig. 3).

Data from pXRF analysis of soil samples and ICP-MS analysis of water samples reveals that there is a positive correlation between total Mn concentration in soil samples and aqueous Mn concentration in water samples taken from carbonate aquifers, with an R^2 of 0.54 (Fig. 4). The same data set shows a slight negative correlation between total Mn concentration in soil samples and aqueous Mn concentration in water

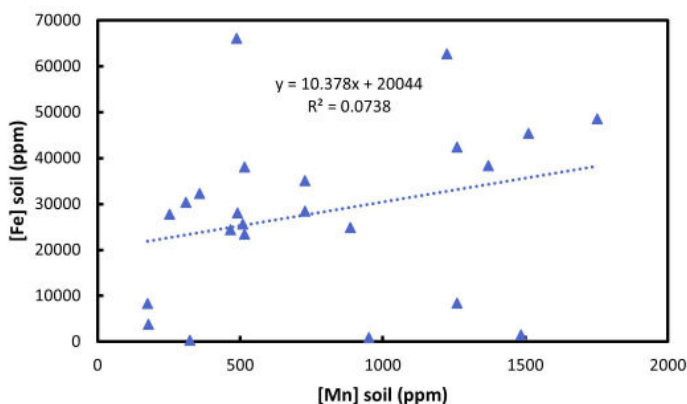


Figure 2. Plot of total Fe concentration versus total Mn concentration in soil samples.

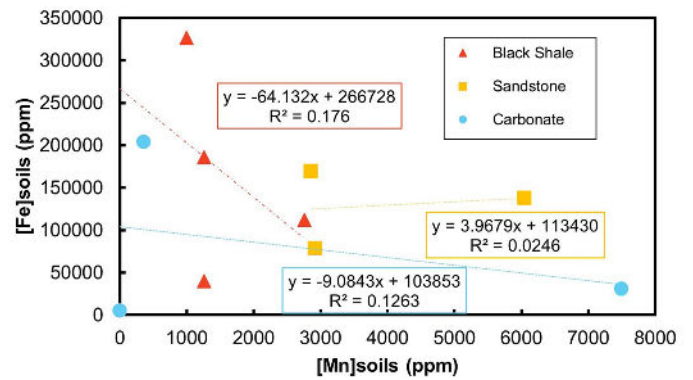


Figure 3. Plot of total Fe concentration in soil versus total Mn concentration in soil broken down by aquifer lithology. Black shale sites shown in red triangles, sandstone sites shown in yellow squares, and carbonate sites shown in blue circles.

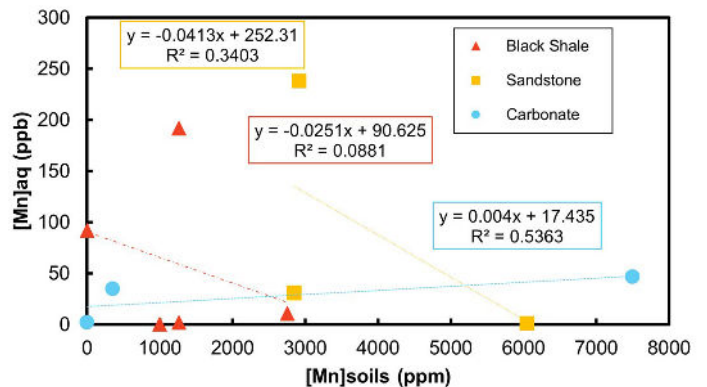


Figure 4. Plot of total Mn concentration in soil samples versus aqueous Mn concentration in water samples broken down by aquifer lithology. Black shale sites shown in red triangles, sandstone sites shown in yellow squares, and carbonate sites shown in blue circles.

samples taken from sandstone aquifers, with an R^2 value of 0.34 (Fig. 4). There is no meaningful trend one way or the other in black shale aquifers (Fig. 4).

DISCUSSION

Black shale aquifers do not exhibit a meaningful correlation between aqueous Mn and total soil Mn. There is a potential negative correlation between aqueous Mn and total soil Mn in sandstone aquifers, with an R^2 of 0.34 (Fig. 2). This negative correlation between aqueous Mn and total soil Mn as observed in sandstone aquifers makes sense; as a system becomes more oxidizing, more Mn oxidizes and precipitates from spring water and becomes trapped in the soil.

