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SURFACE AND SUBSURFACE PROPERTIES REGULATING MANGANESE  
CONTAMINATION OF GROUNDWATER IN THE NORTH CAROLINA PIEDMONT

By

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FINAL REPORT

to the  
Water Resources Research Institute  
of  
The University of North Carolina

For Research entitled

Surface and Subsurface Properties Regulating Manganese Contamination of Groundwater in the  
North Carolina Piedmont

WRI Project 13-05-W

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Submitted by

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## **ABSTRACT**

***Project Title:*** *Surface and Subsurface Properties Regulating Manganese Contamination of Groundwater in the North Carolina Piedmont*

Manganese (Mn) contamination of well water is a widespread problem and increasing concern in North Carolina (NC). Roughly 50% of wells in NC have Mn concentrations exceeding the state standard of 0.05 mg/L. Recent studies have shown that routine consumption of well water with elevated Mn concentrations may lead to increased infant mortality rates, death by cancers, and cognitive impairments in children. In NC, Mn in well water is naturally derived, but specific sources of Mn to groundwater are generally unknown, and concentrations are spatially variable, ranging from <0.01 to >2 mg/L, making it difficult to predict risks to exposure.

The goal of this research was to identify environmental factors that regulate dissolved Mn concentrations in groundwater of the NC Piedmont. In particular, the specific research objectives were to 1) relate the spatial variability of groundwater Mn concentrations to surface and subsurface properties that have been mapped across the North Carolina Piedmont; 2) characterize the hydrogeochemical conditions of Mn-contaminated aquifers, potential sources of Mn, and Mn retention capacities of soil, saprolite and aquifer solids; and 3) develop decision-making tools that support of better management of manganese as a contaminant in groundwater. To accomplish the goal and objectives, chemical analyses of Mn in regolith (soil and saprolite), bedrock, and well-water samples from ten NC Division of Water Resources groundwater research stations were integrated with geospatial analyses of statewide well-water data, soil maps, and geology maps obtained from the US Geological Survey, US Department of Agriculture, North Carolina Geological Survey, NC Department of Health and Human Services, and NC Department of Environment and Natural Resources

Analyses reveal that >1 million people in the Piedmont of the Southeast US are impacted by well water with Mn concentrations  $\geq 0.05$  mg/L, and >387,000 people in the NC Piedmont are exposed to Mn concentrations above this limit. Within the Piedmont, Mn concentrations cluster by soil system, with the Carolina Slate Belt and Triassic Basin systems being particularly affected. Hydrogeochemical results show that a zone of solid-phase Mn-oxide accumulation persists near the water table (~4.6-9.1 m) in saprolite, and solid-phase Mn speciation – as determined by sequential extraction and X-ray absorption spectroscopy analyses – is dominated by primary, less-reactive Mn-bearing minerals at deeper depths. Across the region, dissolved Mn concentrations in wells are generally highest just below the zone of solid-phase Mn-oxide accumulation and decrease with depth. Based on results from adsorption isotherm experiments, Mn in groundwater is ~4 times more likely to adsorb in saprolite than in the bedrock.

Collectively, these results suggest that near-surface cycling has led to Mn repartitioning and delivery to groundwater and is likely to occur for a range of geological parent materials. Following accumulation near the water table, Mn is reductively mobilized and transported downward through a network of bedrock fractures. Manganese concentrations both above the drinking water standard and below detection limits (< 0.01 mg/L) are observed in wells from different depths at nearly every groundwater research site across the Piedmont, suggesting that localized environmental processes at individual well sites could be controlling current Mn concentrations in well water. Therefore, integrated soil-bedrock-system analyses for a specific well site are needed for effective Mn prediction and management.

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## **1. INTRODUCTION**

Over half of North Carolina's population relies on groundwater as their primary drinking water source. In addition, North Carolina is one of the fastest growing states in the United States (US), and with a rapidly increasing population, the demand on groundwater is expected to grow significantly. Currently, more than 2,700,000 residents use privately owned individual wells in NC, which may contain anthropogenic and naturally occurring contaminants (NCGWA, 2007). Until 2008, NC did not require private drinking well testing to ensure adequate water quality and, even currently, annual inspection of wells is optional for homeowners (EHS, 2014). Contaminants in drinking water can pose a serious hazard to human health, and therefore, it is necessary to identify and mitigate the threats to drinking water supplies in order to protect these vital resources.

Manganese (Mn) contamination in drinking water has recently been recognized as a potential threat to human health. In NC, approximately 50% of sampled groundwater wells have naturally occurring Mn concentrations exceeding the state's recommended drinking water standard of 0.05 mg/L (NCDENR, 2011). Studies have shown that consuming Mn in high concentrations or over a long period of time can have neurological effects on humans, called "manganism" (WHO, 2011). Symptoms are described as a "Parkinson's-like syndrome" and can cause muscular weakness, early signs of gout, and cognitive learning impairments in children (WHO, 2011). Recent studies in NC have observed that an increase in groundwater Mn concentrations corresponds to increases in infant mortality rates (IMR) and deaths from cancers (Spangler et al., 2009; Spangler et al., 2010).

Whereas it is known that Mn is naturally occurring in rocks and soils, the specific sources of Mn and the environmental processes and factors that control its delivery to groundwater in NC remain unknown. Manganese concentrations above 0.05 mg/L can be found throughout NC, especially in well water within the Piedmont physiographic region, where concentrations can be over an order of magnitude above the drinking water standard.

The research described here seeks to identify the major sources of manganese contamination in groundwater of the NC Piedmont and characterize the dominant environmental factors controlling the variability of manganese concentrations in well water. Field, laboratory, spectroscopic, and geospatial investigations were integrated in order to understand controls on manganese contamination from a variety of spatial scales. The main goal of this research was to create a working model that assesses the risk of manganese contamination to wells by combining hydrogeochemical factors that influence Mn concentrations with existing well water data. In particular, the specific objectives of this research were to: 1) relate the spatial variability of groundwater Mn concentrations to surface and subsurface properties that have been mapped across the North Carolina Piedmont; 2) characterize the hydrogeochemical conditions of Mn-contaminated aquifers, potential sources of Mn, and Mn retention capacities of soil, saprolite and aquifer solids; and 3) develop decision-making tools that support of better management of manganese as a contaminant in groundwater.

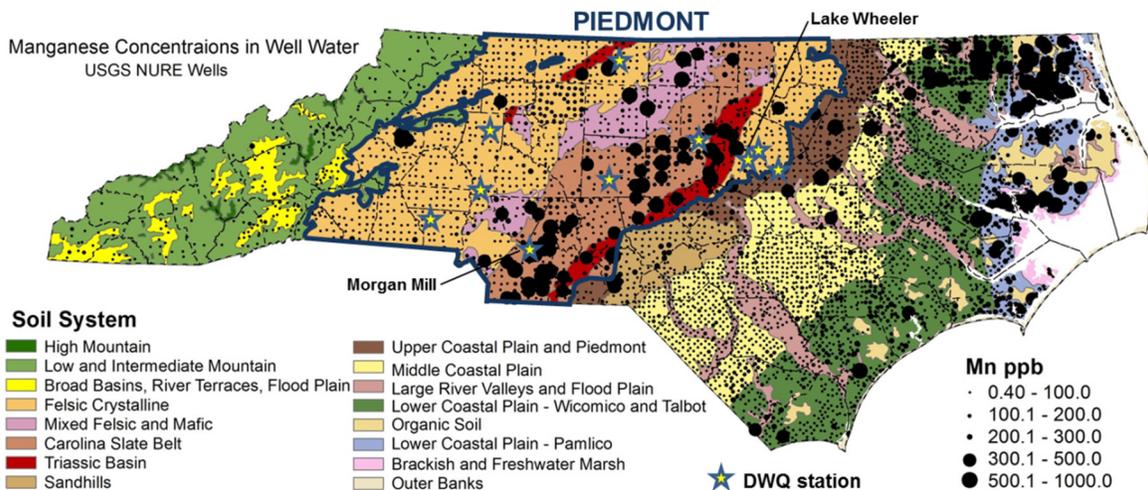
Analyses reveal that >1 million people in the Piedmont of the Southeast US are impacted by well water with Mn concentrations  $\geq 0.05$  mg/L, and >387,000 people in the NC Piedmont are

exposed to Mn concentrations above this limit. Within the NC Piedmont, manganese is delivered to groundwater from saprolite in the near-surface regolith and is subsequently stored in shallower aquifers until transported downward to underlying fractured bedrock aquifers. Distributions of manganese concentrations across the Piedmont reflect patterns of geological weathering and suggest that underlying formations impact concentrations of Mn found in well water. Spatial variability makes it difficult to predict where manganese contamination might occur and therefore an integrated understanding of hydrology and biogeochemistry of localized areas is vital for the protection of human health.

## **2. METHODS**

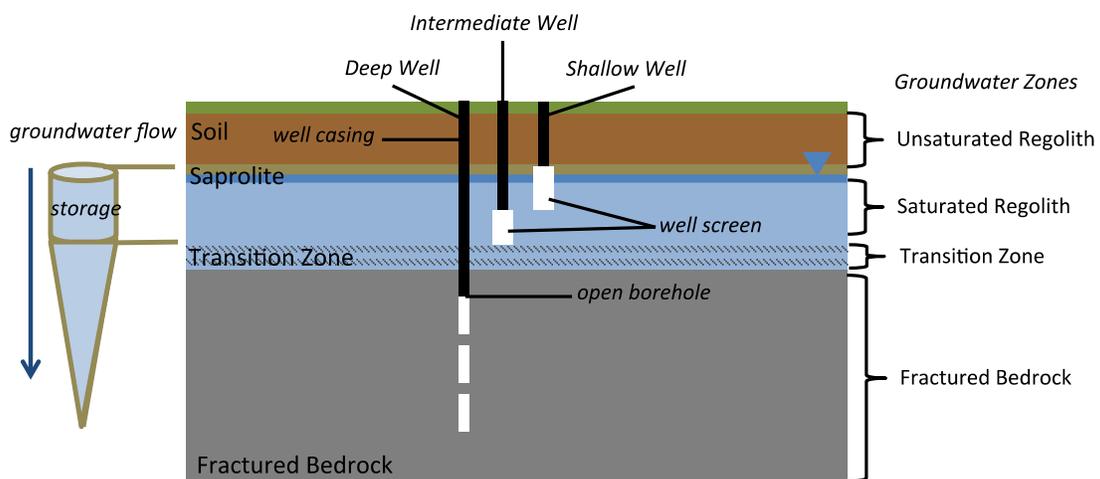
### **2.1. Field site description and hydrogeological overview**

The North Carolina Piedmont is a physiographic region located between the coastal plain to the east and Appalachian Mountains to the west. The dominant soil systems in the Piedmont are Felsic Crystalline, Mixed Felsic and Mafic, Carolina Slate Belt, and the Triassic Basin (**Figure 1**). Although these systems are comprised of numerous soil series with different compositions, each system generally consists of moderately drained soils with some version of loam texture (Daniels et al., 1999). The Piedmont bedrock is mainly composed of igneous and metamorphic rocks and therefore contains mostly crystalline-rock aquifers, although there is a small section containing a siliciclastic-rock aquifer (Lindsey et al., 2006). In general, the Piedmont physiographic region has a rock-saprolite-solum weathering pattern, in which an average of 1-meter thick soil solum overlies a 1 to 25 m thick saprolite layer (Buol and Weed, 1991). Groundwater can flow through all three layers of soil, saprolite, and bedrock, creating different potential sources of Mn to well water.



**Figure 1. Manganese concentrations in well water [USGS National Uranium Resource Evaluation well water database (Smith, 2006)] mapped over NC soil systems [Natural Resources Conservation Service Soil Survey Geographic database (SSURGO, 2014)]. Concentrations are depicted by black filled circles, with values proportional to symbol size. 1 ppb = 1 µg/L = 0.001 mg/L.**

The Piedmont hydrogeologic system is often classified into four zones, including the unsaturated regolith zone (includes soil and some saprolite), the saturated regolith zone (includes saprolite), the transition zone (includes some saprolite and some bedrock), and the fractured bedrock (includes bedrock) (Lindsey et al., 2006) (**Figure 2**). The unsaturated regolith zone provides a medium for the recharge water to infiltrate to the groundwater system, and the saturated regolith zone acts as a reservoir that supplies water to the bedrock through fractures (Lindsey et al., 2006). The transition zone tends to be more permeable than the other zones, thus creating a potential high-flow groundwater system, whereas groundwater only flows through interconnected fractures within the bedrock (Lindsey et al., 2006). The most restrictive layer to groundwater percolation is at the transition from the soil solum to the saprolite, and the water table tends to fluctuate with season within the saprolite, sometimes intersecting the soil surface depending on location (Buol and Weed, 1991).



**Figure 2. Conceptualized cross-section of NC Piedmont physiographic region depicting groundwater flow and well installation.** The NC Piedmont is a complex system in which groundwater flows downward through the regolith and into highly fractured bedrock. The groundwater flow system is classified into four zones: unsaturated regolith, saturated regolith, transition zone, and fractured bedrock. Current wells in place can be installed in the regolith, transition zone, or bedrock, and newly installed wells are generally installed into the bedrock with an open borehole. Conceptual model based on Heath et al. (1994) and Lindsey et al. (2006).

Groundwater Mn concentrations vary spatially and with depth throughout the NC Piedmont. High Mn concentrations can be found within all soil systems and geozones, although the Carolina Slate Belt hosts the greatest percentage of wells with Mn exceeding the drinking water standard (**Figure 1** and below).

