Supporting Information

Soil Weathering As an Engine for Manganese Contamination of Well Water

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- 21 pages, 9 figures, 2 tables -

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Additional Methods

Total solid-phase Mn concentrations. Total solid-phase Mn and Ti concentrations on samples from the Morgan Mill Division of Water Resources (DWR) site were measured by neutron activation analysis at the North Carolina State University 1-MW PULSTAR Nuclear Reactor facility. Fifteen soil, saprolite, and bedrock samples, analyzed singly; 3 duplicate samples; 4 method blanks; and 4 Mn standards were irradiated sequentially for 10 seconds each at 50 kW in the PULSTAR PN terminus. Samples decayed for 10 minutes, and were counted for 5 minutes each on a gamma spectroscopy system.

"Environmentally available" solid-phase Mn concentrations via strong-acid digestions.

To measure strong-acid-digestible Mn concentrations in solid phases, a 2.5-cm-thick slice from the center of all samples was air dried and crushed with a mortar and pestle to pass through a 2mm sieve. Manganese was then analyzed after an acid digestion protocol based on EPA Method 3050B (USEPA, 1996). EPA Method 3050B uses strong acids and determines "environmentally available" Mn, which is Mn not incorporated into silicate minerals but instead tends to be more mobile in the environment.

Samples were digested by first weighing 1 g of sample into digestion tubes with caps. Ten milliliters of 7 M HNO₃ were 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 HNO₃ 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 were 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 30% hydrogen peroxide (H₂O₂) was added

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to the each tube, and then repeated six times. 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. The next day, 10 mL of 12 M HCl were added to each tube, and tubes were vortexed and placed on the rack for 15 minutes. Samples were then filtered using Whatman No. 41 filter papers and diluted to 100 mL. Ten mL aliquots of the digested samples were analyzed for total dissolved Mn by ICP-OES. The detection limit for dissolved Mn was 0.01 mg/L. Duplicate sets of digestions were conducted for all samples.

Sequential extractions. Chemical fractionation of solid-phase Mn was performed using a sequential extraction procedure adapted from McDaniel and Buol (1991) for acid soils in the North Carolina Piedmont. Cores from four of the DWR research stations – LT, MM, NCZP, and LW (Fig. S2) – were chosen for sequential extraction analysis based on their associations with different soil systems and geozones, and their different concentrations of Mn in monitoring wells. The operationally defined extracting solutions for obtaining Mn from exchangeable, organic matter, Mn oxide, amorphous iron oxide and crystalline iron oxide fractions were, respectively: 1 M Mg(NO₃)₂ at a pH of 7, 0.7 M NaOCl at a pH of 8.5, 0.1 M NH₂OH•HCl at a pH of 2, 0.2 M (NH₄)₂C₂O₄•H₂O-0.2 M H₂C₂O₄ at a pH of 3, and a citrate-bicarbonate-dithionite (CBD) extract consisting of 0.3 M Na₃C₆H₅O₇•2H₂O, 0.1 M NaHCO₃ and 1 g Na₂S₂O₄(s) (summarized below) . Residual Mn phases were calculated as the difference between strong-acid-digestible Mn concentrations (by EPA 3050B) and the sum of Mn from the five extraction steps. Triplicate sets of extractions were conducted for all samples.

Extraction solution	Target Mn fraction
1 M Mg(NO ₃) ₂ , pH 7	Exchangeable Mn
0.7 M NaOCl, pH 8.5	Mn in organic matter
0.1 M NH ₂ OH•HCl, pH 2	Mn oxide
0.2 M (NH ₄) ₂ C ₂ O ₄ •H ₂ O, 0.2 M H ₂ C ₂ O ₄ , pH 3	Mn in amorphous iron oxide
0.3 M Na ₃ C ₆ H ₅ O ₇ •2H ₂ O, 0.1 M NaHCO ₃ , 1 g Na ₂ S ₂ O ₄ (s)	Mn in crystalline iron oxide
EPA 3050B procedure	Residual strong-acid-digestible Mn

Summary of sequential extraction solutions, adapted from McDaniel and Buol (1991)

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 according to standard procedures. 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⁻, F⁻, NO₃⁻, $PO_4^{3^-}$, NH_4^+ , and $SO_4^{2^-}$. Samples collected for dissolved organic carbon were filtered into 30 mL glass bottles using the same filter. Samples analyzed for cation content 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. Samples for anion analysis were not acidified. All samples were immediately stored on ice and then stored at 4°C in the dark until analysis.

Samples were analyzed for anions (Cl⁻, F⁻, NO₃⁻, PO₄³⁻, and SO₄²⁻) using a ion chromatograph (DIONEX model 500), with a detection limit of 0.05 mg/L for all anions. Samples were analyzed for nutrients (NO₃⁻, NH₄⁺, and PO₄³⁻) using a flow injection analyzer (LACHAT, Hach model 8000), with detection limits of 0.10 mg/L for N-NO₃⁻ and N-NH₄⁺, and 0.01 mg/L for P-PO₄³⁻. Samples were analyzed for metals 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 1.0μ g/L.

