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## Cover Page Footnote

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# Spatial Variability of Manganese Oxide in Two Soilscapes: Upland-Lowland, and Riparian Buffer-Wetland Boundary-Wetland

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## Abstract

**Background:** This research project describes the development of a quantitative measurement methodology to determine the concentration of manganese oxide ($MnO_x$) in two soilscape positions (Upland- Lowland and Riparian Buffer-Wetland Boundary-Wetland). **Methods:** A reaction between the $MnO_x$ in the soil sample and hydrogen peroxide ($H_2O_2$) was initiated to determine the level of $MnO_x$ reactivity in the soil sample. Data was collected from four sites on Soilscape 1 (Upland, Lowland, and two sites between the Uplands and Lowlands); within each site, five soil profile depths and three sample replicates were measured which comprised a total of 60 samples. Additionally, data was collected from three sites on Soilscape 2 (Riparian Buffer-Wetland Boundary-Wetland), within each site, three soil profile depths and three sample replicates were measured which comprised a total of 27 samples. Measurements were collected and revalidated to assess the accuracy of the measurement protocol. **Results:** Analysis of data collected from the surface layers in Soilscape 1 indicated that the Lowland (Site 4) had the highest level of $MnO_x$ followed by Site 3 with the lowest value occurring at Site 2. A follow up, revalidation study of three of the four sites from the surface layers on Soilscape 1 indicated that the Lowland (Site 4) had the highest level followed by the Midslope (Site 3) with the lowest value occurring at the Upland (Site 1). Therefore, the revalidation study results matched two of the three sites from the initial study. Correspondingly, the data collected from the three sites from the surface layers on Soilscape 2 indicated that the Wetland Boundary had the highest level followed by Riparian Buffer with the lowest value occurring at Wetland. The revalidation study results matched the initial study for each of the three sites from the surface layers on Soilscape 2, which indicated that the Wetland Boundary had the highest level followed by the Riparian Buffer with the lowest value occurring at the Wetland. **Conclusion:** The results of this study can be used to easily determine the spatial variability of $MnO_x$ levels in soilscapes that range from Upland-Lowland and Riparian Buffer-Wetland Boundary-Wetland, and the movement of soluble $MnO_x$ ions within soilscapes by mass flow and/or diffusion processes. In soils with adequate levels of $MnO_x$ ions, the use of this methodology can assist in the delineation of the wetland boundary, which has both an economic and land-use importance to society, because of the importance of the ecological functions of wetland ecosystems.

**Keywords:** Wetlands, Wetland Boundary, Soilscapes, Manganese Oxide ($MnO_x$), Hydrogen Peroxide ($H_2O_2$)

# Introduction

A wetland is an area that has hydrophytic vegetation, hydric soils, and wetland hydrology, as noted in the National Food Security Act Manual and the 1987 Corps of Engineers wetlands delineation manual (Environmental Laboratory, 1987). Wetlands can be either seasonal or permanently saturated and they represent one of the world's most crucial ecosystems that are threatened by human development activities (Mitsch and Gosselink, 2015). On a national basis, it is estimated that around 53% of wetlands present at the time of European settlement in the early 1600s have since been lost from the conterminous United States (WARPT, 2010). Wetlands provide significant economic, social, and cultural benefits, since they are important for primary products, such as timber and fish, and they support recreational and tourist activities. Also, wetlands help to reduce the impacts from storm damage and flooding, maintain good water quality in rivers, recharge groundwater, store carbon, help to stabilize climatic conditions, and control pests (NSW, 2013). The process of defining the boundary of a wetland ecosystem is defined as wetland delineation that aims to provide a legally defensible line that officially outlines the wetland from the non-wetland area on an examined landscape (Environmental Laboratory, 1987; Tiner, 2017). Hydric soils and wetland hydrology are included in the delineation of a wetland with the criteria for their determination being included in the Field Indicators of Hydric Soils in the United States (United States Department of Agriculture, Natural Resources Conservation Service, 2017).