## **2.2. Spatial data sources**

Background well water-quality data were obtained from the United States Geological Survey (USGS) National Uranium Resource Evaluation (NURE) Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) program (Smith, 2006, **Figure 1**) and the NC Department of Health and Human Services (DHHS) Environmental Health Section (EHS) private well database. As part of the NURE program, 5174 wells were sampled across North Carolina from 1976-1978,

with an attempt to create study areas on a 1° x 2° quadrangle basis (Smith, 2006). Well water consisted of private, semi-private, and public water supplies. Water samples were initially analyzed only for uranium, but were later re-analyzed for a wide range of inorganic and organic species, as well as other parameters such as well depth and pH (Smith, 2006). In our study, the NURE dataset was used for a baseline understanding of Mn concentrations in well water across North Carolina and the NC Piedmont. The NURE data for North Carolina were geocoded using ArcGIS then clipped to the Piedmont physiographic region. Manganese concentrations, well depth, and pH were used for comparisons to samples collected from more recent field sampling across the NC Piedmont.

In addition to the NURE data, the NC Department of Health and Human Services (DHHS) Environmental Health Section (EHS) provided a dataset of Mn concentrations in wells from 2008-2011 that was also used in this study for further evaluation of Mn concentrations in groundwater. The DHHS dataset contains well water data from 8926 private drinking wells across all 100 counties of NC that were constructed, repaired, or abandoned on or after July 2008 (Session Law 2006-202). A variety of different analytes, but not well depth, are contained in the DHHS dataset. Data were clipped to the Piedmont physiographic region and spatially projected using the longitude and latitude coordinates associated with each well.

Additionally, soil map data were obtained from the Natural Resources Conservation Service Soil Survey Geographic database (SSURGO, 2014), and geology map data were accessed from NC Geologic Survey maps (NCGS, 1985). County-level estimates of population and household well use were obtained from U.S. Census data (U.S. Census Bureau, 2014).

### **2.3. Spatial analyses**

The population of people possibly affected by manganese in well water was calculated based on the USGS NURE dataset (Smith, 2006) and U.S. Census county-level estimates of population and household well use (U.S. Census Bureau, 2014). The estimate was calculated as;

$$\text{Population Impacted} = \sum(\text{TP} * \% \text{WW}) * \text{TF}_{\text{threshold conc}} * \text{AP}$$

Where:

TP: is the total county population

%WW: the percent of the county population using well water

TF: fraction of county wells above the Mn threshold (0.05, 0.1, 0.2, 0.3, 0.5 mg/L)

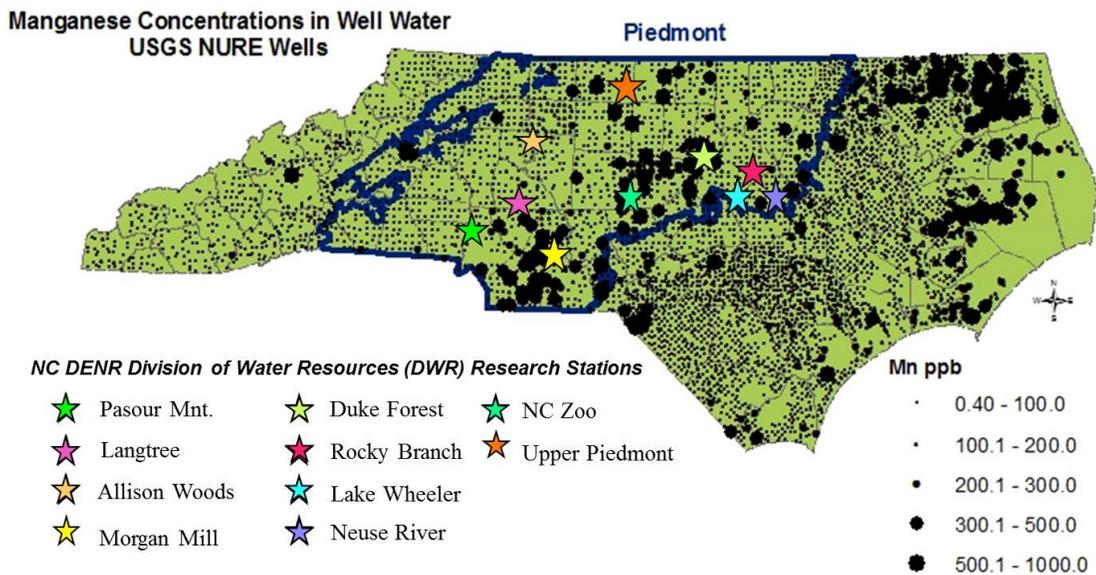
AP: The percent of the county land area within the piedmont region

The NURE data were joined to the county-level population estimates using a geographic information system. For each county the fraction of wells above the threshold manganese concentration was calculated and recorded. When only a part of a county fell within the piedmont physiographic region, the percent of the land area within the Piedmont was used to reduce the estimate of people impacted. The estimate assumes a uniform population density within a county and that the NURE samples collected are representative of the county and spatially unbiased.

The spatial variability of groundwater Mn concentrations was related to surface and subsurface properties of the Piedmont. Existing statewide well-water quality data [from the USGS National Uranium Resource Evaluation (Smith, 2006) and the NC Department of Public Health private well testing database (NC DENR, 2011)], soil map data [Natural Resources Conservation Service Soil Survey Geographic database (SSURGO, 2014)], and geology map data [NC Geologic Survey maps (NCGS, 1985)] were assembled and linked. The data sources were integrated, analyzed, and visualized using the Geographical Information System (GIS) program ArcMap ver. 10.1 and the statistic software R.

#### **2.4. Sample collection**

Geological cores, soil samples, and well water samples were obtained from ten North Carolina Department of Environmental and Natural Resources (NCDENR) Division of Water Resources (DWR) research stations (**Figure 3** and **Table 1**). Geological cores were originally drilled and extracted by well drillers during the installation of the well clusters for each research station. All original geological cores began at surface depth and extended to as deep as 61 meters, were placed in multiple boxes provided by DWR, and were stored across the state in various warehouses. An average of 12 subsamples for the geological cores from eight of the ten research stations were retrieved in May and June 2013 for this study. Samples were chosen from the geological cores to obtain a representation of the unsaturated regolith, saturated regolith, transition zone, bedrock, and any transition between those zones. Samples were placed into storage bags and stored in a dark box at room temperature for laboratory experiments.



**Figure 3. Locations of NC Division of Water Resources groundwater monitoring research stations superimposed on map of Mn concentrations in well water (Smith, 2006). 1 ppb = 1 µg/L = 0.001 mg/L.**

**Table 1. DWR groundwater and monitoring research stations used for well water and geological core collection.**

<b>Groundwater and Monitoring Research Station</b>	<b>Acronym</b>	<b>Geozone</b>	<b>Soil System</b>
Lake Wheeler Road	LW	Raleigh and Charlotte	Felsic Crystalline
Duke Forest	DF	Carolina Slate	Carolina Slate Belt
Neuse River Waste Water Treatment Plant	NRWWTP	Felsic Intrusive	Felsic Crystalline
Rocky Branch	RB	Raleigh and Charlotte	Felsic Crystalline
Upper Piedmont	UPRS	Milton	Felsic Crystalline
NC Zoo	NCZP	Carolina Slate	Carolina Slate Belt
Morgan Mill	MM	Carolina Slate	Carolina Slate Belt
Pasour Mountain	PM	Carolina Slate	Felsic Crystalline
Langtree Peninsula	LT	Raleigh and Charlotte	Felsic Crystalline
Allison Woods	AW	Inner Piedmont	Felsic Crystalline

Wells in all study sites were sampled for Mn concentrations following a well water sampling protocol by NCDENR DWR (NCDENR and USGS, 2008). Water levels were measured in each well at the site before sampling. Prior to sampling, 3 pore volumes of water were purged from shallow and intermediate wells and 1-1.5 pore volumes of water were purged from deep wells using a SS Geosub 12 Volt DC Sampling pump and controller (Geotech Environmental Equipment, Inc.), Monsoon Purging pump (Geotech Environmental Equipment, Inc.), Grundfos (Geotech Environmental Equipment, Inc.), or a peristaltic pump (Pine Environmental Services, Inc.) depending on location and well depth. Water samples were filtered using in-line 0.45-micron filters (Dispos-a-filters, Geotech Environmental, Inc.) into 30 mL HDPE bottles, acidified using concentrated nitric acid, then stored on ice until permanently stored at 4°C. All pumps were de-contaminated after each use by rinsing inside and out with a soapy water and then deionized water according to the NCDENR DWR protocol (NCDENR and USGS, 2008). Samples were analyzed for Mn by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer model 2000 DV) at the North Carolina State University Department of Soil Science Environmental and Agricultural Testing Service (EATS) laboratory.

### **2.5. Well water analysis**

Temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and specific conductance were measured using an YSI Plus multi-probe for each DWR research station samples, and were recorded when these parameters reached steady values. Alkalinity was measured using a field alkalinity titration kit (Hach Company). Following purging, samples were filtered using a 0.45-micron filter (Dispos-a-filters, Geotech Environmental, Inc.) into 30 mL HDPE bottles for chemical analyses of dissolved Mn, As, Ca, Fe, K, Mg, Na, P, S, Si, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>. Samples collected for dissolved organic carbon (DOC) were filtered into 30 mL glass bottles. Cation samples were acidified to pH ~3 using trace-metal-grade concentrated nitric acid, and DOC and nutrient samples were acidified with trace-metal-grade

concentrated hydrochloric acid. Anion samples were not acidified. All samples were immediately stored on ice and then stored at 4°C in the dark until analysis.

Anion samples ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ ) were analyzed using a ion chromatograph (DIONEX model 500), with a detection limit of 0.05 mg/L for all anions. Nutrient samples ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ ) were analyzed using a flow injection analyzer (LACHAT, Hach model 8000), with detection limits of 0.10 mg/L for N- $\text{NO}_3^-$  and N- $\text{NH}_4^+$ , and 0.01 mg/L for P- $\text{PO}_4^{3-}$ . Metals were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer model 2000 DV), in which the detection limit was 0.05 mg/L for Ca, Fe, K, Mg, Na, P, S, and Si and 0.01 mg/L for Mn. Arsenic was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Varian Model 820) with a method detection limit of 1.0  $\mu\text{g/L}$ .

## **2.6. Total and “environmentally available” concentrations of Mn in solids**

To measure Mn concentrations in solid phases, a one-inch thick slice from the center of all samples was air dried and crushed with a mortar and pestle to pass through a 2-mm sieve. Total Mn concentrations were measured on select samples via Neutron Activation Analysis at the North Carolina State University 1-MW PULSTAR Nuclear Reactor facility. Detection limits were < 10  $\mu\text{g/g}$ .

“Environmentally available” Mn was then analyzed on all solid-phase samples after an acid digestion protocol based on EPA Method 3050B (EPA, 1996). This method uses strong acids that test for “environmentally available” Mn, which is Mn not incorporated into silicate minerals but instead tends to be more mobile in the environment. In duplicate, samples were digested by first weighing 1 g of sample into digestion tubes with caps. Ten mL of 7 M  $\text{HNO}_3$  was added to each tube, which was then vortexed, placed in a digestion block and heated to 95°C for 15 minutes. Samples were taken off the block and 5 mL of 14 M  $\text{HNO}_3$  were added, and tubes were vortexed and replaced on the rack for 30 minutes. This step was repeated. Digestion tube caps were removed and the tubes heated on the block for 2 hours. After 2 hours, tubes were removed from the block, caps were replaced, and 2 mL of DI water was added to each tube. One mL of  $\text{H}_2\text{O}_2$  was added to the each tube and then repeated six times so that a total volume of 6 mL was added per tube. Uncapped tubes were replaced on the block for two more hours. After 2 hours the caps were replaced, and tubes were removed and set aside overnight. Ten mL of HCl were added to each tube, vortexed, and placed on the rack for 15 minutes. Samples were then filtered using Whatman 41 filter papers and diluted to 100 mL. Ten mL aliquots of the digested samples analyzed for total dissolved Mn by using ICP-OES. The detection limit for dissolved Mn using the ICP-OES was 0.01 mg/L.

## **2.7. Sequential extractions**

Fractionation of subsurface Mn was performed using a sequential extraction procedure adapted by McDaniel and Buol (1991) for acid soils in the North Carolina Piedmont. Cores from four out of the DWR research stations – LT, MM, NCZP, and LW – were chosen for sequential extraction analysis based on their associations with different soil systems and geozones, and their

different levels of Mn in monitoring wells (**Figure 3**). The extracting solutions for obtaining Mn from exchangeable, organic matter, Mn oxide, amorphous iron oxide and crystalline iron oxide fractions were, respectively: 1 M  $\text{Mg}(\text{NO}_3)_2$  at a pH of 7, 0.7 M NaOCl at a pH of 8.5, 0.1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  at a pH of 2, 0.2 M  $(\text{NH}_4)_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ -0.2 M  $\text{H}_2\text{C}_2\text{O}_4$  at a pH of 3, and a citrate-bicarbonate-dithionite (CBD) extract consisting of 0.3 M  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot 2\text{H}_2\text{O}$ , 0.1 M  $\text{NaHCO}_3$  and 1 g  $\text{Na}_2\text{S}_2\text{O}_4(\text{s})$ . Residual Mn phases were calculated as the difference between total Mn concentrations (by EPA 3050b acid digestion) and the sum of Mn from the five extraction steps.

## **2.8. X-ray absorption spectroscopy analysis**

Sediment samples were analyzed by X-ray absorption spectroscopy (XAS) at ambient temperature on beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) under dedicated conditions (3 GeV, 500 mA) using an unfocused beam. X-ray absorption near edge structure (XANES) spectra for the sediments were collected in fluorescence mode on a 100-element Ge detector. A rhodium mirror was used and a channel-cut Si(220)  $\phi=90^\circ$  monochromator (beam size = 2 mm vertical x 10 mm horizontal) was detuned an additional 50% to reject higher order harmonics. The energy scale was calibrated to the derivative maxima (6,539 eV) of a Mn metal foil. Samples were mounted on polycarbonate holders with Kapton tape windows and 2-9 scans were collected depending on Mn sediment concentration.