Manganese X-ray absorption near-edge structure (XANES) spectroscopy and linear combination fitting of data. 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 monochromator (beam size = 2 mm vertical × 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 concentration.

A wide range of manganese standards were used in the linear combination fitting of the XANES data. Below is a list of the standards used in initial assessment of the fitting. Standards in **bold** were used in the final fits of the sediment samples in addition to the bedrock. The minerals were obtained from the Smithsonian Institute, the Mineral Research Company, or from other researchers. Standard spectra are shown in Figure S8.

Norrishite: K(Mn⁺³₂Li)Si₄O₁₀O₂ from Smithsonian with ID NMNH 170706, Locale: New South Wales Australia, Hoskins Mine

Dr. Cara Santelli, Smithsonian:

Metaswitzerite: Mn₃(PO₄)₂·4 H₂O from Smithsonian with ID NMNH 170124, Locale: unknown Bermanite: Mn²⁺Mn³⁺₂(PO₄)₂(OH)2·4H₂O from Smithsonian with ID NMNH 149978, Locale: Mesquitella and Mangaulde

Gaudefroyite Ca₄Mn⁺³_{3-x}(BO₃)₃(CO₃)(O,OH)₃ from Smithsonian with ID NMNH R16209, Locale: Morocco, Ant-Atlas

Cryptomelane:K(Mn⁴⁺,Mn²⁺)₈O₁₆ from Smithsonian with ID NMNH 128327, Locale: South Africa, Kuruman District, Smart Farm

Mineral Research Company:

Purpurite: (Mn,Fe)PO₄ from the Mineral Research Company, Locale: Namibia Parsettensite: K_{1.2}Mn₈(Si,Al)₁₂O₂₆(OH)₁₀ Mineral Research Company, Locale Foote Lithium Mine Compnay, Foote Mine, North Carolina

Dr. Dean Hesterberg, North Carolina State University: Hureaulite: Mn₅(PO₄)₂(PO₃(OH))₂ •4H₂O

Dr. Peggy O'Day, University of California, Merced: Bixbyite: $(Mn^{+3}Fe^{+3})_2O_3$ Magnosite: $Mn^{2+}O$ δ- $Mn^{4+}O_2$ Todorokite: $(Na,Ca,K)_2(Mn^{+4},Mn^{+3})_6O_{12}\bullet 3-4.5(H_2O)$ Pyrolusite: β- $Mn^{4+}O_2$ Ramsdellite: $Mn^{4+}O_2$ Ramsdellite: $Mn^{4+}O_2$ Manganite: γ - $Mn^{3+}O(OH)$ Feitknechtite: β - $Mn^{3+}O(OH)$ Heterosite: $(Mn^{+3},Fe^{+3})PO_4$ Tephroite: $Mn^{+2}_2SiO_4$ **Rhodochrosite**: $Mn^{2+}CO_3$ **Birnessite**: $(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5 H_2O$ **Hausmanite**: α - $Mn^{2+}Mn^{3+}_2O_4$ **Groutite**: $Mn^{3+}O(OH)$

In general, the standards used in the final fits represent the different possible Mn oxidation states in the samples and therefore demonstrate differences between soil/saprolite and bedrock. The standards used were natural samples so mixed Mn valence state may exist, particularly with the birnessite and groutite.

Fitting analyses were performed over the range of 6350-6590 eV without an energy shift parameter for the calibrated data. In addition to the pure standards, the spectrum from a corresponding bedrock sample was used in the fitting of soil, saprolite, and transition-zone samples because pure-mineral standards alone could not accurately account for features in their XANES spectra.

Initial screening of the data was performed using the method from Manceau et al. (2012) by fitting all of 21 spectra in the fit and allowing negative components. The most negative component was removed from the next iteration until all non-zero components were removed. From there, of the remaining components, a representative spectra for each oxidation state was used in a combinatorial fit, and each negative component was re-introduced into the fit one-byone to ensure no false minima were obtained during removal of components. Principal component analysis (PCA) of the data (Figure S9) indicates up to three components, but the third component is small compared to the other two components, indicating it is in some but not all samples. Accordingly, fitting was constrained to the bedrock plus 1 Mn standard with the exception of two samples (Lake Wheeler 11.3 meters and NCZP 5.9 meters), where the addition of another component was necessary to improve the fit. In general, fits shown in Figures 3 and S7 represent those with the best R-factor unless a) the best fit incorporated >2 components, b) one component represented <5% of the fit (a value below the typical uncertainty of linear combination fits), c) the R-factor (goodness-of-fit metric) for an alternate fit was within 0.007 of the R-factor for the "best fit", AND d) an alternate fit was consistent with the rest of the soil/saprolite column. Fitting results, including "best fits" and any alternate fits also summarized in Table S2.