However, carbonate aquifers display a positive correlation between aqueous Mn and total soil Mn. It should be noted that all carbonate soil samples in

this data set were obtained from the Maple Flats Pond complex, a group of ponds with thick clay layers overlying Antietam quartzite alluvial cobbles on top of carbonates (Buhlmann et al., 1999). Dissolution of the carbonates resulted in the formation of these sinkhole ponds, while the thick clay layer allows these ponds to periodically fill and retain water for extended periods of time (Fleming & Alstine, 1999). Thus, these ponds are unique systems in that there is no contribution of Mn to these waters from groundwater systems (with the exception of Spring Pond), thus all Mn in these ponds must be derived exclusively from soil weathering. Therefore, if aqueous Mn can only be derived from soil weathering in these cases, it follows that increasing soil concentrations will result in increased aqueous Mn in the corresponding springs and seeps.

One alternative explanation that does bear mentioning is that carbonate aquifers often have higher bicarbonate concentrations than other aquifer rock types and therefore stabilize manganese carbonate minerals such as rhodochrosite, MnCO_3 . Rhodochrosite is more soluble (with a pK_{sp} value of 10.39) than Mn (oxyhydr)oxide minerals such as birnessite (pK_{sp} of 15.62), pyrolusite (pK_{sp} of 17.84), and manganite (pK_{sp} of 18.26) (Harris, 2016). However, the alkalinity of these waters from the Maple Flats Pond complex are no greater than the springs and seeps in sandstone and shale aquifers here studied (Croy, 2022), thus this explanation is less likely than the soil weathering hypothesis.

Although there are no clear correlations between total Fe concentration in soil and total Mn concentration in soil when broken down by lithology (Fig. 3), plotting all data together reveals a positive correlation (Fig. 2). The broad range of Fe concentrations makes the observed small R^2 very likely, even though it is clear there is a general positive relationship between total soil Fe concentration and total soil Mn concentration (Fig. 2). Generally speaking, a positive correlation between total Fe concentration in a soil core and total Mn concentration is logical. Mn and Fe behave similarly from a redox perspective (Harris, 2016). Both aqueous Fe and Mn are most stable as divalent cations. When oxidized to 3+ they will precipitate out as an Mn/Fe (oxyhydr)oxide mineral.

Overall bulk Mn concentrations found in this study differ somewhat from what past studies have found. A survey of wells from across the United States found bulk Mn concentrations of anywhere between 300 to 800 ppm (Cannon et al., 2017). Data from pXRF analysis in this current study returned bulk Mn concentrations much higher than found in Cannon et al. (2017). The data in Cannon et al. (2017) was collected around wells all across the United States, including data from areas that may not be particularly susceptible to having elevated levels of Mn in groundwater. Considering that the average bulk Mn concentration in soil worldwide is 650 ppm, some samples from Cannon et al. (2017) clearly have bulk Mn concentrations below average. It is also worth considering that Cannon et al. (2017) used data collected from around wells, not springs. Soil around springs is much more likely to interact with groundwater than soil around a well (Tolman, 1937). Surface or rainwater that might be more likely to interact with soil around a well, may be very different from groundwater from a chemical perspective.

CONCLUSION

Understanding what factors are correlated with high manganese concentrations in groundwater is a public health imperative. Analyzing the chemistry of the soil around springs is a good way to help build that understanding. This study found that there is a general positive correlation between total Fe concentration in soil and total Mn concentration in soil. This study also found that different aquifer lithologies display different relationships between total Mn concentration in soil and total aqueous Mn concentration, with carbonate aquifers displaying a positive relationship and black shale and sandstone aquifers displaying negative relationships. These relationships give valuable information about the source of Mn contamination in systems. A positive correlation between total Mn concentration in soil and total aqueous Mn suggests that the soil itself may be the major source of aqueous Mn contamination. A negative correlation suggests that the redox conditions of a system control where Mn appears in the system. A more oxidizing system may cause Mn to end up as oxides in soil, whereas a more reducing system may cause Mn to mobilize and end up in the water.

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