The data collection and analysis approaches used are discussed by Kelly et al. (2008). XANES data were generally collected over three energy ranges of -200 to -50 eV, -50 to 50 eV, and 50 to 300 eV relative to a given edge energy, with smaller step sizes and larger counting times used in the region bracketing the edge (-50 to 50 eV). XANES spectra were averaged, baseline corrected with a linear model, and normalized to an edge step of 1 using the IFEFFIT suite of computer programs in the Athena and Artemis software. Estimates of proportions of various chemical species present in the samples were made using the linear combination fitting (LCF) routine in Athena to determine the combination of scaled XANES spectra from standards that gave the best-fit to sample spectra. Fitting analyses were performed over the range of 6350 eV-6590 eV without an energy shift parameter for the calibrated data. Standards used in the LCF fitting included a range of Mn(III/IV) oxides. Additionally, a background bedrock sample was used in the fitting as the standards alone could not accurately recreate the sediment XANES spectra. Proportions of XANES spectra for standards that yield the “best fits” (lowest or near-lowest statistical goodness of fit) to sample spectra when summed are considered as being estimates of analogous species in the ash samples. The sums of weighting factors on fitting standards were 99-107% (Morgan Mill), 97-107% (Langtree), 92-115% (NC Zoo), and 93-103% (Lake Wheeler), and these were normalized to a sum of 100%.

## **2.9. Adsorption isotherms**

Batch adsorption isotherm experiments were conducted to quantify Mn sorption onto regolith and bedrock samples from the Morgan Mill and Langtree research stations. Experiments were conducted within a custom-built anaerobic glovebox with a 97:3  $\text{N}_2:\text{H}_2$  environment. Two liters of anaerobic water were made by boiling and purging with nitrogen gas. After several hours, the

bottle was sealed and placed into the glovebox where experimental solutions were made. A background solution of 0.1 M NaCl and 0.025 M HEPES [4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid] in 1.0 L of anaerobic water was buffered to a pH of 7.0, roughly the average pH of NC groundwater. A Mn standard of 12 mg/L was made using  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 500 mL of the buffered salt solution.

Saprolite, transition, and bedrock samples were tested for each site. In triplicate, nine different concentrations of  $\text{Mn}^{2+}$  were applied to each sample: 0 mg/L, 0.2 mg/L, 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 3.0 mg/L, 5.0 mg/L, 7.5 mg/L, and 10.0 mg/L. One gram of regolith or bedrock sample was added to 15 mL centrifuge tubes, and Mn-standard and buffered-salt solutions were added in certain volumes to obtain the desired Mn concentration. Controls were run for all samples, and included: 0 mg/L of added Mn in the buffered salt solution with solids added (triplicate), no solid and 1 mg/L Mn in the buffered salt solution (duplicate), and no solid with 0 mg/L Mn added to the buffered salt solution (duplicate). Samples were shaken for 48 hr with pH-adjustment after 24 hr and 48 hr if necessary, filtered, and acidified under anaerobic conditions. The resulting filtered and acidified samples were analyzed for Mn by ICP-OES.

The Freundlich model was applied to isotherm data to describe the distribution of Mn between the solid phase and aqueous phase at equilibrium. The empirical equation used was  $q = K_d c^N$ , where  $q$  is the mass of Mn sorbed per mass of solid-phase material,  $K_d$  is the partitioning coefficient,  $c$  is the concentration of Mn in solution in equilibrium, and  $N$  is the exponential fitting parameter. Dissolved Mn (mg/L) was corrected for desorption of Mn already present on the solid-phase material (i.e., data from controls with 0 mg/L Mn plus solid) and then plotted against adsorbed Mn (mg/kg) data. The plotted data were then linearized to obtain the values for the Freundlich equation and fitted to the model. The partitioning coefficient was used for comparison among samples.

### **3. RESULTS**

#### **3.1. Concentrations of Mn in well water**

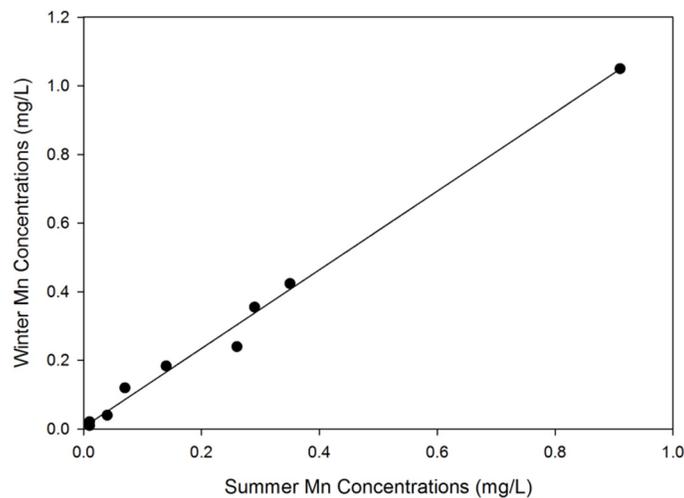
##### *3.1.1. Manganese distributions in well water*

Manganese concentrations in well water are spatially variable across the Piedmont physiographic region, and concentrations range from the below 0.001 mg/L to greater than 1 mg/L (**Figure 1**). For reference, the North Carolina Mn recommended drinking water guideline is 0.05 mg/L. The average concentrations of Mn in well water for the DWR, NURE, and DHHS datasets were 0.17 mg/L, 0.06 mg/L, and 0.10 mg/L, respectively (**Table 2**). Forty-three percent of the DWR wells, 27% of NURE wells, and 27% of DHHS wells had Mn concentrations greater than or equal to 0.05 mg/L. Roughly 50% of counties and 90% of DWR research stations within the NC Piedmont had one or more wells containing Mn concentrations above the standard of 0.05 mg/L.

**Table 2. Manganese concentrations, well depth and pH from the NURE and DHHS datasets compared to collected samples from DWR research stations.**

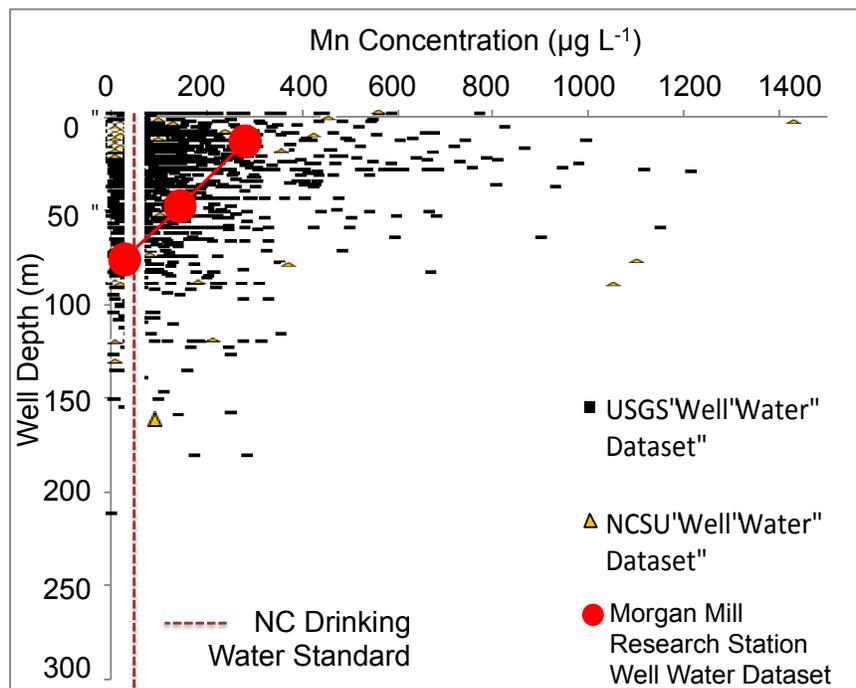
	DWR (n=46)				NURE PIEDMONT (n=1867)				DHHS PIEDMONT (n=4426)			
	Avg	Max	Min	Med	Avg	Max	Min	Med	Avg	Max	Min	Med
<b>Depth (m)</b>	43.34	161.54	3.05	46.00	22.02	365.76	0.00	15.24	-	-	-	-
<b>pH</b>	6.29	7.62	4.92	6.07	6.60	8.90	4.50	6.60	-	-	-	-
<b>Mn (mg/L)</b>	0.17	1.42	0.01	0.03	0.06	2.42	0.00	0.02	0.10	7.50	0.03	0.03

Among the sampled DWR wells, Mn concentrations in well water showed little variability ( $R^2 = 0.99$ ) between summer and winter (**Figure 4**). The lack of change of Mn concentrations (and other groundwater constituents) with season could suggest that groundwater pulled from wells tends to be relatively unaffected by short-term surface changes and that subsurface processes control the groundwater chemistry. A change in season could slow or increase the biotic and abiotic rates at which minerals are broken down and their constituents released into the aqueous phase. However, since the groundwater table is several meters below the surface, the relevant geochemical processes controlling Mn in well water are likely less affected by outside factors and instead are more likely to be influenced by processes that occur in the deeper saturated regolith, transition zone, and bedrock. Moreover, although annual rainfall in the Piedmont is on average 45 inches/year, the groundwater recharge rate (i.e. the downward movement of surface water to groundwater) is roughly 8 inches/year (NCDWR, 2009; Mew and Spruill, 2000). Given that groundwater recharge rates are relatively low and that wells are generally open over many meters, it is probable that any seasonal influences on Mn concentrations were masked from samples.



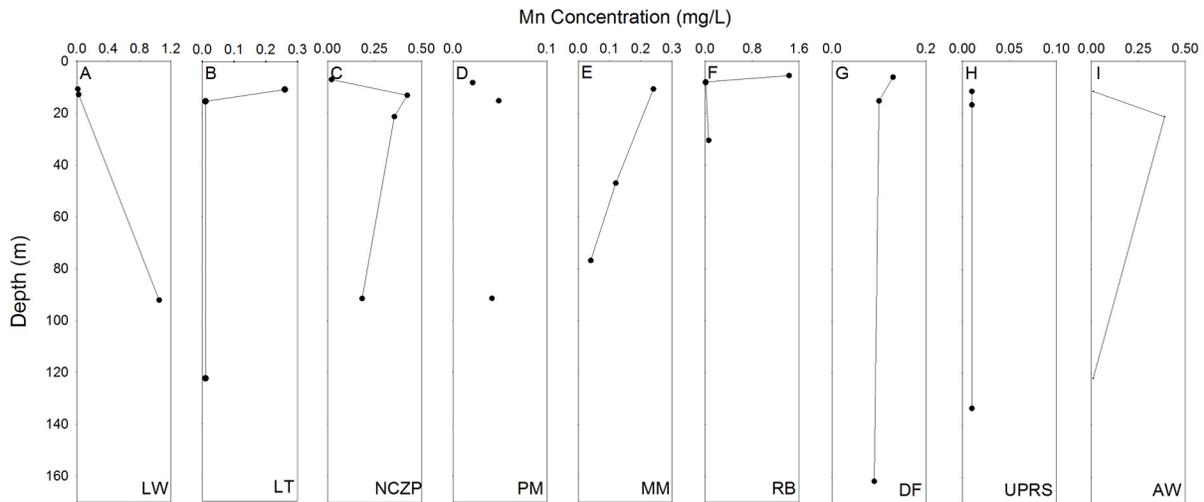
**Figure 4. Seasonal comparison of manganese concentrations in DWR monitoring wells.** Wells from four research stations - LT, LW, MM, and NCZP - were sampled in both the summer of 2013 and in the winter of 2013-14 to obtain seasonal comparisons of Mn concentrations. Samples had a strong linear relationship ( $R^2 = 0.99$ ).

Manganese concentrations in NC Piedmont well water were generally highest at shallower depths; the majority of wells with Mn > 0.05 mg/L are shallower than 50 m deep, and the highest Mn concentrations (> 0.5 mg/L) were generally found in wells shallower than ~30 m deep (**Figure 5**). Bulk data collected from the NURE program for the Piedmont suggested that Mn concentrations are largest at relatively shallower depths as compared to deep bedrock aquifers, where concentrations tend to be low.



**Figure 5. Depth distribution of Mn concentrations in well water** from USGS National Uranium Resource Evaluation well water database (Smith, 2006) (black squares), our collected samples from >50 wells at 9 NC DWR groundwater research stations (yellow triangles), and our analyses from samples collected at the Morgan Mill DWR research station (red circles). 1 ppb = 1 µg/L = 0.001 mg/L.

Depth distributions from monitoring well clusters consisting of shallow, intermediate, and deep wells within each DWR research station showed a more localized trend of decreasing Mn concentration with well depth (**Figure 6**). In seven out of the nine research stations, Mn concentration decreased from shallow or intermediate wells to deep wells. In one well Mn was lower at shallow depths, and in another Mn concentration remained roughly constant as a function of depth. Maximum Mn concentrations among the seven well sites with decreasing concentrations with depth ranged from 0.01 mg/L to 1.43 mg/L (**Figures 6 B-F, G, I**). At the only station (LW) where Mn concentrations increased with depth, Mn changed from 0.01 mg/L to 1.05 mg/L (**Figure 6A**). According to the DWR data, the average concentration of Mn was highest in shallow wells at a concentration of 0.20 mg/L. However, the median concentration of Mn was highest for deep wells at a concentration of 0.07 mg/L. Out of the 46 DWR wells sampled, 42% of shallow wells, 31% of intermediate wells, and 56% of deep wells had concentrations greater than 0.05 mg/L, although these percentages are partially biased by well clusters in Mn-contaminated areas with more deep wells than shallow or intermediate wells.



**Figure 6. Manganese concentrations with well depth for 9 DWR research stations.** Seven DWR research stations showed a decrease in Mn concentration from shallow or intermediate wells to deep wells, one showed an increase, and one remained constant. Monitoring wells from a single cluster are shown for every research station except PM, in which a shallow, intermediate, and deep well were analyzed from separate well clusters within the research station (no lines connecting points).