Bedrock Mn XANES spectra show differences from location to location, but resolving their different mineral components was not possible with our XANES standards. The geology of the area indicates that the Mn can possibly be in silicates or phosphates, and spectra indicate all four bedrocks are a mixture of Mn(II) and Mn(III) with differing proportions, and there is a possible Mn(IV) phase in NCZP.

Mass-transfer coefficient calculation. The mass-transfer coefficient, τ , is a commonly used dimensionless metric that quantifies accumulation or depletion of an element within a

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weathering profile, relative to its bedrock abundance and corrected for the concentrations of an immobile element (Brantley and Lebdeva, 2011). We used Ti as a representative immobile element and calculated τ for Mn (denoted $\tau_{Mn,Ti}$) as:

$$\tau_{Mn,Ti} = \left[\frac{c_{Mn,w}}{c_{Mn,p}}\right] \left[\frac{c_{Ti,p}}{c_{Ti,w}}\right] - 1 \tag{S1}$$

where $C_{Mn,w}$ is the concentration of Mn at a given depth in the regolith, $C_{Mn,w}$ is the concentration of Mn in the bedrock, $C_{Ti,w}$ is the concentration of Ti at the corresponding depth in the regolith, and $C_{Ti,p}$ is the concentration of Ti in the bedrock. Neutron activation analysis results were used for the concentrations in these calculations. $\tau_{Mn,Ti} > 0$ represents Mn accumulation within the weathering profile whereas $\tau_{Mn,Ti} < 0$ represents Mn depletion, relative to bedrock abundances. **Figure S1.** Conceptualized cross-section of NC Piedmont physiographic region (after Lindsey et al. (2006), Heath (1980), and Heath (1994)), 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. Within the DWR research sites, the regolith was ~7 to 11.6 m thick, and the transition zone went to depths of ~12.9 to 21 m. Our survey indicates that existing wells have been installed in the regolith, transition zone, or bedrock whereas newly installed wells are generally installed into the bedrock with an open borehole.



Figure S2. Locations of the North Carolina Division of Water Resources (DWR) Groundwater Monitoring and Research Stations, with USGS NURE well water Mn concentrations (Smith, 2006) and plotted over North Carolina Piedmont soil systems (SSURGO, 2014). Station notations: AW = Allison Woods; LT = Langtree Peninsula; PM = Passour Mountain; MM = Morgan Mill; DF = Duke Forest; RB = Rocky Branch; LW = Lake Wheeler; NRWWTP = Neuse River Wastewater Treatment Plant; NCZP = North Carolina Zoological Park; UPRS = Upper Piedmont Research Station.



Figure S3. Manganese concentrations from the North Carolina Department of Health and Human Services (DHHS) private well water database, 2008-2011, plotted over NC Piedmont soil systems (SSURGO, 2014).



Figure S4. Manganese concentrations from USGS NURE well-water data (Smith, 2006) distributed within NC Piedmont soil systems (SSURGO, 2014). Black dots represent data points that are considered outliers based on the statistical analysis. The solid line within the box represents the median Mn concentration and the dotted line represents the average Mn concentration. The horizontal red line is 0.05 mg/L, the NC drinking water standard and US Environmental Protection Agency Secondary Maximum Contaminant Level (SMCL). The numbers for each soil system represent the number of wells with Mn > 0.05 mg/L out of the total number of wells sampled for that portion of the Piedmont. The highest maximum, mean, and median Mn concentrations are found in wells from the Carolina Slate Belt, followed by the Triassic Basin and then the Mixed Felsic/Mafic system.



Figure S5. Solid- and aqueous-phase manganese concentration depth profiles from each NC DWR research station. Well-water concentrations are shown with blue points (linked by solid lines) located at the centers of well screens, and well-screen intervals are shown with light gray bars. Solid-phase Mn concentrations represent "environmentally available" Mn concentrations obtained with a strong-acid digestion, EPA Method 3050B (USEPA, 1996); solid-phase Mn concentrations generally peak within the saprolite layer at each location. Average water table depths (blue dotted lines) represent the average depth to groundwater for all wells at a site, measured prior to sampling in summer of 2013. Monitoring wells from a single cluster are shown for every research station except Passour Mountain, in which a shallow, intermediate, and deep well were analyzed from separate well clusters within the research station. No cores were available for the Passour Mountain or Rocky Branch sites, and wells were inaccessible at the Neuse River Wastewater Treatment Plant (NRWWTP).