In general, the most common soil features used to identify hydric soils are based on iron (Fe) which imparts red, yellow, and brown colors to well and moderately well drained soils (Soil Science Division Staff, 2017). When soils are waterlogged for an extended time period, microbial respiration can lead to anaerobic conditions in which iron and manganese (Mn) oxides are reduced to the soluble forms that diffuse from the soil matrix to zones of oxidation. The ions are then oxidized as well as precipitated in the form of redoximorphic features (United States Department of Agriculture, Natural Resources Conservation Service, 2017). The redox (Eh) ladder indicates that Mn oxides are used as an alternate electron acceptor by microbes before using Fe oxides, therefore Mn becomes reduced and subsequently mobile in the soil solution before reduced Fe (ferrous) ions (Sylvia et al., 1999; Coyne, 1999; Gambrell, 1996). However, in the dry down phase when the waterlogged soil has experienced an extended period of reduction, upon return of aerobic conditions, the ferrous Fe ions will oxidize before the manganous Mn ions which migrate along an extended diffusion gradient away from the source pool (wetland or waterlogged zone).

Iron-based soil features have been more readily accepted as part of the methods for delineation of wetlands, but the presence of Mn should be considered as important based on its role in biogeochemical cycling within seasonally and permanently saturated ecosystems that possess hydric soils. Soils that do not reflect typical redoximorphic features that are associated with the typical hydric soil morphological characteristics are called "Problem Soils" (United States Department of Agriculture, Natural Resources Conservation Service, 2017). Soil conditions such as red parent material, low organic carbon levels, and high pH levels are associated with calcareous material or saline conditions; as a result, these soils are difficult to define as hydric soils while also creating an issue when attempting to categorize the landscape as a wetland. Presently, the presence of ferrous iron in the soil is determined by using the photochemical dye, alpha alpha dipyridyl, but the majority of the tests are qualitative based on the positive reaction producing a faint to bright red color with increasing concentrations of reduced iron in the soil sample (United States Department of Agriculture, Natural Resources Conservation Service, 2017). This test can provide a quantitative measure of ferrous iron in solution when measured against a ferrous iron standard with selected concentration levels and a corresponding gradient in color development. A quantitative test of ferrous iron is beneficial when comparing soils from different geologic materials or the soils' potential to supply a concentrated zone of iron oxides that tends to occur in the wetland boundary.

The presence of Mn oxide in a soil sample can be measured qualitatively using the reaction with hydrogen peroxide which produces an exothermic reaction accompanied by fizzing, bubbles, and potentially a smoke plume as hydrogen gas is evolved from the reaction. A quantitative measure of Mn oxide is beneficial as a tool in examining the movement of soluble ions and the precipitation in concentrated zones on seasonally wet and wetland soilscapes that exhibit different hydrodynamic conditions. Herein, a novel method (GOTTP) is described; the authors hypothesize that this method will accurately and consistently measure manganese oxide (MnOx) by measuring the reaction between MnOx and hydrogen peroxide ($H_2O_2$). This project sought to identify patterns of movement and concentration of MnOx in two soil ecosystems.

In theory, Site 4 should have the highest MnOx reactivity level, because the greatest amount of manganese should be precipitated in the landscape position that is farthest from the source point (Site 1) in saturated periods and the flow through zone (Sites 2 and 3) during seasonally wet periods. The Wetland Boundary (WB) should have the highest $MnO_x$ reactivity level, because the greatest amount of manganese should be precipitated in the landscape position that is between the source pool (Wetland, WL) in saturated periods and the flow through zone (Riparian Buffer, RB) during seasonally wet periods. The investigators hypothesized that the level of MnOx reactivity is the greatest at the Lowland sites as compared with the Upland sites; further, the level of MnOx reactivity is higher at the WB sites as compared with the WL sites. The results of this study can be used to increase the pool of scientific knowledge gathered from this new quantitative method that may contribute to determination of hydric soils as part of the wetland delineation process.

# Materials and Methods

## Site Selection

On Soilscape One, four sites were selected which represented Uplands (Sites 1 and 2) and Lowlands (Sites 3 and 4) landscape positions. Soil samples were collected from five depths within each soil profile from the sites. Sample 1 was collected from a depth of 0-2 inches, Sample 2 was collected from a depth of 2-4 inches, Sample 3 was collected from a depth of 4-6 inches, Sample 4 was collected from a depth of 6-8 inches, while Sample 5 was collected from a depth of 8-10 inches. Soil samples were packaged in plastic bags and transported to the laboratory for testing. The second trial was conducted a separate scientist for revalidation, three sites were selected which represented Upland (Site 1), MidSlope (Site 3), and Lowland (Site 4) landscape positions. Soil samples were tested from the same depths as Samples 1-3 of the first trial.

