The Distribution and "Problematic" Nature of F21 (Red Parent Material) Hydric Soils

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ABSTRACT

It has long been recognized that soils derived from certain red parent materials (RPM) fail to develop hydric features typical of wetlands, creating problematic situations for wetland delineators. To address this issue, the National Technical Committee for Hydric Soils approved Field Indicator F21 (Red Parent Material) to identify these areas. For red soils to qualify as problematic, they must have Color Change Propensity Index (CCPI) values below 30. Based on CCPI analyses of more than a thousand soil samples collected from around the country, a national draft map has been compiled identifying areas that are likely to contain soils derived from problematic RPM. Although progress has been made in recognizing the geographical extent of these problem soils (occurring in association with sedimentary, hematite-rich "red bed" deposits, and the alluvial and glacial materials derived from them), the cause of their "problematic" nature remains uncertain. In this study, three mineralogical and pedological hypotheses, that are mostly related to the hematitic mineralogy of the associated iron oxides, have been identified as possible causes of the "problematic" nature of these soils. Several methods have been employed to evaluate these hypotheses, including XRD work to examine Al-substitution in hematite and hematite crystallite size in RPM versus non-problematic RPM soils. Preliminary results from these investigations are presented.

PROJECT BACKGROUND

- Soils derived from certain Red Parent Materials (RPM) are difficult to identify as hydric in the field (i.e. "problematic") during the delineation of wetlands required by CWA regulations (USACE, 2012) (**Figure 1**).
- The NTCHS has addressed these situations with the adoption of the F21 Red Parent Material Field Indicator in all Major Land Resource Areas (USDA-NRCS, 2010), and requires soils to qualify as "problematic" with a Color Change Propensity Index (CCPI) less than 30 (USDA-NRCS, 2010; Rabenhorst & Parikh, 2000).
- Based on CCPI analyzes of more than 1000 soil samples from around the country, problematic RPM soils and their derivative lithologies have been observed to occur as/in association with sedimentary, hematite-rich, "red bed" deposits.
- Current literature suggests that the cause of problematic RPM soils might be related to mineralogical characteristics inherited from their parent materials (Elless & Rabenhorst, 1994), but the actual cause of their "problematic" nature remains uncertain.