Figure S6. Solid-phase Mn concentration depth profiles based on fractions generated from sequential extractions (McDaniel and Buol, 1999) of cores from three research stations. Mn oxides are most prevalent in the near-surface and decrease with depth, while residual material, based on strong-acid digestion (USEPA, 1996) comprises the majority of solid-phase Mn in the bedrock.



Figure S7. Manganese X-ray absorption near-edge structure (XANES) spectra and linear combination fits from three NC DWR sites. Data are shown with solid black lines. Linear-combination fits using Mn(IV)-oxide standard, Mn(III)-oxide standard, and respective bedrock XANES spectra are shown with dotted red lines. Mn is found within both Mn(III,IV) oxide and residual Mn(II,III)-bearing bedrock minerals in the chemically and physically weathered soil and saprolite, but only bedrock minerals comprise the Mn phases within the bedrock and physically weathered transition zone. Data from presented and relevant alternate fits are provided in Table S2. Bore-log profiles for each site are provided to the left of each XANES plot.





Figure S8. Manganese XANES standard spectra used in linear combination fitting.



Figure S9. Manganese XANES principal component analysis cumulative variance plot.

					Division of	Water R	esources	5					
Shallow (n=12)					I	Intermediate (n=16)				Deep (n=18)			
Parameters	Avg	Max	Min	Med	Avg	Max	Min	Med	Avg	Max	Min	Med	
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/c㎡)	131.99	422.40	14.60	110.70	186.66	630.00	40.00	117.75	279.93	1106.00	127.00	203.65	
pН	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)	121.32	255.40	-282.70	134.20	111.98	239.70	-116.00	142.50	21.83	159.80	-151.10	45.10	
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	
HCQ⁻(mg/L)	53.07	223.26	2.44	17.69	46.73	192.76	3.66	27.45	102.70	184.22	17.08	135.42	
F (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	
CI (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	
NO3 (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	
PO4 (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	
SO4 (mg SO4/I	.) 7.59	31.00	0.17	1.85	7.75	72.00	0.20	1.75	53.91	750.00	0.43	8.95	
NH4 (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	
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	
As (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 (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 (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 (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 (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	
Mn (ug/L)	204.6	1430.0	10.0	21.0	106.2	423.7	10.0	15.5	196.2	1100.0	10.0	70.0	
Na (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	
P (mg/L)	0.06	0.06	0.05	0.06	0.07	0.07	0.06	0.07	0.06	0.06	0.05	0.06	
S (mg/L)	2.20	9.19	0.05	0.47	2.70	22.80	0.05	0.54	17.02	231.00	0.10	2.78	
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	

Table S1. Chemical groundwater analyses for shallow, intermediate, and deep NC DWR wells.

Table S2. Combinatorial fit data for XANES fits shown in Figures 3 and S7. Data shown are not normalized to 1, and any components shown here that represented <5% of the fit were omitted from the figures. R-factors represent statistical goodness of fit. Alternate fit data for which R-factors are better than those for the fits shown in Figures 3 and S7 are provided, and primary justification for choosing other fits is provided in the notes at the bottom of the table.

Decision District Infection of Europe Infection of Europe Infection of Europe 3.1 0.48 0.55 0.002 4.1 0.82 0.25 0.002 4.7 0.21 0.76 0.000 5.7 0.51 0.48 0.001 7.2 0.78 0.24 0.01 0.001 12.8 1.00 0.01 0.002 0.002 Morgan Mill – alternate fits 4.1° 0.79 0.27 0.002 Lake Wheeler – fits in Figure S7 1.2 0.21 0.78 0.002 Lake Wheeler – fits in Figure S7 1.2 0.21 0.78 0.001 1.3 0.31 0.40 0.26 0.001 14.9 0.81 0.11 0.26 0.001 25.6 0.73 0.97 0.032 0.002 7 0.97 0.05 0.0033 0.001 13.7 0.81 0.19 0.05 <th>Denth (m)</th> <th>Bedrock</th> <th>Birnessite</th> <th>Groutite</th> <th>Rhodochrosite</th> <th>Hausmanite</th> <th>R-factor</th>	Denth (m)	Bedrock	Birnessite	Groutite	Rhodochrosite	Hausmanite	R-factor		
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	0.9 0.1	0.40		0.14	0.40	0.14	0.004		

Primary justification for presenting fit with near-lowest statistical goodness of fit:

^aNear-lowest fit included secondary mineral that matched the rest of the soil/saprolite column ^bNear-lowest fit included secondary mineral that matched the rest of the soil/saprolite column ^cNear-lowest fit included secondary mineral that matched the rest of the soil/saprolite column ^dNear-lowest fit included secondary mineral that matched the rest of the soil/saprolite column ^eNear-lowest fit included secondary mineral that matched the rest of the soil/saprolite column ^fDid not use introduction of a new phase unsupported by the rest of the soil/saprolite column

Supporting Information References

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