On Soilscape Two, three sites were selected which represented the Wetland (Site 1), Wetland Boundary (Site 2) and Riparian Buffer (Site 3) landscape positions. Soil samples were collected and packaged from 3 depths: 0-2 inches, 5-7 inches, and 10-12 inches. As before, soil samples were packaged and transported to the laboratory for testing. The second trial was conducted by a separate scientist but following the same protocol.

## Method

The method used to measure $MnO_x$ in the study is novel, so the authors have taken the liberty to use the initials of their last names to label the method GOTTP, in reference to Griffin, Onweni, Thomas, Timms, and Polk.

GOTTP Protocol for Determining Soil $MnO_x$ Levels

1) Assemble a standard metal lab stand with a vertical post for attachment of a vertical clamp used to hold the digital timer.

2) Weigh approximately 2 grams of soil sample in an aluminum weighing boat using an electronic balance.

3) Place the weighed soil in a 15 mL graduated conical centrifuge tube with 0.5mL serial measurement indices. The soil should occupy approximately 2 mL volume within the tube.

4) Record initial level of the solution in the Centrifuge Tube (Time 0:00), then immediately start the timer

5) Using a syringe, add 2 mL of 3% hydrogen peroxide to the soil sample in the centrifuge tube.

6) Record level of the solution after each 15-second interval for the complete duration of the monitoring cycle (total of 7 minutes).

7) Repeat method for each additional sample

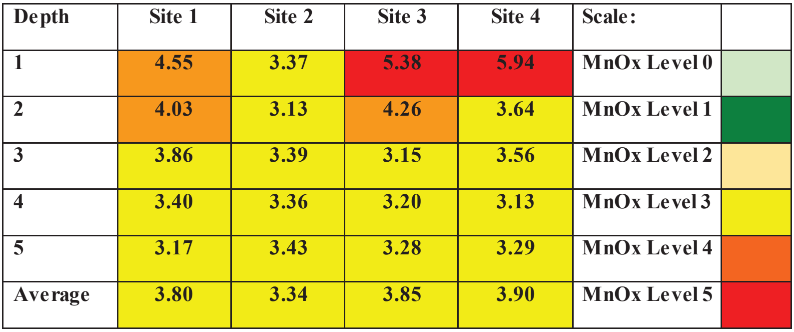
## Experimental Design and Data Analysis

On Soilscape One on the first trial, 3 replicate soil samples were tested from each of the 4 sites and 5 depths that represented a grand total of 60 samples. Tests were conducted on samples and the results from the data that was gathered were used to compare the sites using descriptive and inferential statistical analyses. The statistical analyses were used to determine the level of $MnO_x$ reactivity that should theoretically be greatest at the Lowland sites as compared with the Upland sites. For the second trial, 3 replicate soil samples were tested from 3 sites and 3 depths that represented a grand total of 27 samples. A smaller number of samples were measured due to elimination of one of the intermediate sites.

## Results and Discussion

Results gathered from the Soilscape One, indicated that Site 4 had a grand average $MnO_x$ reactivity level of 3.90cc that was the highest compared to the other sites (Table 1). These results corresponded with the hypothesis that Site 4 should have the highest $MnO_x$ reactivity level. Using a geographic site location analysis, the data indicated that the highest $MnO_x$ level, 5.94cc, occurred at the surface of Site 4 (4.1), which illustrated that the diffusion of manganese proceeded from the source point (Site 1) to the Site 4 at which point manganese ions precipitated within the soil matrix. Site 3 indicated an elevated $MnO_x$ level (5.38cc) at the surface (3.1), which corresponded with this site location serving as a flow through and discharge zone for soluble Mn ions during alternating wet-dry conditions. Site 1 had elevated levels (4.55cc and 4.03cc) in the surface (1.1 and 1.2) due to the naturally occurring $MnO_x$ nodules that migrate to the surface of the sandy soil during the natural weathering and erosion processes on this landscape. Site 2 is clearly the flow through zone based on the lower $MnO_x$ levels (3.13-3.43cc) that were recorded in the surface (Depth 1) and lower surface (Depth 2) sampling zones. This site provided a clear indication of the dynamic nature of the $MnO_x$ in these soils that receive an average of 44 inches of rainfall per year which promotes ample opportunity for redox processes to drive the dissolution (depletion) and precipitation (concentration) of mineral oxides.