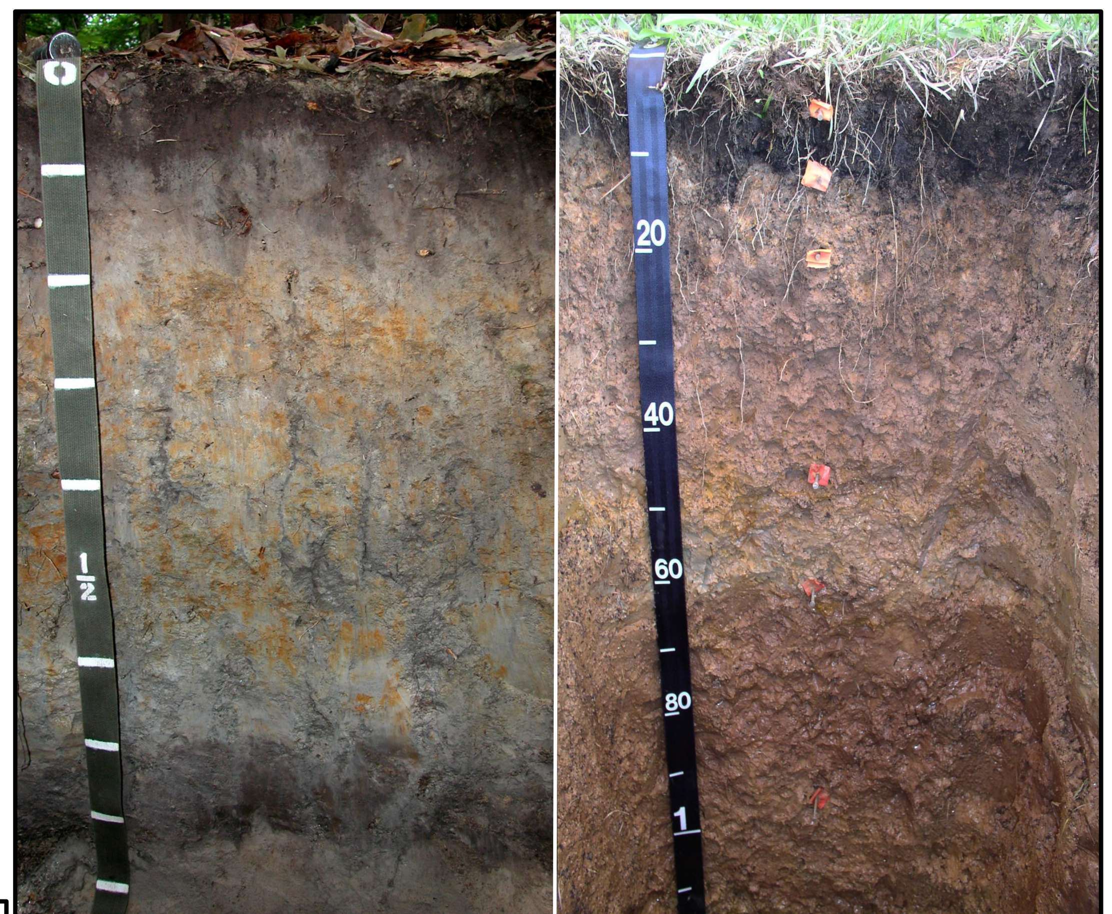

Figure 1. Hydric soils derived from problematic red parent materials (right) demonstrate far weaker expression of redoximorphic features than typical hydric soils (left).