The depth variability of dissolved Mn concentrations suggests that certain subsurface layers are more susceptible to Mn release to groundwater than others. In particular, higher concentrations of manganese within shallow and intermediate wells may reflect Mn mobilization at or below the water table, where the onset of reducing conditions would stimulate in situ reductive dissolution of Mn oxide minerals and Mn mobilization to groundwater. If groundwater was being pulled from wells near a source of high Mn, then it would be more likely to observe higher concentrations of dissolved Mn at or around these depths. Because groundwater generally moves downward from the reservoir to the bedrock (Lindsey et al., 2006), Mn released at upper layers could contribute to concentrations observed at deeper depths through Mn transport. Once delivered to bedrock aquifers, Mn could be distributed through the NC Piedmont's highly fractured groundwater system.

### 3.1.2. Exposure to Mn through in well water

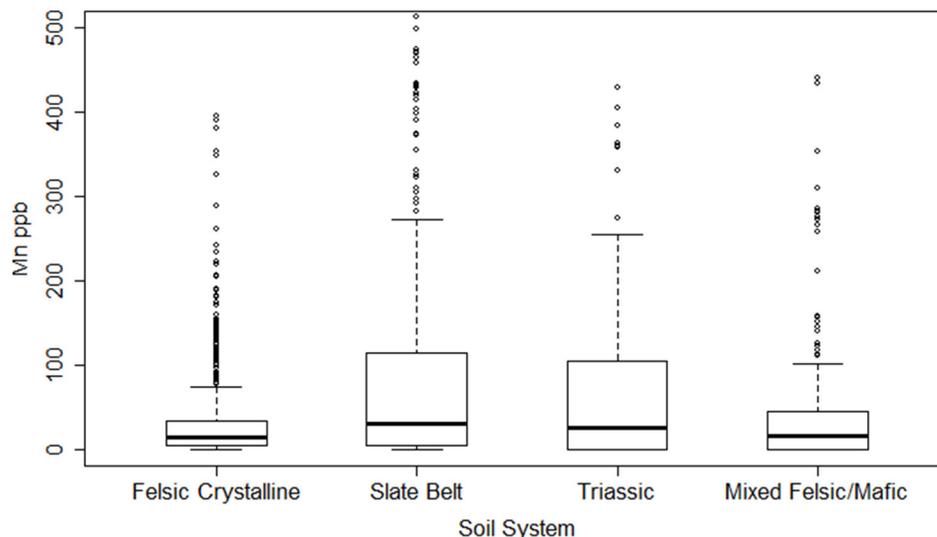
Based on spatial analyses of Mn distributions and water-use census data, over 387,000 people in the NC Piedmont are exposed to drinking water with Mn concentrations above the NC standard of 0.05 mg/L (**Table 3**). Across the entire southeastern US Piedmont, it is estimated that 1 million people are drinking water above the NC standard. Although 0.05 mg/L is not a health-based standard, NC's state toxicologist Dr. Kenneth Rudo stated that adverse health effects could be observed in people consuming Mn concentrations as low as 0.1 mg/L (Rudo, 2014). Based on a health-based standard of 0.1 mg/L, we calculate that over 240,000 people are likely impacted in NC and over 535,000 people may be impacted in the Southeastern US Piedmont region. Concentrations much greater than this occur throughout the NC Piedmont and thousands are still impacted (**Table 3**).

**Table 3. Estimate of number of people exposed to Mn in well water above different concentrations within the NC and Southern US Piedmont**

<b>Mn (mg/L)</b>	<b>People Exposed in NC Piedmont</b>	<b>People Exposed throughout Southern Piedmont (VA,NC,SC,GA)</b>
≥ 0.05	387,566	1,008,445
≥ 0.1	244,423	536,911
≥ 0.2	98,198	188,788
≥ 0.3	58,375	106,071
≥ 0.4	22,943	45,404
≥ 0.5	2,878	9,183

*3.1.3. Correlations of Mn concentrations with soil, and geologic properties in the NC Piedmont*

The distribution of Mn in groundwater is spatially heterogeneous across the southeastern Piedmont (**Figure 1**). In North Carolina, concentrations above 0.05 mg/L are widespread and are observed in all mapped geological formations and soil systems. Manganese concentrations cluster by soil system in the Piedmont, with the Carolina Slate Belt and Triassic Basin systems being particularly affected (**Figures 1 and 7**). The highest Mn concentrations are found in wells located in the Carolina Slate Belt system, with a mean concentration of 108 µg/L and a maximum concentration of 2420 µg/L, compared to the NC drinking water guideline of 50 µg/L. However, within other systems, elevated Mn concentrations may also exist in well water. For instance, the lowest average Mn concentrations are found in wells located in the Felsic Crystalline system, but even there, >17% of wells have measured concentrations greater than the NC drinking water guideline of 50 µg/L.



**Figure 7. Manganese well water concentration data** (Smith, 2006) **and soil system** (SSURGO, 2014). The highest maximum, mean, and median Mn concentrations are found in the Carolina Slate Belt, followed by the Triassic Basin and then the Mixed Felsic/Mafic system. 1 ppb = 1 µg/L = 0.001 mg/L.

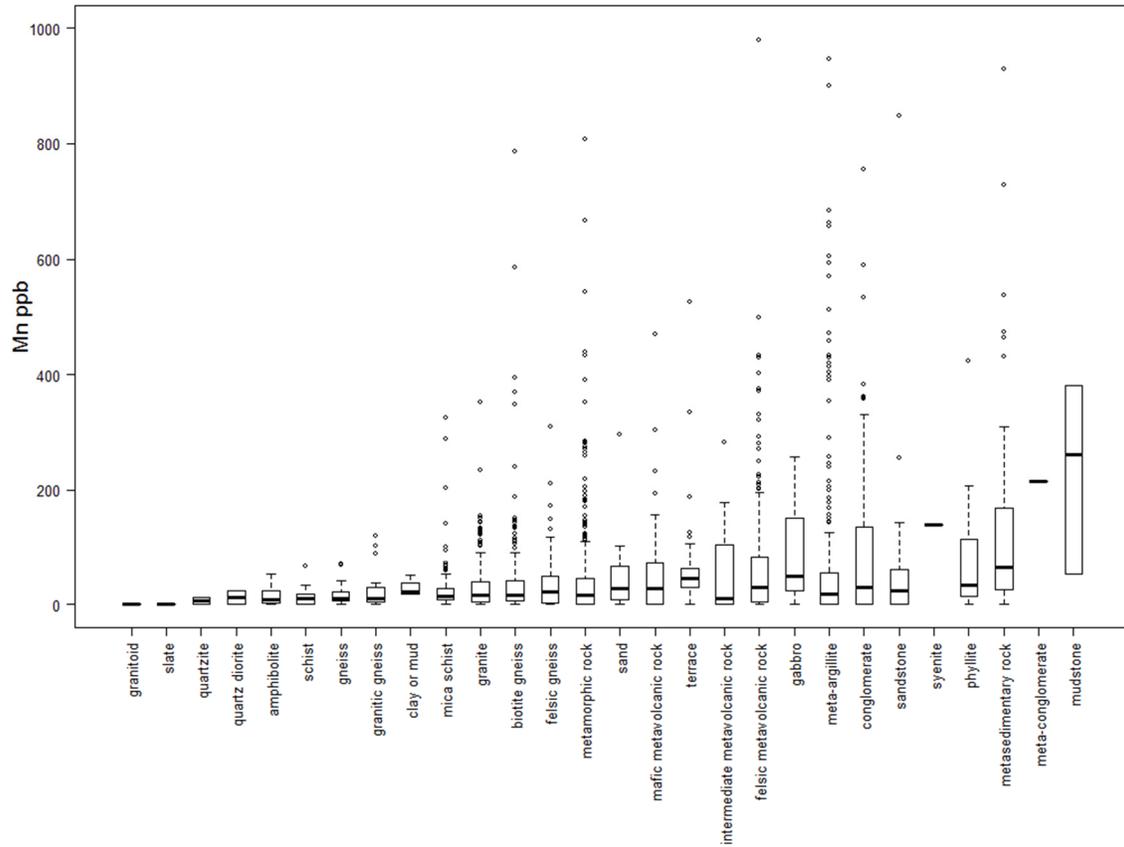
Using data across the Piedmont, we examined associations between Mn concentrations and soil properties hypothesized to influence Mn release and transport (**Table 4**). Well-water Mn concentrations are negatively correlated with the sand fraction and hydraulic conductivity of soils, but positively correlated with the silt fraction of soils. Across the Piedmont, these correlations are weak. However, the textural relationships may suggest that Mn in well water may be associated with finer particles, such as those Mn oxides; such hypotheses are supported by geological data and chemical analyses described below.

**Table 4. Correlation matrix of Mn concentration in well water** (USGS National Uranium Resource Evaluation well water database) **and soil properties** (Soil Survey Geographic database) In the table, mn\_ppb = Mn concentration in well water; sandtotal\_r = % sand fraction of soil texture; silttotal\_r = % silt; claytotal\_r = % clay; om\_r = organic matter content; ksats\_r = hydraulic conductivity; ecec\_r = cation exchange capacity of soil.

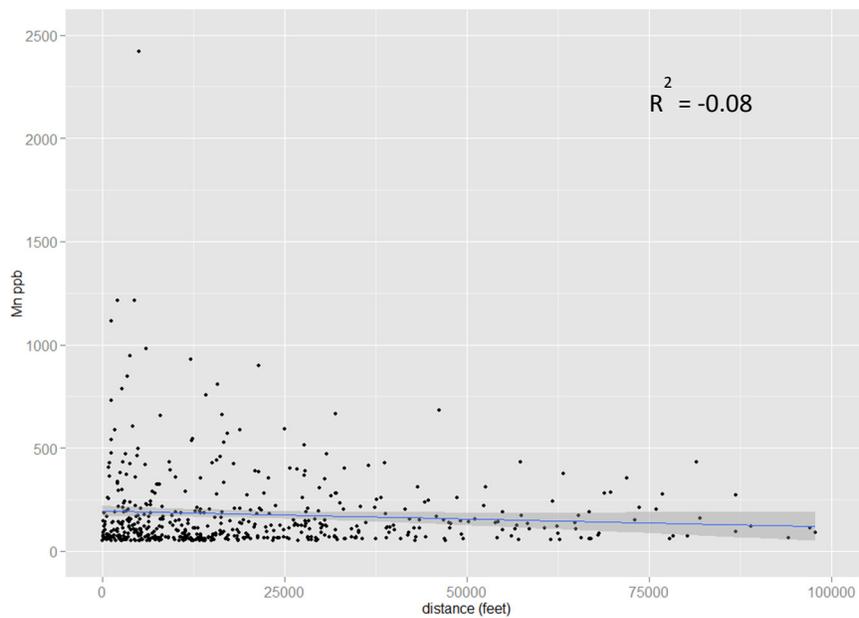
	mn_ppb	sandtotal_r	silttotal_r	claytotal_r	om_r	ksats_r	ecec_r
mn_ppb	1.00	-0.15	0.18	0.00	0.01	-0.05	0.05
sandtotal_r	-0.15	1.00	-0.94	-0.63	-0.12	0.73	-0.35
silttotal_r	0.18	-0.94	1.00	0.33	0.16	-0.58	0.30
claytotal_r	0.00	-0.63	0.33	1.00	-0.05	-0.72	0.30
om_r	0.01	-0.12	0.16	-0.05	1.00	-0.04	0.90
ksats_r	-0.05	0.73	-0.58	-0.72	-0.04	1.00	-0.23
ecec_r	0.05	-0.35	0.30	0.30	0.90	-0.23	1.00

By assessing well water concentrations in terms of mapped geologic/aquifer properties, we have found that the highest Mn concentrations are associated with sedimentary and unconsolidated rock classes, with igneous rocks being the least likely to host wells with high Mn concentrations (**Figure 8**). High Mn concentrations are associated with more weathered rocks and finer-grained rocks, which may indicate sources of Mn to groundwater such as secondary minerals like Mn oxides.

Spatial analyses also indicate a weak association between Mn concentrations in well water and the distance of wells to mapped faults and dykes (**Figure 9**). Faults and dikes are common within the Carolina Slate Belt and Triassic Basin, where well-water Mn concentrations are highest, potentially enabling transport of dissolved Mn from the near-surface to aquifers. Many faults and dykes within the Piedmont have yet to be mapped by geologists, complicating this analysis. Accordingly, future analyses could target smaller areas where the best mapping coverage of these geologic features exists.



**Figure 8. Manganese well water concentration data** (Smith, 2006) **and rock type** from mapped geologic rock type (NCGS, 1985). 1 ppb = 1  $\mu\text{g/L}$  = 0.001 mg/L.



**Figure 9. Mn well water concentration** (Smith, 2006) **and distance to mapped fault or dyke**. A weak association exists between Mn concentration and distance of the well from faults/dykes. 1 ppb = 1  $\mu\text{g/L}$  = 0.001 mg/L.

## **3.2. Groundwater chemistry and controls on Mn concentrations**

### *3.2.1. Spatial and depth variations of bulk groundwater chemistry*

Samples from the DWR research stations were used to characterize NC Piedmont groundwater chemistry (**Table 5**). Groundwater composition tended to vary among location in the NC Piedmont and less so with depth, although some slight differences were noted. The average conductivity for shallow, intermediate, and deep wells was 132  $\mu\text{S}/\text{cm}^2$ , 186  $\mu\text{S}/\text{cm}^2$ , and 280  $\mu\text{S}/\text{cm}^2$  respectively (**Table 5**). Average values of redox potential (Eh), -0.08 V and -0.09 V, were similar for shallow and intermediate wells respectively, but decreased in deep wells to -0.18 V (**Table 5**). Average alkalinity increased in deeper wells to 103 mg/L  $\text{CaCO}_3$  from concentrations of 53 mg/L  $\text{CaCO}_3$  and 47 mg/L  $\text{CaCO}_3$  in shallow and intermediate wells, respectively (**Table 5**). pH was variable within all well depths, ranging between 5.0 and 8.0 in all categories. Based on relative proportions of the major ions, groundwater tended to be classified mostly as a calcium type to no dominant type for cations and a bicarbonate type for anions.