**Table 1** Comparison of average manganese oxide reactivity levels (cc) on Soilscape One at Sites 1, 2, 3, and 4 are presented by depth and averaged by site. The color of the cell indicates the level of MnOx.



| Depth | Site 1 | Site 2 | Site 3 | Site 4 | Scale: | |
|---|---|---|---|---|---|---|
| 1 | 4.55 | 3.37 | 5.38 | 5.94 | MnOx Level 0 | 🟩 |
| 2 | 4.03 | 3.13 | 4.26 | 3.64 | MnOx Level 1 | 🟩 |
| 3 | 3.86 | 3.39 | 3.15 | 3.56 | MnOx Level 2 | 🟨 |
| 4 | 3.40 | 3.36 | 3.20 | 3.13 | MnOx Level 3 | 🟨 |
| 5 | 3.17 | 3.43 | 3.28 | 3.29 | MnOx Level 4 | 🟧 |
| Average | 3.80 | 3.34 | 3.85 | 3.90 | MnOx Level 5 | 🟥 |

Results gathered from the second iteration of experiments on Soilscape One indicated that Lowland (Site 4) had a grand average $MnO_x$ reactivity level of 5.01cc that was the highest compared to the other sites (Table 2). These results matched, with a variance of 0.61, the initial project work which indicated that the testing procedure can produce repeatable results that may not produce the same numerical data, but the trends as related to the null and research hypotheses remained intact.

**Table 2** Comparison of average manganese oxide reactivity levels on Soilscape One at Upland (Site 1), MidSlope (Site 3), and Lowland (Site 4) are presented by depth and averaged by site. The color of the cell indicates the level of MnOx.

| Depth | Upland (Site 1) | MidSlope (Site 3) | Lowland (Site 4) |
|---|---|---|---|
| 1 | 4.43 | 4.81 | 6.25 |
| 2 | 4.04 | 3.90 | 4.09 |
| 3 | 5.01 | 3.00 | 4.68 |
| Average | 4.49 | 3.90 | 5.01 |

| Scale: | |
|---|---|
| MnOx Level 3 | 🟨 |
| MnOx Level 4 | 🟧 |
| MnOx Level 5 | 🟥 |
| MnOx Level 6 | 🟪 |

The geographic site location analysis data indicated that the highest $MnO_x$ level occurred at the surface of the Lowland (Site 4), MidSlope (Site 3) data indicated an elevated $MnO_x$ level at the surface, and the lowest values occurred at (Upland) Site 1. The Lowland (Site 4) surface had a level of 6.25cc, which was the highest level recorded during this monitoring cycle, also the value was higher than the initial testing value of 5.94cc.

Results gathered from the Soilscape Two indicated that the WB had a grand average $MnO_x$ reactivity level of 3.87cc which was higher than the RB level of 3.64cc and the WL level of 3.07cc (Table 3). These results corresponded with the hypothesis that WB should have the highest $MnO_x$ reactivity level. Using a geographic site location analysis, the data indicated that the highest $MnO_x$ level occurred at the surface of WB with a value of 5.26cc, which illustrated that the diffusion of manganese proceeded from the source pool to the WB at which point manganese ions precipitated within the soil matrix. The WL levels were the lowest during the monitoring cycle which corresponded with lower redox conditions that lead to diffusion of the soluble Mn ions, therefore the WL served as a zone of loss of Mn ions (source pool) with subsequent gain or concentration of Mn ions in the WB and even in the RB during the wettest climatic periods.

**Table 3** Comparison of average manganese oxide reactivity levels on Soilscape Two at Riparian Buffer (RB), Wetland Boundary (WB), and Wetland (WL) by depth averaged by site. Two trials are compared: Initial measurements are listed with 1 and follow-up is listed as 2.

| Depth | RB 1 | RB 2 | WB 1 | WB 2 | WL 1 | WL 2 | Range 1 | Range 2 | Scale: |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.45 | 3.59 | 5.26 | 5.06 | 3.00 | 3.07 | 2.26 | 2.00 | MnOx Level 0 |
| 2 | 3.95 | 4.04 | 3.29 | 3.39 | 3.11 | 3.34 | 0.84 | 0.70 | MnOx Level 1 |
| 3 | 3.53 | 3.35 | 3.05 | 3.41 | 3.10 | 3.38 | 0.47 | 0.05 | MnOX Level 2 |
| Avgerage | 3.64 | 3.66 | 3.87 | 3.95 | 3.07 | 3.26 | 0.80 | 0.69 | MnOX Level 3 |
| | | | | | | | | | MnOX Level 4 |
| | | | | | | | | | MnOX Level 5 |