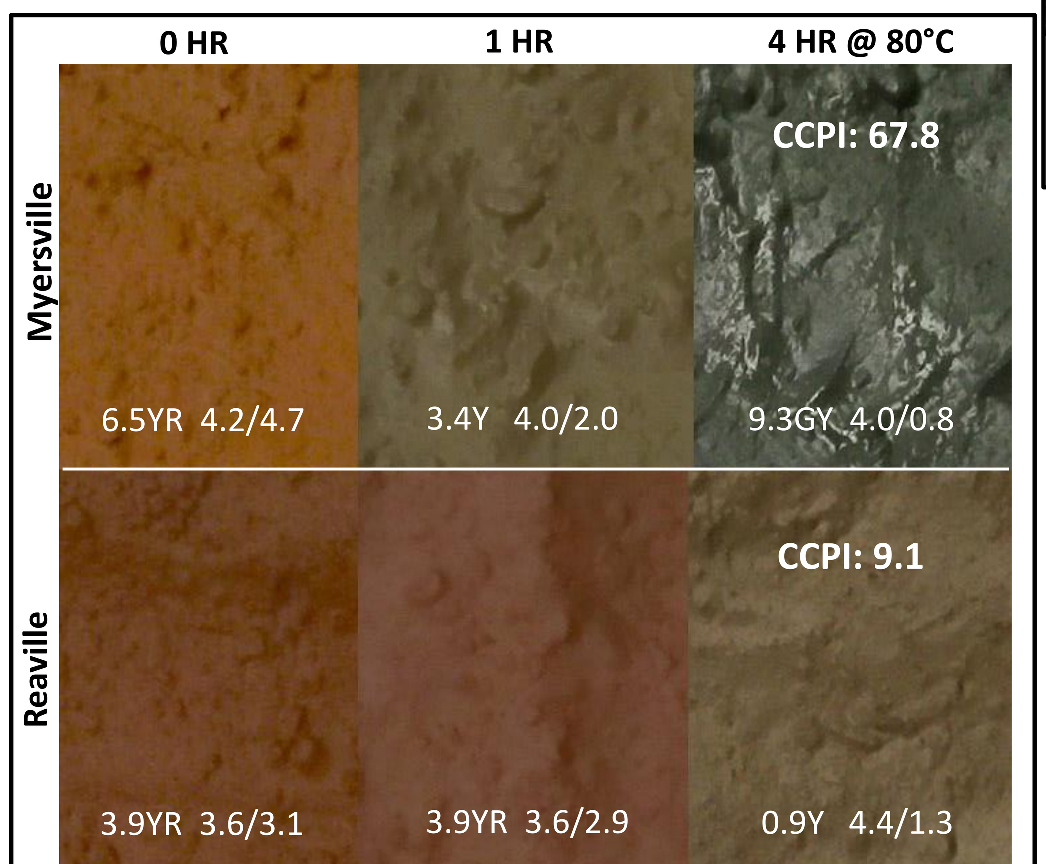

Figure 2. CCPI results of Bt samples from the Myersville (top) and Reaville (bottom) series. For CCPI, soils are incubated under various conditions and then their color is measured, after: 1) immediately following saturation with no sodium dithionite (reducing agent) at 25°C; 2) with sodium dithionite after 1 hour @ 25°C; and 3) with sodium dithionite after 4 hours @ 80°C. Colors measured are used to calculate a CCPI value indicative of the resistance of soils to form redoximorphic features. Reaville soils are more resistant to color change than Myersville soils and qualify as "problematic."

THE MAPPING AND DISTRIBUTION OF F21 RPM

- Soil samples of potentially problematic RPM soils were solicited from gov't agencies (USDA-NRCS, USACE), the Kellogg Soil Survey Laboratory (KSSL), and private sector soil scientists. Contact was made via a project letter sent to offices of the USDA MLRA and USACE wetland regions.
- A brief soil description (horizons, depths, colors, redox), GPS coordinates, a best assessment of soil series sampled, and geological information (age, formation name, etc.) were requested to accompany soil samples.
- Soils were identified as problematic based on the Color Change Propensity Index (CCPI) (Rabenhorst & Parikh, 2000). Color was determined using a Konica Minolta digital colorimeter, measured three times per sample. Munsell hue, value, and chroma were recorded to the nearest 0.1 unit. Soils were grouped into classes of "problematic" if CCPI < 30, "non-problematic" if CCPI > 40, and "questionable" if CCPI is between 30 and 40 (**Figure 2**).
- Problematic RPM series were investigated to identify all associated series within the same lithology using reports from project participants, OSDs, soil series extent maps, and NRCS block diagrams.
- Series formed from problematic RPM were tied to digital soil (gSTATSGO) and geological (USGS geology) units to produce a national guidance map showing where problematic RPM soils might occur and the application of field indicator F21 might be appropriate (**Figure 3**).