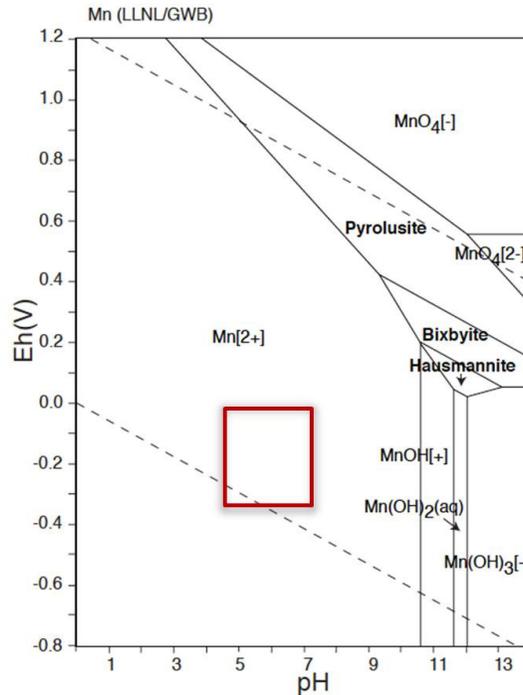
### *3.2.2. Redox conditions*

Mn oxides, which tended to be the most common forms of environmentally “available” solid-phase Mn observed within our cores (see below), require reducing conditions, acidic conditions, or both to promote their dissolution into groundwater (Adriano, 2001; Stumm and Morgan, 1996; Dixon and Schulze, 2002). Although there was no clear relationship between Mn concentrations and pH in well water, average Eh values ranged from -0.08 V to -0.18 V (**Table 5**), which are much lower than the general redox potential range for the reduction of Mn(IV) to Mn(II), 1.4 to 0.2 V (Dixon and Schulze, 2002). Based on pH and Eh measurements,  $\text{Mn}^{2+}$  is the most stable Mn phase within the groundwater from wells across the Piedmont DWR sites (**Figure 10**). Because Mn(IV) is insoluble and Mn(III) is only soluble in the presence of strong complexing agents (Morgan, 2000), reducing conditions, which promote Mn(II) production, are more likely to promote buildup of dissolved Mn in groundwater (McDaniel and Buol, 1991; Bricker, 1965; Adriano, 2001).

Manganese concentrations were generally below regulatory limits when dissolved oxygen (DO) concentrations were  $> \sim 50\%$  saturation ( $\sim 4$  mg/L at 25°C) and  $\text{NO}_3^-$  was present in well water. In contrast, Mn concentrations were elevated when DO and  $\text{NO}_3^-$  were found at low concentrations, supporting the notion that Mn reduction is required for dissolution of Mn to groundwater. Iron and  $\text{SO}_4^{2-}$  concentrations did not trend with Mn concentrations.

**Table 5. Chemical groundwater analyses for shallow, intermediate, and deep DWR well sites.**

Parameters	Shallow (n=12)				Intermediate (n=16)				Deep (n=18)			
	Avg	Max	Min	Med	Avg	Max	Min	Med	Avg	Max	Min	Med
Mn (mg/L)	0.20	1.43	0.01	0.02	0.11	0.42	0.01	0.02	0.20	1.10	0.01	0.07
Depth (m)	8.41	11.58	3.05	9.45	16.55	24.38	7.92	16.00	92.18	161.54	30.48	91.44
Temp (°C)	16.29	19.60	13.70	16.37	16.27	17.50	15.00	16.20	16.96	18.21	15.70	16.90
DO (mg/L)	4.60	9.09	0.29	5.19	4.75	9.07	0.50	4.23	2.56	7.50	0.02	2.12
Spec. Conduc. (µS/cm <sup>2</sup> )	131.9	422.4	14.6	110.7	186.6	630.0	40.0	117.7	279.9	1106.0	127.0	203.6
pH	5.75	7.27	4.92	5.79	6.01	7.41	5.03	5.69	6.90	7.62	5.57	7.21
ORP (mV)	121.3	255.4	-282.7	134.2	111.9	239.7	-116.0	142.5	21.8	159.8	-151.1	45.1
Eh (V)	-0.08	0.06	-0.28	-0.07	-0.09	0.04	-0.32	-0.06	-0.18	-0.04	-0.35	-0.15
DOC (mg C/L)	15.24	79.00	0.50	1.20	12.00	80.00	0.60	1.30	16.13	84.00	0.60	1.30
CaCO <sub>3</sub> (mg/L)	53.07	223.2	2.44	17.69	46.73	192.7	3.66	27.45	102.7	184.22	17.08	135.4
F <sup>-</sup> (mg/L)	0.09	0.24	0.05	0.05	0.09	0.20	0.05	0.05	0.17	0.39	0.05	0.15
Cl <sup>-</sup> (mg/L)	6.91	17.00	1.00	4.00	6.26	28.00	1.20	3.55	8.88	25.00	1.10	3.75
NO <sub>3</sub> <sup>2-</sup> (mg N/L)	1.70	12.00	0.05	0.09	2.62	12.00	0.05	0.38	1.46	11.00	0.05	0.05
PO <sub>4</sub> <sup>3-</sup> (mg P/L)	< 0.05	<0.05	<0.07	< 0.08	< 0.05	< 0.05	< 0.05	< 0.05	<0.05	0.00	0.00	<0.05
SO <sub>4</sub> <sup>2-</sup> (mg SO <sub>4</sub> /L)	7.59	31.00	0.17	1.85	7.75	72.00	0.20	1.75	53.91	750.00	0.43	8.95
NH <sub>4</sub> <sup>1+</sup> (mg N/L)	0.15	0.67	0.10	0.10	1.41	2.50	0.31	1.41	7.11	14.00	0.22	7.11
As <sup>3+</sup> (µg/L)	0.74	1.40	0.35	1.00	0.81	1.00	0.35	1.00	4.48	26.14	0.35	1.00
Ca <sup>2+</sup> (mg/L)	11.10	45.60	0.24	4.80	21.54	91.71	1.49	9.20	42.32	261.00	8.48	24.04
Fe <sup>3+</sup> (mg/L)	0.28	1.71	0.02	0.05	0.09	0.77	0.02	0.05	0.37	4.36	0.02	0.05
K <sup>+</sup> (mg/L)	1.80	4.07	0.21	1.52	2.56	5.72	0.58	2.56	2.66	16.30	0.42	1.32
Mg <sup>2+</sup> (mg/L)	2.78	8.44	0.27	2.10	4.38	14.26	0.46	2.97	5.05	7.72	0.86	5.41
Na <sup>1+</sup> (mg/L)	9.64	21.80	0.68	8.57	12.17	30.58	2.16	10.52	13.10	31.60	2.74	13.63
Si (mg/L)	10.66	18.50	3.13	9.03	13.47	22.20	6.15	13.00	13.49	21.70	9.13	11.85



**Figure 10. Manganese pH-Eh stability diagram**, modified from Morgan (2000), The red box outlines the span of measured pH and Eh values from > 50 wells across our field area, indicating that Mn<sup>2+</sup> is the stable form of Mn in aquifers.

### 3.2.2. Solubility of potential Mn-bearing minerals

In order to evaluate the potential for dissolution of Mn-bearing minerals, we calculated saturation indices based on the groundwater chemistry measured in well water. Only six wells were oversaturated with a Mn-bearing mineral in the MINTEQ database, and in each case the mineral was MnHPO<sub>4</sub>(s) (**Table 6**). Instead, NC Piedmont groundwater underlying the DWR research stations was undersaturated with respect to numerous Mn-bearing minerals (**Table 6**). The observation of an undersaturated groundwater system in regards to Mn-bearing minerals identifies the thermodynamic drive for mineral dissolution, and could indicate that Mn concentrations may persist or even increase in the future. However, it is unknown if the identified undersaturated minerals are actually present in the subsurface because the minerals were generated from measured groundwater constituents using a theoretical modeling program. Moreover, the rates of dissolution of Mn oxides are often slow and can limit environmental processes, and thus the dissolution of the minerals present may not necessarily contribute substantially to Mn concentrations in groundwater (Martin, 2005). Future research into subsurface mineralogy and dissolution could play a key role in understanding possible contributors to Mn in groundwater.

**Table 6. Saturation indices for Mn-bearing minerals in DWR research station wells computed from Visual MINTEQ.**

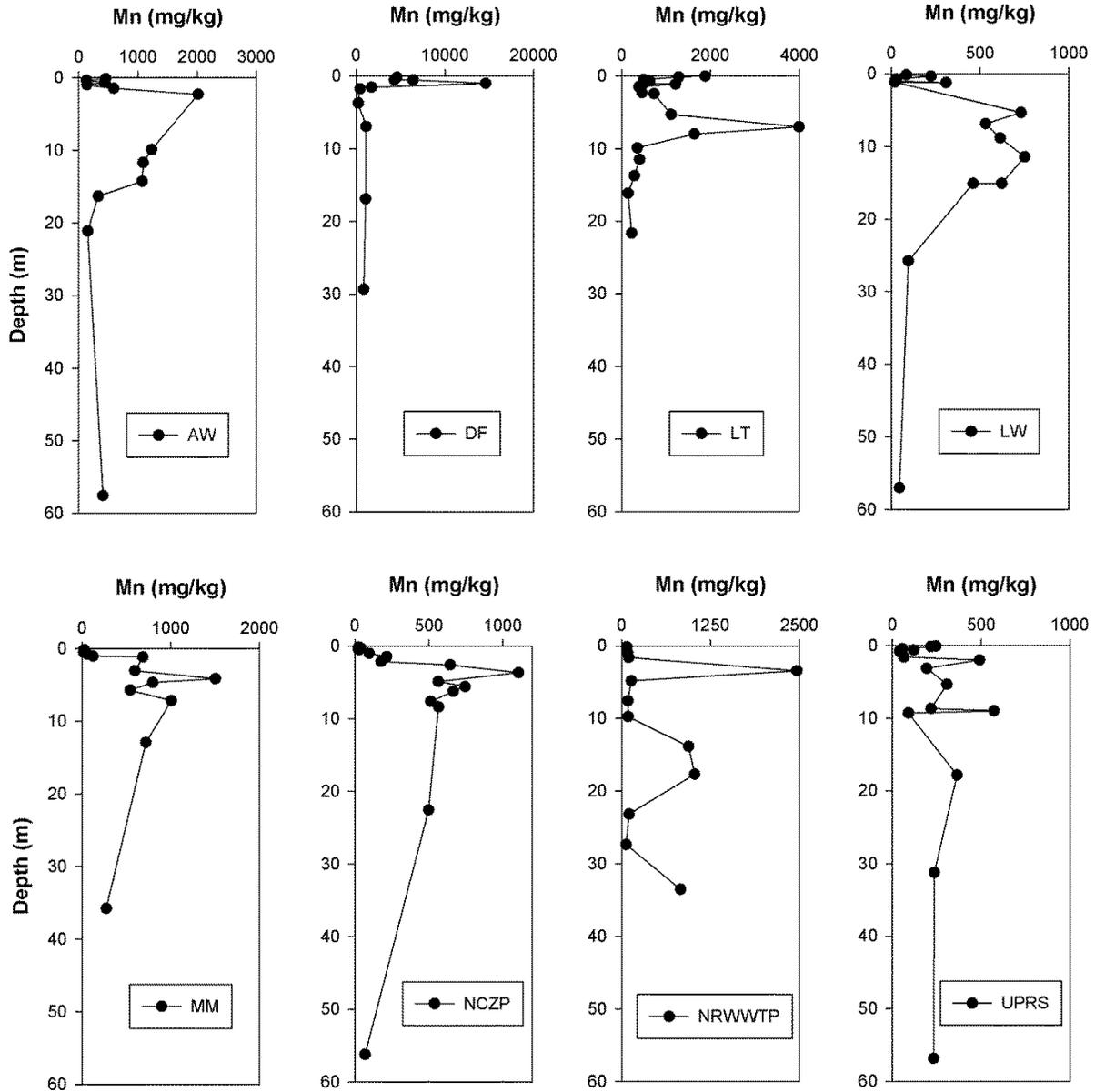
<b>Saturation Indices for Mn-bearing Minerals in DWR Well Sites (n=28<sup>a</sup>)</b>			
<b>Mineral</b>	<b>Number of wells under-saturated</b>	<b>Number of wells over-saturated</b>	<b>Saturation Index Range</b>
Hausmannite	28	0	-68.54 to -11.80
Manganite	28	0	-25.60 to -2.39
Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (s)	28	0	-74.19 to -14.15
MnCl <sub>2</sub> :4H <sub>2</sub> O(s)	28	0	-50.96 to -14.15
MnCO <sub>3</sub> (am)	28	0	-14.29 to -0.89
MnHPO <sub>4</sub> (s)	22	6	-20.96 to 1.85
MnSO <sub>4</sub> (s)	28	0	-35.17 to -11.44
Pyrochroite	28	0	-21.04 to -7.07
Pyrolusite	28	0	-40.01 to -1.78
Rhodochrosite	28	0	-13.80 to -0.40

<sup>a</sup>PM and NCZP are not incorporated due to lack of available alkalinity data.

### **3.3. Solid-phase chemistry and controls on Mn concentrations**

#### *3.3.1. Manganese concentrations in solid phases*

Concentrations of “environmentally available” Mn in solid-phase profiles across the NC Piedmont tended to peak in saprolite within the regolith near the water table (between 2 m and 9 m depth) and decreased significantly below that peak (**Figure 11**). Soil and residuum layers generally had lower Mn concentrations at the surface with a slight peak of Mn concentration with depth. Manganese concentrations in the bedrock were the lowest of the profile and were significantly less than those in the saprolite layer. Concentrations of Mn in soil and residuum, saprolite, and bedrock varied among research stations. Overall, although there was variability in concentrations among locations, Mn concentrations generally decreased slightly with depth in soil layers, increased and reached a maximum in saprolite, then decreased throughout the rest of the depth profile (**Figure 11**).



**Figure 11. Solid-phase “environmentally available” Mn concentrations with depth for eight geological cores collected from DWR research stations.** Similar trends of maximum concentrations within the saprolite layer and then a significant decrease into the bedrock were observed throughout the NC Piedmont. DF’s maximum concentration was observed in the soil, however a second peak was still observed in the saprolite.

