

EVALUATION OF MEHLICH-3 FOR THE DETERMINATION OF CATION EXCHANGE CAPACITY IN KANSAS SOILS

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ABSTRACT

Soil testing laboratories across the United States have implemented the Mehlich-3 (M3) extraction method for phosphorus (P) and other nutrients. Though M3 is known to work well as a multinutrient extractant, it raises concerns for measuring exchangeable cations, particularly in calcareous soils. The objectives of this study were (a) to evaluate M3 as an extractant for base cations for Kansas soils, (b) to identify a range of soil pH where M3 may be a suitable replacement for ammonium acetate (AA), and (c) to examine the relationship between cation exchange capacity (CEC) summation and CEC displacement. A study was conducted evaluating 308 soils collected from across Kansas and extracted using both the M3 and AA soil extraction methods. Cation exchange capacity was estimated using the summation approach from measurements of both the M3 and AA, and the displacement method. Results indicate a strong correlation among M3 and AA methods for K, Mg, and Na ($R^2 = .98, .96, .97$, respectively). However, these relationships were considerably weaker for extractable Ca ($R^2 = .78$), where extractable Ca was higher in the M3 extracts for high pH soils. Estimated CEC was also affected by soil pH for the M3 method, with an estimated critical pH value of 7.3. Extractable Ca and CEC for soils with a pH below 7.3 showed a strong correlation between M3 and AA methods ($R^2 = .9$). Using M3 as a multinutrient extractant can improve turnaround time for sample analysis in soil testing laboratories. However, the use of the M3 procedure in soils with a pH of 7.3 or above will likely result in overestimation of exchangeable Ca and CEC.

INTRODUCTION

The Mehlich-3 (M3) soil test procedure allows for the simultaneous measurement of numerous essential plant nutrients in soils, including phosphorus (P), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), manganese (Mn), zinc (Zn), and copper (Cu) (Mehlich, 1984). This has lent to the wide adoption of the M3 procedure by soil testing labs across the United States. Using a single extraction for multiple nutrients helps streamline the daily workflow, reduce labor and operating costs in the laboratory, and improve turnaround times for routine soil fertility analyses. These multinutrient extractions also allow laboratories to take full advantage of modern laboratory equipment's ability to measure multiple elements simultaneously, such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In Kansas, the M3 procedure is currently used to assess plant-available P and K, but exchangeable base cations and CEC estimates are determined using a neutral ammonium acetate (AA)

extracting solution. This AA procedure is well established for the extraction of exchangeable base cations in soils (Ciesielski et al., 1997; Normandin et al., 1998; Sumner & Miller, 2018) and is a recommended procedure for the North Central Region (Nathan & Gelderman, 2015).

Given its potential cost savings, the M3 procedure is an attractive option for soil testing laboratories. However, data relating M3 extractable base cations to the standard procedures are nonexistent for Kansas soils. This study aimed to (a) investigate the relationship between M3 and AA extractable base cations and CEC in Kansas agricultural soils; (b) identify a soil pH range at which these two methods can be used interchangeably; and (c) examine the relationship between CEC summation and CEC by displacement (not shown, see Rutter et al., 2022).

MATERIALS AND METHODS

Soil samples were randomly selected to represent a range of soils and geographic regions across Kansas, USA. A total of 308 samples were included in this study and selected from field-production soil samples collected from the 0-to-15 cm depth and submitted to the Kansas State University Soil Testing Laboratory from July through December 2019. Samples were dried at 40 °C and ground to pass a 2-mm sieve using a flail-type soil grinder. Dried and ground samples were stored at room temperature until analysis (Gelderman & Mallarino, 2012). All extraction procedures used in this study are described in the Recommended Soil Testing Procedures for the North Central Region handbook (Nathan & Gelderman, 2015).

Relationships between the various soil test parameters were investigated using linear and nonlinear least-squares regression analysis. All statistical analyses were performed using R version 4.05 (R Core Team, 2021) and visualized using the 'ggplot2' graphics package (Wickham, 2016) in RStudio (RStudio Team, 2021). Nonlinear regression models were fit using self-starting functions from the 'nlraa' package (Miguez, 2021). The significance of all statistical tests and comparisons were evaluated at the 95% confidence level ($\alpha = .05$). For a more detailed description of the laboratory and statistical methods used in this study please refer to the accompanying paper by Rutter et al. (2022).