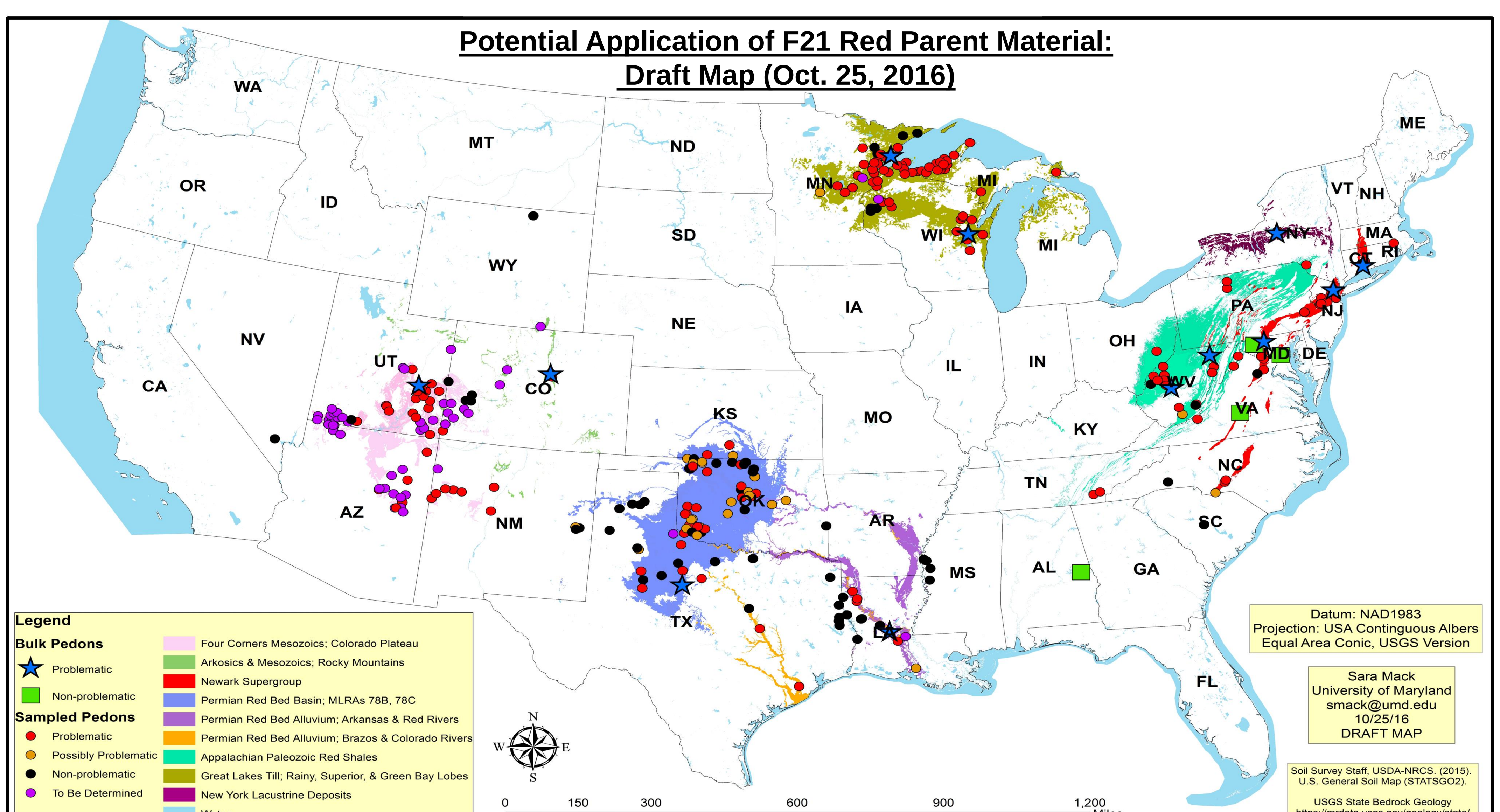

Figure 3. Map of areas where problematic RPM soils and geologies are recognized (thus application of the F21 RPM indicator is appropriate), based on CCPI analyses of soil samples submitted for the RPM project. Approximately 10 "groups" of soils and their associated geologies have been identified as problematic RPM, all in association with sedimentary, hematite-rich "red bed" deposits, or the alluvial, colluvial, and/or glacial materials derived from them. No problematic RPM has been identified in HI, AK, or Puerto Rico. Star and square points on the map are locations where bulk samples were collected to explore the cause of problematic RPM.

WHAT CAUSES THE "PROBLEMATIC" NATURE OF F21 RPM SOILS? -- THREE WORKING HYPOTHESES

1. The physical occlusion of iron oxides within rock fragments preserved across a range of particle size fractions (sand, silt, clay) within RPM soils, that would not be present in soils derived from other lithologies.

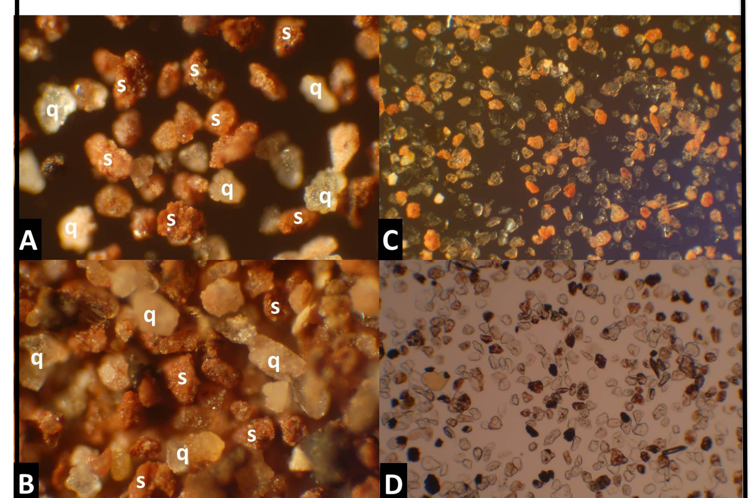

Figure 4. Photomicrographs of VFS (A & B) and CoSi (C & D) fractions from the Bt horizon of the Reaville soil (CCPI = 10). Note that in addition to individual mineral grains (mostly quartz - q), there are also many red shale(s) fragments present, which essentially are microaggregates of lithified material. A, B and C were taken with incident light, while D was taken with plane polarized transmitted light. C and D are the same field of view. Frame length for A and B is 800 µm; frame length for C and D is 300 µm.