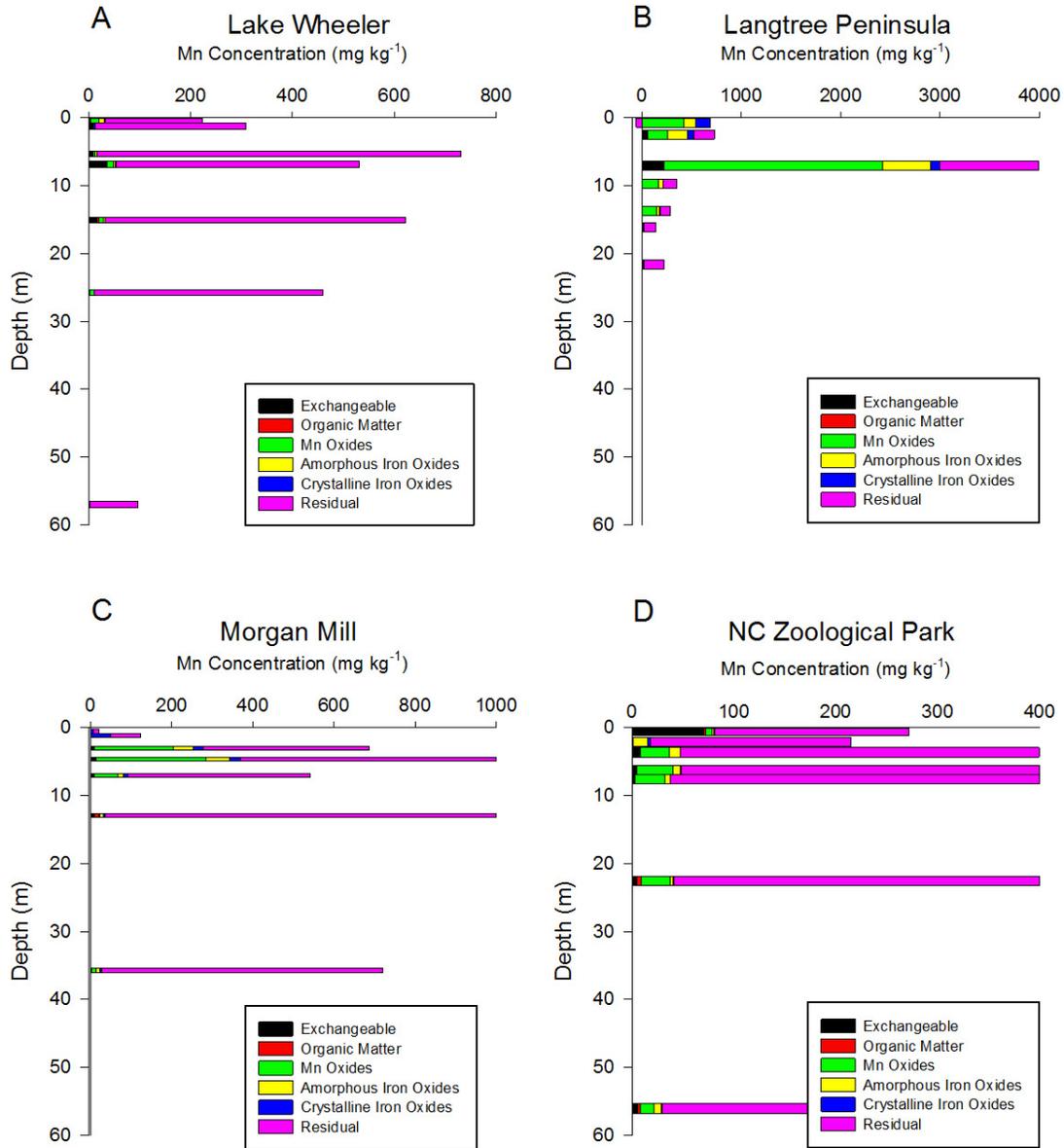
### 3.3.2. Manganese speciation and fractionation with depth

Sequential extractions revealed that Mn tended to be most closely associated with residual and Mn-oxide fractions within the Piedmont subsurface for MM, NCZP, LT, and LW (**Figure 12**). Samples from depths of the maximum Mn concentration in the subsurface profile for three out of the four research stations showed a larger percentage of Mn oxides than other depths, but all

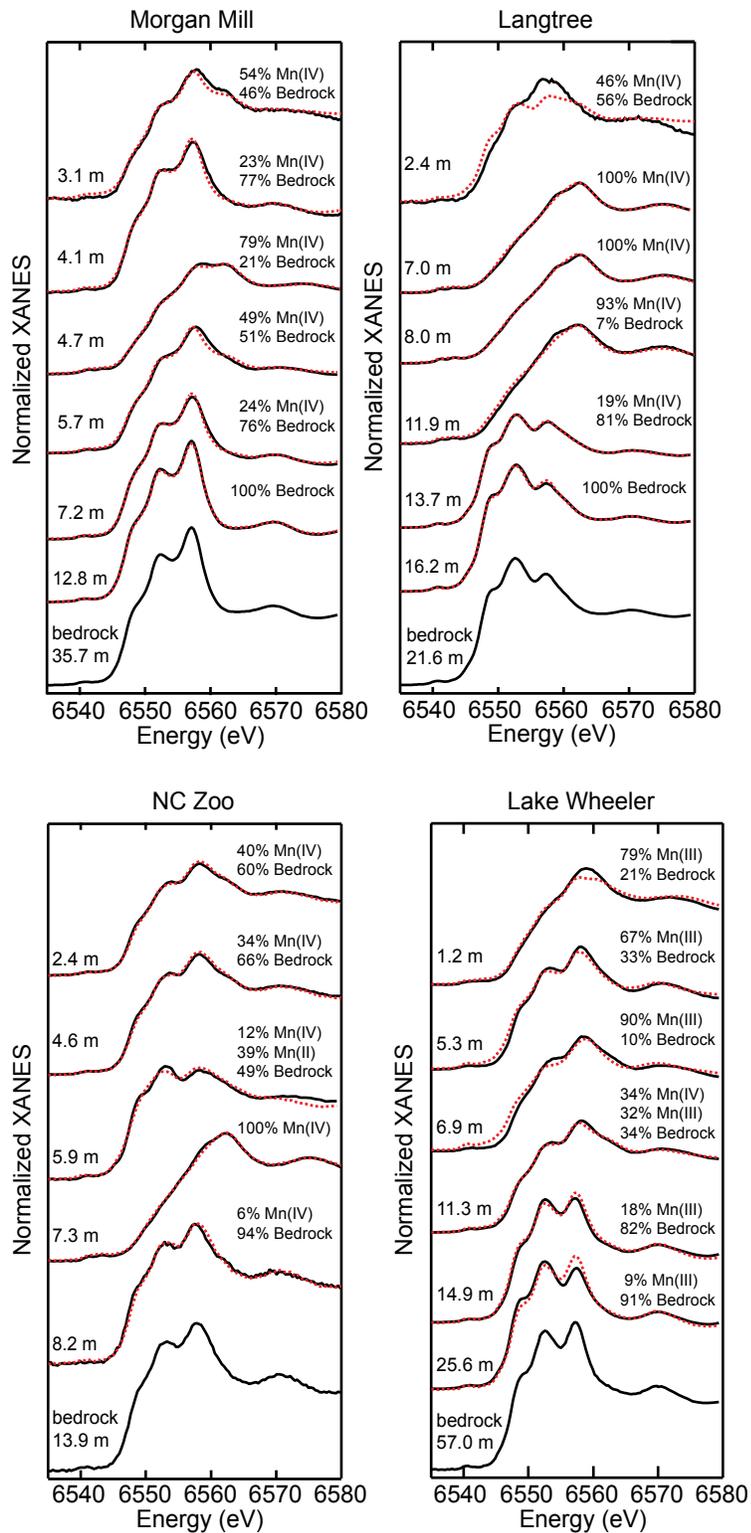
depths were largely dominated by residual fractions. MM and LT had higher concentrations of Mn oxides within their cores and were less dominated by residual Mn-bearing phases than the cores of NCZP and LW (**Figure 12**).

The highest concentrations of Mn in exchangeable and Mn oxide fractions occurred shallower in the subsurface for each research station (**Figure 12**). MM, NCZP, LT, and LW's highest exchangeable Mn concentrations were 14 mg/kg (at 4.6 m), 215 mg/kg (at 7 m), 70 mg/kg (at 0.46 m), and 36 mg/kg (at 6.8 m), respectively. Highest concentrations of Mn within Mn oxide fractions were 269 mg/kg (at 4.6 m), 2202 mg/kg (at 7 m), 36 mg/kg (at 6.2 m), and 16 mg/kg (at 0.33 m). Although absolute concentrations were small from core to core, proportions of Mn found within amorphous iron oxide and crystalline iron oxide phases were higher throughout the entire MM core as compared to the NCZP and LW cores. Only small concentrations of Mn were associated with the organic matter extracted fraction for all depths of all cores. Proportions of Mn found within residual fractions tended to increase with depth for all cores.

Linear combination fitting of the Mn K-edge XANES was performed using the bedrock as the background mineral phase and identifying the change in the bedrock minerals to secondary Mn (III/IV) oxides as a function of depth (**Figure 13**). The bedrock was an unidentified mixture of Mn (II) and Mn(III) silicates. Samples from four research sites (Morgan Mill, Langtree, North Carolina Zoo, and Lake Wheeler) were analyzed and showed Mn speciation varied with depth. X-ray adsorption near-edge structure (XANES) spectroscopic analyses indicate that Mn is primarily found within Mn(III,IV)-oxide and residual Mn(II,III)-bearing bedrock minerals throughout solid-phase profiles, although Mn oxides are only found in considerable quantities within the chemically weathered soil and saprolite.



**Figure 12. Solid-phase Mn concentrations with depth based on fractions generated from sequential extractions of cores from 4 research stations. Mn oxides are most prevalent in the near-surface and decrease with depth, while residual material increases with depth and is most prevalent in the bedrock.**

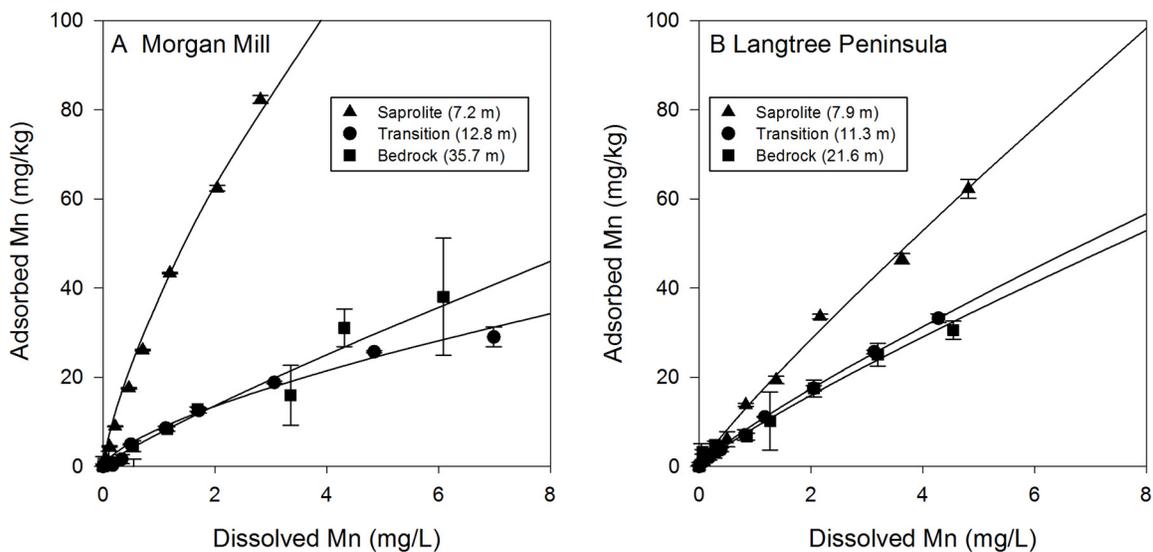


**Figure 13. Mn X-ray adsorption near-edge structure (XANES) spectroscopic analyses of solid phases from four research sites. Mn is found within both Mn(IV) oxide and residual Mn(II,III)-bearing bedrock minerals in the surface, although Mn oxides are only found in considerable quantities within the soil and saprolite.**

#### 4.4. Sorption capacity of solid-phase materials for Mn

Saprolite layers at MM and LT demonstrated the highest sorption capacity for dissolved Mn, whereas bedrock layers and transition layers had a lower equivalent sorption intensity (**Figure 14**). Saprolite, transition, and bedrock material for MM and LT had some concentration of Mn desorb from the solid-phase that was not originally added in the batch isotherm experiment. MM samples at 7.2 m, 13.1 m, and 35.7 m with no concentrations of Mn added had 0.30 mg/L, 0.35 mg/L, and 0.39 mg/L of Mn desorb or dissolved, respectively. LT samples at 7.9 m, 11.3 m, and 21.6 m with no concentrations of Mn added had 2.29 mg/L, 0.58 mg/L, and 0.28 mg/L of Mn desorb, respectively. Measured aqueous concentrations were corrected by these values for presented isotherm plots and calculations.

Calculated Freundlich  $K_d$  values for the saprolite layer within MM and LT were 37.8 L/kg (7.2 m) and 15.3 L/kg (7.9 m), respectively.  $K_d$  values for transition and bedrock layers within MM were 8.5 L/kg (12.8 m) and 7.4 L/kg (35.7 m).  $K_d$  values for transition and bedrock layers within LT were 9.6 L/kg (11.3 m) and 8.7 L/kg (21.6 m). Based on these data, saprolite at 7.2 m from MM showed a comparatively higher sorption intensity for Mn than saprolite at 7.9 m from LT (**Figure 14**). At MM, Mn was over 4 times more likely to partition onto the saprolite from the aqueous phase than it was to the transition or bedrock material. Manganese in the aqueous phase was only twice as likely to partition onto the saprolite than onto transition or bedrock material in the LT samples.