Results gathered from the Soilscape Two follow-up research project work indicated that the WB had a grand average $MnO_x$ reactivity level of 3.95cc which was higher than the RB level of 3.66cc and the WL level of 3.26cc (Table 3). The results matched the initial project work which provided another indication that the testing procedure can produce repeatable results. The geographic site location analysis data indicated that the highest $MnO_x$ level occurred at the surface of WB with a value of 5.06cc, which was similar to 5.26cc from the initial testing period. Also, the WL levels were the lowest during the monitoring cycle which matched the initial results. The RB Depth 2 value was 4.04cc, which was the second highest reactivity level recorded across the three sites that corresponded with the diffusion of Mn oxides from the wetland boundary into the subsurface of the RB during the wettest period when the Mn ions were mobile in the soil water solution with subsequent precipitation upon intercepting oxidized conditions.

## Conclusions

In conclusion, the most important points gathered from this research include the following. 1) The project results from Soilscape One corresponded with the research hypothesis. The Lowland (Site 4) should have the highest MnOx reactivity level, due to concentration of ions in this zone that either moved by mass flow or diffusion from the Upland (Site 1) or by through flow in the Upland (Site 2) and MidSlope (Site 3) soils. 2) The project results from Soilscape Two corresponded with the research hypothesis that the WB site should have the highest MnOx reactivity level, due to concentration of ions in this zone that diffused from the WL site. 3) The GOTTP method used in this research project, based upon the reaction between MnOx and $H_2O_2$, serves as a new, quantitative method of wetland delineation and determination of Mn ions present in various soilscape positions. 4) the GOTTP method, when compared to soils with no manganese and elevated manganese levels, can be used to produce repeatable results that can support scientific investigations of soluble Mn ions and precipitated Mn

Oxides produced during fluctuating hydrodynamic conditions in wetlands, hydric, and seasonally wet soils.

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## References

Coyne, M.S. ((1999). Soil microbiology: an exploratory approach. (Delmar Publishers, Albany, N.Y.

Environmental Laboratory. (1987). Corps of Engineers wetlands delineation manual. United States Army Corps of Engineers. Waterways Experiment Station Technical Report Y-87-1.

Gambrell, R.P. 1996. Manganese, Chapter 24. In Methods of Soil Analysis, Part 3.

Chemical Methods – SSSA Book Series no. 5. (Soil Science Society of America and American Society of Agronomy, Madison, WI.

Mitsch, W.J. and Gosselink, J.G. (2015). Wetlands. Fifth Edition. John Wiley & Sons.

NSW. (2013). New South Wales, Australia. Office of Environment & Heritage. Retrieved from http://www.environment.nsw.gov.au/wetlands/WhyAreWetlandsImportant.htm

Soil Science Division Staff. (2017). Soil survey manual. Ditzler, C., Scheffe, K., and Monger,

H.C. (eds.). USDA Handbook 18. (Government Printing Office, Washington, D.C.

Sylvia, D.M., Fuhrmann, J.F., Hartel, P.G., and Zuberer, D.A. (1999). Principles and applications of soil microbiology. 2nd Edition. (Pearson Education, Inc., Upper Saddle River, N.J., 2005).

Tiner, R.W. (2017). Wetland Indicators: A Guide to Wetland Formation, Identification, Delineation, Classification, and Mapping, Second Edition. CRC Press. Taylor & Francis Group.

United States Department of Agriculture, Natural Resources Conservation Service. (2017).

Field Indicators of Hydric Soils in the United States, Version 8.1. Vasilas, L.M., Hurt, G.W. and Berkowitz, J.F. (eds.). USDA, NRCS, in cooperation with the National Technical Committee for Hydric Soils. Retrieved from http://www.nrcs.usda.gov/wps/portal/nrcs/main/soils/use/hydric.

WARPT. (2010). Wetland-At-Risk Protection Tool. Retrieved from http://www.wetlandprotection.org/estimate-wetland-loss.html (2010).