2. The substitution of Al for Fe in the crystalline structure of hematite within RPM soils versus non-RPM soils. It has been shown that in the case of goethite, increased Al-substitution decreases reductive dissolution of the mineral.

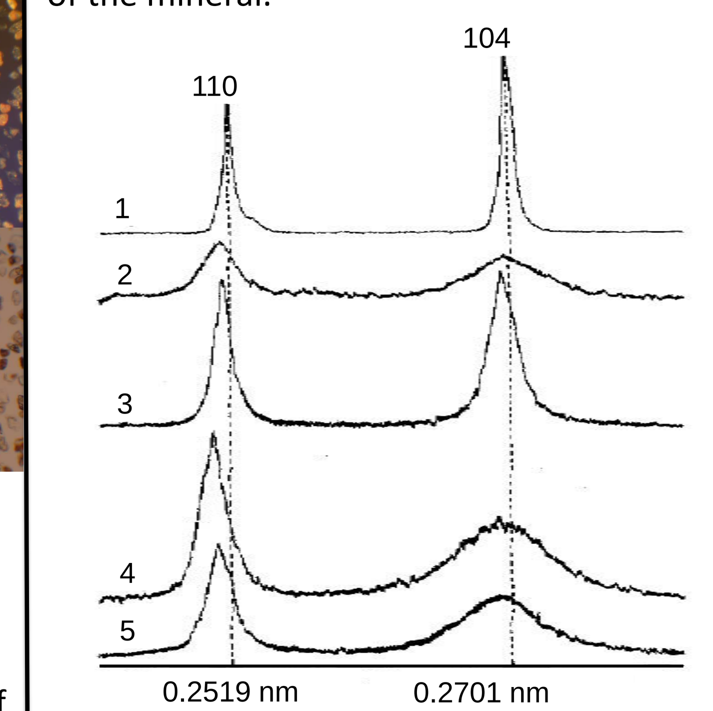

Figure 5. X-ray diffractograms of hematite synthesized with increasing amounts of Al (from 1 to 5). Peak shifts in (104) and (110) d-spacings indicate increasing Al-substitution within hematite (Schwertmann et al., 1977).

3. Larger crystal sizes of hematite within RPM soils versus non-RPM soils. Large crystal sizes of hematite (evidenced by the dark red colors of the soils and parent materials that qualify as problematic RPM) may result in a lower reactive surface area for chemical reduction reactions.

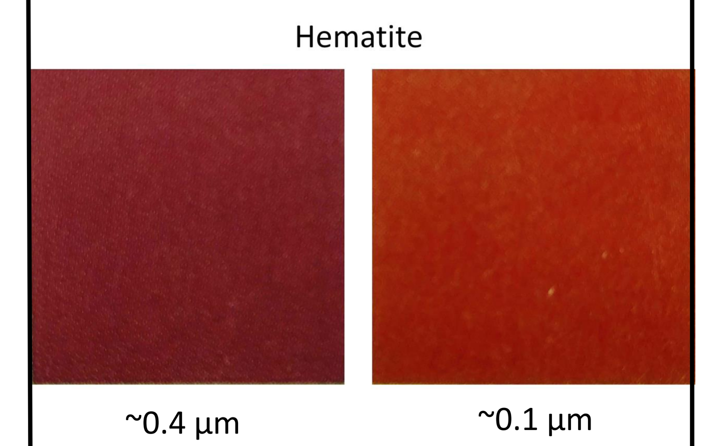

Figure 6. Hematite with larger crystals has darker and more purplish colors than smaller crystals that are a brighter red (figure from Schwertmann, 1993). Colors of larger hematite crystals correspond to the current color requirements of the F21 RPM Indicator (7.5YR or redder, value and chroma ≤ 4) (USDA-NRCS, 2010).

IDENTIFYING THE CAUSE OF THE "PROBLEMATIC" RPM: METHODOLOGY

Hypothesis 1:

- Selected samples will be fractionated into various particle size fractions (sands, silts, clays) (Kittrick & Hope, 1973).
- Individual fractions will be analyzed for their CCPI (Rabenhorst & Parikh, 2000). Evidence for physical occlusion will be assessed by whether different fractions exhibit dramatic differences and/or similarities in CCPI.
- Fractions may also be observed in thin section and/or under a (petrographic) microscope pre- and post-CCPI analyses for evidence of physical occlusion.