**Figure 14. Manganese adsorption isotherms.** Adsorption isotherm data for MM and LT DWR research stations (symbols) fitted with a Freundlich isotherm model (lines). Data are for saprolite, transition zone, and bedrock samples. Error bars represent standard deviation of triplicate analyses; unseen error bars are smaller than the plotted symbol size. Data are normalized for solid mass but are not corrected for surface area.

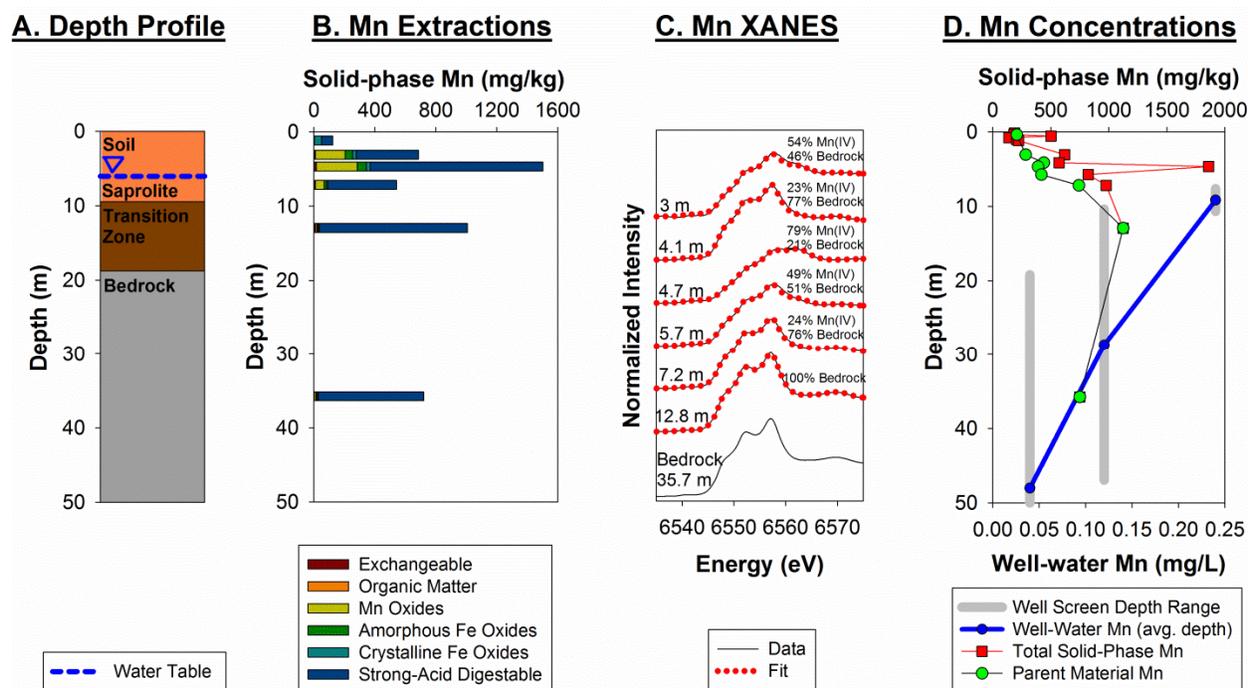
## **4. DISCUSSION**

Based on our findings, we propose a conceptual model for the main processes driving Mn contamination of well water in the NC Piedmont. Following years of bedrock weathering at the near-surface, Mn has repartitioned from primary minerals to secondary, Mn-oxide minerals. Manganese oxides accumulate above the water table, where redox conditions allow, but once saturated, reductively dissolve. Manganese that enters the aqueous phase can migrate downward, due to natural flow processes of the region (Heath, 1994). Manganese downward transport may be partially facilitated by surficial faults and dykes, as well as bedrock fractures. Bedrock solids, which are dominated by primary mineral phases, have little capacity to retain dissolved Mn, and as a result, Mn that enters aquifers stays partitioned in the aqueous phase and is able to contaminate well water. We synthesize our data below, using results from the Morgan Mill groundwater research site as a representative example.

### **4.1. Weathering and manganese near-surface repartitioning**

Based on solid and aqueous chemical profiles, we posit that active weathering above aquifers can serve as an “engine” transforming Mn to enable delivery of high concentrations to groundwater. Prior research on Mn contamination of groundwater has focused on geological characteristics of deeper aquifers when considering influences on Mn concentrations (Kiracofe et al., 2015; Homoncik et al., 2010; Groschen et al., 2009; Fisher and Davidson, 2007; Flanagan et al., 2014). However, soil mineral weathering also plays key roles controlling the distribution and flux of redox-labile elements, such as Mn (Brantley and Lebedeva, 2011). Pedogenetic processes can influence the downward transport of solutes to aquifers, impacting groundwater quality and human exposure to contaminants via well-water consumption. Whereas surface-derived anthropogenic influences to groundwater quality are well recognized, the effects of natural soil processes on contaminant distributions and exposure remain underappreciated and poorly characterized.

The Piedmont physiographic region has a rock-saprolite-solum wreathing pattern, in which an average of 1-meter thick soil solum overlies 1-25 m of saprolite (Buol and Weed, 1991; **Figure 15A**). The soil and saprolite are chemically weathered layers, and the physically weathered transition zone overlies the bedrock. Chemical weathering of parent materials during pedogenesis repartitions Mn from primary to secondary phases. Sequential extractions and X-ray adsorption near-edge structure (XANES) spectroscopic analyses indicate that Mn is primarily found within Mn(III,IV)-oxide and residual Mn(II,III)-bearing bedrock minerals throughout solid-phase profiles, although Mn oxides are only found in considerable quantities within the chemically weathered soil and saprolite (**Figures 12, 13, and 15B, C**).



**Figure 15. Summary data from Morgan Mill.** **A.** Depth profile for Division of Water Resources (DWR) research site, Morgan Mill, with chemically weathering soil and saprolite, physically weathering transition zone, and bedrock. The water table separates zones of oxygen and water influx. **B.** Sequential extractions (McDaniel and Buol, 1991) of soil and saprolite (<10 m) from Morgan Mill indicate Mn phases are dominated by oxide and residual fractions. **C.** Soil and saprolite XANES spectra are fit with different proportions of the bedrock and Mn(IV)-oxide standard spectra, indicating partial weathering of parent material in the regolith. **D.** Field data from Morgan Mill. Total solid-phase Mn concentrations (via neutron activation analysis) reach a sharp maximum within the saprolite, just above the water table. Well-water Mn is highest in wells screened just below the solid-phase peak, and concentrations decrease with depth.

Solid-phase Mn-concentrations reach a sharp maximum within the saprolite, generally just above the water table (**Figures 11, 15D**), characteristic of a “depletion-enrichment” profile (Brantley and Lebedeva, 2011) and reflecting primary mineral dissolution, leaching of Mn, and precipitation of Mn oxides. Proportions of Mn within primary mineral phases, based on total Mn and XANES fit data (**Figure 15C**), are depleted closer to the surface (**Figure 15D**), and concentrations of Mn oxides increase to the water table (**Figure 15B**). The decrease of Mn oxides below the water table within the saprolite and the high aqueous concentrations of Mn in wells screened just below the solid-phase peak (**Figure 15D**) suggest the reductive release of Mn, a process influenced by the system hydrology.

#### ***4.2. Hydrologic controls on Mn release and downward transport***

Hydrologic features superimposed on weathering patterns create conditions that mobilize Mn to groundwater. Weathering of parent materials increases the availability of Mn by creating secondary Mn (III,IV) oxides that are susceptible to dissolution under reducing conditions; the location of the water table within the saprolite creates a geochemical gradient promoting

(microbial) reduction. Across the NC Piedmont, the water table is roughly coincident with the maximum peak of solid-phase Mn concentrations, and groundwater is devoid of dissolved oxygen, with redox chemistry generally below the potential of Mn reduction (**Table 5** and **Figure 10**), creating conditions favorable to release of Mn into solution. Accordingly, the highest well-water Mn concentrations are typically found in shallow wells, screened just below the water table and solid-phase Mn maximum (**Figures 5, 15**).

Once into solution, Mn(II), as the  $Mn^{2+}$  cation, may be retained by adsorption to mineral surfaces and organic matter, but overall, re-oxidation, especially in the absence of dissolved oxygen, is relatively slow (Morgan, 2000), and with limited sorption (**Figure 14**), Mn(II) may be transported with natural flow patterns to contaminate wells. The unsaturated regolith zone (soil + saprolite) provides a medium for the recharge water to infiltrate to the groundwater system, and the saturated regolith zone (saprolite) acts as a reservoir that supplies water to the bedrock through fractures (Lindsey et al., 2006; Heath, 1994; Heath, 1980). Net groundwater flow at the field scale is downward, and contaminants from surficial sources, including nitrate and pesticides, have been observed in well water throughout Piedmont aquifers (Lindsey et al., 2006), highlighting the link between groundwater recharge, water chemistry, and groundwater quality. Domestic wells may be screened over 10s of meters to access water from bedrock fractures (**Figure 15D**), and downward delivery of Mn, at least to the upper depths of well screens, could lead to high concentrations in wells even if mixed with low-Mn water from deeper depths.

#### **4.3. Controls on Mn depletion from the near-surface**

At the Morgan Mill research site, repartitioning of Mn in the near-surface has resulted in a net loss of Mn. Roughly 40% of the initial Mn has been depleted from the soil and saprolite, based on the solid-phase Mn profile in **Figure 15**, assuming an initial soil/saprolite parent-material Mn content equivalent to that in bedrock, and assuming bulk densities and material compaction as defined previously for the Piedmont (Pavich, 1986). Given an annual vertical recharge rate of 16 cm/yr (Heath, 1994), a soil/saprolite thickness of 15 m (Heath, 1980), a porosity of 0.3  $m^3/m^3$  (Heath, 1980), and the solid-phase density of quartz ( $\sim 2.7 \text{ g/cm}^3$ ), only  $1.1 \times 10^{-3}$  mg Mn per kg soil/saprolite would need to be released per year to maintain Mn concentrations of 0.2 mg/L in groundwater (roughly the maximum concentration observed at our Morgan Mill site). Solid-phase Mn concentrations reach  $\sim 2000$  mg/kg in Piedmont saprolite (**Figures 11, 15**), thereby providing a natural reservoir for feeding Mn into groundwater. Although Mn loss from the regolith may have also occurred due to erosion and efflux to rivers (Herndon and Brantley, 2011), current depth profiles and hydrological and geochemical gradients suggest that Mn delivery to groundwater is also an important process.

#### **4.4. Spatial variability, uncertainty, and alternate scenarios**

Soil weathering and redox partitioning conspire to increase the availability and mobilization of potentially dangerous Mn concentrations to groundwater, and the spatial variability in well-water Mn concentrations observed at the field-site and regional scales may reflect variability in bedrock parent material, weathering rates, and/or local hydrology. Although total solid-phase Mn concentrations

are sufficient to provide elevated well-water Mn concentrations across the Piedmont, the deep weathering profiles and water tables within the Felsic Crystalline series trap Mn in Mn oxides to deeper depths within the chemically weathering regolith, as evidenced at the Langtree site (**Figures 6, 11, 12, 13**). In contrast, the intersection of the water table within the chemically weathering zones of the Carolina Slate Belt (Morgan Mill, NC Zoological Park sites) may enable downward delivery of dissolved Mn below the regolith. Detailed hydrogeochemical assessments are needed for improved predictions about the specific distributions of Mn in well water and resulting risks for human exposure.

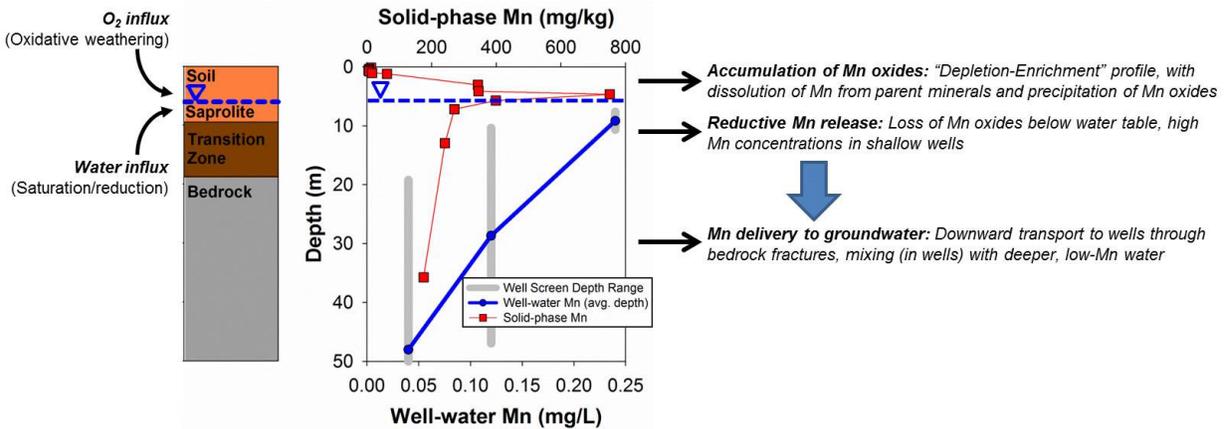
Importantly, a mechanism of near-surface delivery of Mn to groundwater does not preclude additional processes from influencing Mn concentrations. Indeed, dissolution of bedrock may release Mn to groundwater, and indeed, mineral saturation calculations do indicate that groundwater may be undersaturated with respect to a number of common Mn-bearing minerals. Dominant drivers on Mn concentrations may vary spatially and temporally, and further work teasing out the relative contributions of Mn to well water is paramount for managing the emerging contaminant.