Hypotheses 2 & 3:

- Total Fe oxide content of soils will be determined via a dithionite-citrate-bicarbonate extraction (Mehra & Jackson, 1960; Fanning et al., 1970).
- Mineralogy of clay fractions of samples will be characterized using X-Ray Diffraction (XRD). Clay fractions will be boiled for 1 hour with 5 M NaOH to dissolve some silicates and concentrate Fe fractions (Kampft & Schwertmann, 1982). Fe oxides in clays may be further concentrated using High-Gradient Magnetic Separation (Schulze & Dixon, 1979).
- Al-substitution in hematite will be determined by observing shifts in (104) and (110) peaks (Schwertmann et al., 1977; Figure 5) (Hypothesis 2).
- Mean crystallite size of hematite at (104) and (110) peaks will be calculated using the Scherrer equation (Klug & Alexander, 1974) (Hypothesis 3).

PRELIMINARY RESULTS

Particle Size Fraction(s)	CCPI
Bulk Clay (< 2 um)	9.3
Fine Silt	9.6
Medium Silt	10.5
Coarse Silt	8.4
VF + F Sands	5.9
Medium Sand	8.4
VC + C Sands	13.2

Table 1. CCPI measurements of Reaville particle size fractions to evaluate for possible physical occlusion. Clay fractions (existing mainly as individual particles) have similar CCPI values as larger size fractions (that contain lithified microaggregates). This indicates that resistance to color change may not be related to physical occlusion of Fe oxide within aggregate grains.

Scherrer Equation
(for calculating crystallite size - L)

$$L = K\lambda/\beta\cos\theta$$

λ = 0.15418 nm (CuKα)

β = FWHM

θ = 33.3 degrees [Hematite (104)]

K = constant (0.9)