## **5. SUMMARY AND CONCLUSIONS**

Manganese contamination of well water is a widespread problem and increasing concern in North Carolina. Roughly 50% of wells in NC have Mn concentrations exceeding the state standard of 0.05 mg/L. Analyses reveal that >1 million people in the Piedmont of the Southeast US are impacted by well water with Mn concentrations  $\geq 0.05$  mg/L, and >387,000 people in the NC Piedmont are exposed to Mn concentrations above this limit. Within the Piedmont, Mn concentrations cluster by soil system, with the Carolina Slate Belt and Triassic Basin systems being particularly affected. Manganese concentrations in NC Piedmont well water were generally highest at shallower depths, and concentrations may be associated with fine-textured soils and rocks.

Based on our findings to date, we propose a conceptual model for the main processes driving Mn contamination of well water in the NC Piedmont (**Figure 16**). Following years of bedrock weathering at the near-surface, Mn has repartitioned from primary minerals to secondary, Mn-oxide minerals. Manganese oxides accumulate above the water table, where redox conditions allow, but once saturated, reductively dissolve. Manganese that enters the aqueous phase can migrate downward, due to natural flow processes of the region (Heath, 1994). Manganese downward transport may be partially facilitated by surficial faults and dykes, as well as bedrock fractures. Bedrock solids, which are dominated by primary mineral phases, have little capacity to retain dissolved Mn, and as a result, Mn that enters aquifers stays partitioned in the aqueous phase and is able to contaminate well water.

This new model for Mn cycling and transport in the Piedmont will allow for better selection of well drilling locations and depths throughout the Piedmont. However, future work should seek further evaluate the robustness of our proposed model in the face of alternate explanations and quantify Mn delivery rates between surface and subsurface zones.



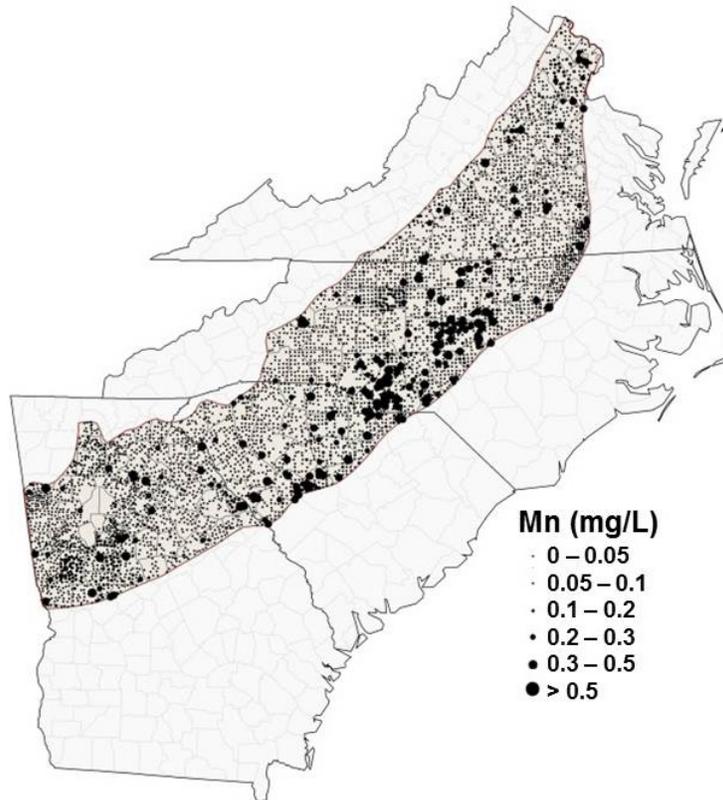
**Figure 16. Conceptual model for Mn repartitioning and delivery to groundwater.** **Left.** Depth profile for the Morgan Mill research site, with chemically weathering soil and saprolite, physically weathering transition zone, and bedrock. The water table separates zones of oxygen and water influx. **Center.** Field data from Morgan Mill. Solid-phase Mn concentrations reach a sharp maximum within the saprolite, just above the water table. Well-water Mn is highest in wells screened just below the solid-phase peak, and concentrations decrease with depth. **Right.** Interpretation of Mn profiles, highlighting the weathering, redox cycling, and transport processes leading to Mn in well water.

## 6. RECOMMENDATIONS

### 6.1. Management of Mn in Piedmont well water

Research in from this project motivates an improved understanding of the factors controlling high Mn concentrations in groundwater. Manganese is an emerging contaminant, and its adverse impacts to human health are being increasingly revealed. Elevated concentrations of Mn are found throughout groundwater of the Southern Piedmont (**Figure 17**), and the extent of the region along the eastern US indicates that our research findings could be applicable beyond our individual research sites.

From a management perspective, results from this study suggest that, rather than based on county averages, risks from Mn in wells would be better assessed based on associations with geological units and depth of casing in the groundwater zones – information that is frequently familiar to experienced well drillers but that has been overlooked in health-based studies. For example, the highest concentrations of Mn were generally observed in shallower wells, so implementation of deeper cased wells should be considered for future well installations. Unfortunately, Mn concentrations occur in extremely high concentrations throughout the NC Piedmont, and it is therefore important for well drillers and public health personnel to encourage annual well testing to private well homeowners since there is currently no enforcement to have wells tested every year. However, with background research and careful well installation management, it is possible that groundwater with low concentrations of Mn could be accessed for most any well location.



**Figure 17. Well water Mn concentrations in the Southern Piedmont.** Data from Smith et al. (2006). We estimate >1 million people drink well water with Mn > 0.05 mg/L.

## **6.2. Research needs**

Because the soil-bedrock continuum is a dynamic system, it must continue to be studied in order to better understand the controls on Mn contamination. Further work could include additional geological assessment in terms of transport pathways and sources of Mn to groundwater, research into subsurface mineralogy and dissolution, investigation into the significance of parent material and the rate of weathering on Mn accumulation in the subsurface, and holistic integration of hydrological and biogeochemical processes for modeling risks of Mn contamination in wells. Each of these efforts would help evaluate the robustness of our proposed model in the face of alternate explanations and quantify Mn delivery rates between surface and subsurface zones.

Manganese concentrations both above the drinking water standard and below detection limits are observed in wells from different depths at nearly every groundwater research site across the Piedmont, suggesting that localized environmental processes at individual well sites could be controlling current Mn concentrations in well water. Therefore, integrated soil-bedrock-system analyses for a specific well site are needed for effective Mn prediction and management. Future analyses could target smaller areas where the best mapping coverage of water chemistry and geologic features exists, and spatial statistical models could be applied to quantify relationships inferred from hydrogeochemical modeling.

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## **APPENDIX 1: List of Abbreviations and Symbols**

AW	Allison Woods
DENR	Department of Environment and Natural Resources
DF	Duke Forest
DHHS	Department of Health and Human Services
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DWR	Division of Water Resources
EATS	Environmental and Agriculture Testing Service laboratory
EHS	Environmental Health Section
HSSR	Hydrogeochemical and Stream Sediment Reconnaissance
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
LT	Langtree Peninsula
LW	Lake Wheeler
MM	Morgan Mill
Mn	Manganese
NC	North Carolina
NCGS	North Carolina Geological Survey
NCZP	North Carolina Zoological Park
NRWWTP	Neuse River Waste Water Treatment Plant
NURE	National Uranium Resource Evaluation
ORP	Oxidation-reduction potential

PM	Pasour Mountain
RB	Rocky Branch
SSRL	Stanford Synchrotron Radiation Lightsource
SSURGO	Soil Survey Geographic database
UPRS	Upper Piedmont Research Station
US	United States
USGS	United States Geologic Survey
WRRRI	Water Resources Research Institute
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy

## **APPENDIX 2: List of Project Outputs To Date**

### **Presentations**

\*indicates efforts at communication of results to end users and policy makers.

‡indicates presentation by student

‡Gillispie, E., Austin, R., Rivera, N., Bolich, R., Amoozegar, A., Duckworth, O., and Polizzotto, M. *Integrated soil-bedrock system analyses reveal near-surface manganese repartitioning and release to groundwater in North Carolina*. Geological Society of America Annual Meeting, Baltimore, MD, November 2015. Poster presentation.

\*‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Advanced Well Workshop, Wilmington, NC, May 2015. Invited Presentation.

Polizzotto, ML. *Understanding the Fate of Soil Contaminants for Protection of Human Health*. NC State University Department of Soil Science Spring Seminar Series, Raleigh, NC, April 2015. Invited presentation.

‡Gillispie, EC., Austin, R., Rivera, N., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Integrated soil-bedrock system analyses reveal near-surface manganese repartitioning and release to groundwater in North Carolina*. Soil Science Society of America Annual Meeting, Long Beach, CA, November 2014. Oral presentation.

Polizzotto, ML., Gillispie, EC., Austin, R., Rivera, NA., Abraham, J., Wang, S., Bolich, R., Bradley, P., Duckworth, O.W., Amoozegar, A., and Hesterberg, D. *Manganese near-surface repartitioning and delivery to groundwater in North Carolina*. Goldschmidt Geochemistry Conference, Sacramento, CA, June 2014. Oral presentation.

\*‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Advanced Well Workshop, Asheville, NC, May 2014. Invited Presentation.

‡Sams, A., Gillispie, E., and Polizzotto, M. *Characterizing the aqueous chemistry of aquifers with low and high manganese in the North Carolina Piedmont*. NCSU Undergraduate Research Symposium, Raleigh, NC, April 2014. Poster Presentation.

\*‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Water Resources Research Institute of the University of North Carolina System Annual 2014 Conference, Raleigh, NC, March 2014. Poster Presentation.

‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. 9<sup>th</sup> Annual NC State University Graduate Research Symposium, Raleigh, NC, March 2014. Poster Presentation.

\*‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Guilford County Well Contractors Day, Greensboro, NC, February, 2014. Invited Presentation.

‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Soil Science Society of North Carolina Annual Meeting, Raleigh, NC, January 2014. Poster presentation.

‡Gillispie, EC., Austin, R., Abraham, J., Wang, S., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Sources and variability of manganese in well water of the North Carolina Piedmont*. Soil Science Society of America Annual Meeting, Tampa, FL, November 2013. Poster presentation.

\*‡Gillispie, E., Polizzotto, M., and Bolich, R. *Sources and variability of manganese concentrations in well water of the NC Piedmont*. 29<sup>th</sup> Annual Onsite Water Protection Conference, Raleigh, NC, October 2013. Invited presentation.

‡Gillispie, EC., Austin, R., Bolich, R., Bradley, P., Amoozegar, A., Duckworth, O., Hesterberg, D., and Polizzotto, ML. *Characterizing the sources and variability of manganese in well water of the North Carolina Piedmont*. 12<sup>th</sup> International Conference on the Biogeochemistry of Trace Elements, Athens, Georgia, June 2013. Poster presentation.

### **Publication in preparation**

Gillispie, EC., Austin, RE., Rivera, NA., Amoozegar, A., Duckworth, OW., Abraham, J., Wang, S., Bolich, R., Bradley, P., and Polizzotto, ML. (2015) Manganese near-surface repartitioning and release to groundwater in the North Carolina Piedmont. In late-stage preparation for *Proceedings of the National Academy of Sciences*.

### **M.S. Thesis**

Gillispie, EC. (2014) *Sources and Environmental Factors Controlling Manganese Distributions in Well Water of the North Carolina Piedmont*. North Carolina State University M.S. Thesis. 115 pp.

### **Undergraduate Thesis**

Sams, AC. (2014) Characterizing the Aqueous Chemistry of Aquifers with Low and High Manganese in the North Carolina Piedmont. North Carolina State University Undergraduate Thesis. 36 pp.

### **Efforts at technology transfer or communication of results to end users, policy makers, or others**

To date, we have communicated results to end users and policymakers through formal presentations and discussions. Well drillers and environmental health officials have been targeted at presentations at the NC Onsite Water Protection Conference (October 2013), the Guilford County Well Contractors Day (February 2014), the Water Resources Research Institute of the University of North Carolina System Annual Convergence (March 2014), and Advanced Well Workshops in Asheville, NC (May 2014) and Wilmington, NC (May 2015).

## **APPENDIX 3: Students and Postdoctoral Scholars Trained through Project**

### **M.S. Student**

- Elizabeth Gillispie: M.S. Soil Science, North Carolina State University, 2014

### **Undergraduate Students**

- Matthew Church: B.S. Environmental Science, North Carolina State University, TBD
- Cory Connell: B.S. Environmental Technology, North Carolina State University, 2014
- Christine Knight: B.S. Environmental Science, North Carolina State University, 2014
- Allison Sams: B.S. Environmental Science, North Carolina State University, 2014

### **Postdoctoral Scholars**

- Megan Andrews: Soil Science, North Carolina State University
- Nelson Rivera: Soil Science, North Carolina State University

### **Narrative of Student Involvement**

One M.S. student (Elizabeth Gillispie), four undergraduates (Allison Sams, Cory Connell, Christine Knight, and Matthew Church), and two post-docs (Nelson Rivera and Megan Andrews) participated in this project.

Research in the project comprised Elizabeth Gillispie's M.S. thesis. She led the field work and laboratory experiments, and she also contributed to the geospatial analyses presented here. Elizabeth gained experience in interdisciplinary and multi-scale research approaches, and her research efforts were coupled with professional development opportunities. She has delivered numerous presentations at academic and professional meetings. For her work on this project, Elizabeth was awarded the Hugh Hammond Bennett Scholarship from the Hugh Hammond Bennett Chapter of the Soil and Water Conservation Society, in recognition of advanced study that contributes to sound use of soil and water resources. She also received student presentation awards for presentations about this project to the Soil Chemistry Division of the Soil Science Society of America (November 2014) and the North Carolina Water Resources Research Institute (March 2014).

Four undergraduates participated in the project by assisting with field work and laboratory experiments. The students collected and analyzed data, performed experiments, and presented results in lab group meetings. One student, Allison Sams, developed an Honors undergraduate thesis as part of the project, and another student used the project as a springboard for graduate school (Christine Knight: University of Michigan). A third student secured a consulting job through his activities with the project. Three of the undergraduates majored in Environmental Science, and the fourth majored in Environmental Technology at NC State University.

The two post-docs collected and analyzed spectroscopic data in order to define the speciation of Mn in solid phases.