For Reaville: Hematite (104), L = 69 nm

Figure 8. Problematic Reaville Clay (< 2 µm) Diffractograms

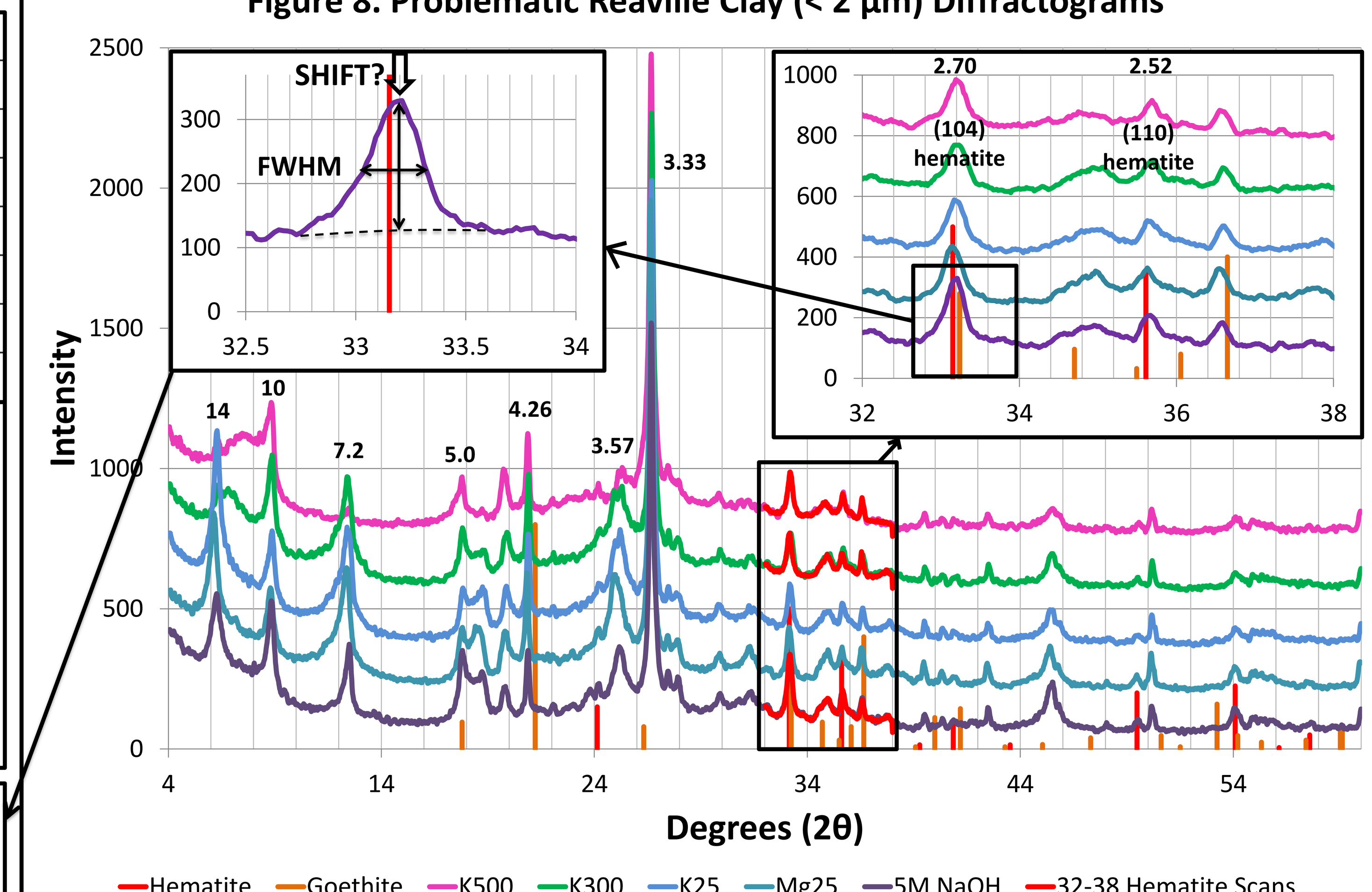

Figure 8. Diffractograms characterizing the mineralogy of the problematic Reaville clay (< 2 µm) fraction. 32-38 degree insets highlight characteristic peaks of hematite. Full Width at Half Maximum (FWHM) will be determined for hematite peaks using the Scherrer equation to estimate mean crystallite size of hematite crystals to compare among problematic and non-problematic RPM soils.

CONCLUSIONS

- Problematic RPM (i.e. F21 applicable) soils occur in association with sedimentary, "red bed" deposits, with hematite as the predominant iron oxide mineral.
- Preliminary CCPI values of particle size fractions for the Reaville series suggest physical occlusion is not the cause of the "problematic" nature of RPM, and instead is likely related to characteristics of the hematite mineral inherited from the soil parent materials.

FUTURE WORK

- Continued CCPI analysis of remaining soil samples to refine RPM mapping and the updating of F21 national draft maps.
- Send MLRA and USACE regional-specific maps of problematic RPM to field offices for final comment.
- Quantification of total Fe oxide content in samples (DCB extraction).
- CCPI analyses of various particle size fractions for other RPM samples.
- Examination of fractions pre- and post-CCPI analyses.
- Calculations and comparisons of mean crystallite size in hematite.
- Calculations and comparisons of Al-substitution in hematite.

REFERENCES

Elless, M. P., & Rabenhorst, M. C. (1994). Hematite in the Shales of the Triassic Culpeper Basin of Maryland. *Soil Science*, *158*(2), 150-154.

Rabenhorst, M. C. & Parikh, S. (2000). Propensity of Soils to Develop Redoximorphic Color Changes. *Soil Science Society of America Journal*, 64, 1904-1910.

NRCS Soil Survey Staff. General Soil Map (gSTATSGO) Database for the Conterminous United States. United States Department of Agriculture, Natural Resources Conservation Service. Available online at https://gdg.sc.egov.usda.gov/. December 1, 2014 (FY2015 official release).

United States Army Corps of Engineers. (2012). *Regional Supplement to the Corps of Engineers Wetland Delineation Manual: Northcentral and Northeast Region* (Version 2.0, ERDC/EL TR-12-1). J. S. Wakeley, R. W. Lichvar, C. V. Noble& J. F. Berkowitz (Eds.). Vicksburg, MS: U.S. Army Engineer Research and Devel. Center.

United States Department of Agriculture, Natural Resources Conservation Service. (2010). *Field Indicators of Hydric Soils in the United States: A Guide for Identifying and Delineating Hydric Soils* (Version 7.0). L. M. Vasilas, G. W. Hurt & C. V. Noble (Eds.). USDA-NRCS, in cooperation with the National Technical Committee for Hydric Soils.

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