RESULTS AND DISCUSSION

Soil pH ranged from approximately 4.4 to 8.2 with a median of 6.67, but followed a bimodal distribution with distinct modes at approximately 6.0 and 7.5 pH. Soil OM contents ranged from approximately 8 to 96 g kg⁻¹ with a median of 30 g kg⁻¹. Soil CEC ranged from approximately 9 to 39 meq 100 g⁻¹ with a median value of 19.7 meq 100g⁻¹. The range and distributions of these parameters (Figure 1) illustrate the need for laboratories to use adequate methods and consider the wide range of soils they may receive from this region.

Potassium, Magnesium, and Sodium

Extractable Ca, K, Mg, and Na were compared between M3 and AA procedures. Mehlich-3 and AA extractable K, Mg, and Na were highly correlated with near 1:1 relationship with slope coefficients of 0.99, 1.02, and 1.01 for K, Mg, and Na, respectively (Figure 1). High R^2 coefficients (Figure 1) suggest that M3 and AA extracted these cations from similar soil pools across a wide range of soil pH and SOM contents. Ammonium acetate extractable base cations are commonly interpreted as representing the "exchangeable" pool, and these results suggest that a similar interpretation for M3-K, -Mg, and -Na is appropriate in Kansas soils.

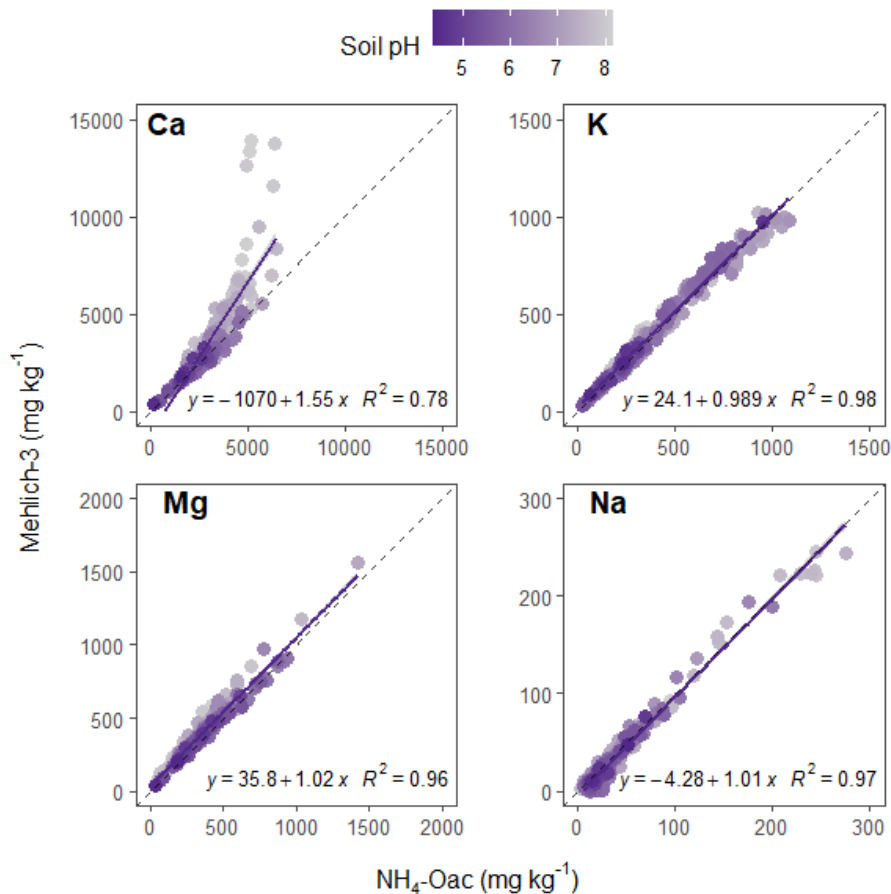


Figure 1. Relationship between Mehlich-3 and Ammonium Acetate extractable calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na). Soil pH is indicated by the color of the dots, where lighter shades denote higher pH values. The dashed line indicates the 1:1 ratio. The fit of a linear regression model is indicated by the solid line and equations in each panel.

However, M3 extracted substantially more Ca than AA in some soils, and the slope (1.55) and R^2 (0.78) of the linear model fit to the Ca data indicate a relatively poor fit between M3 and AA when compared to K, Mg, and Na (Figure 1). Soil samples with

high pH generally resulted in higher M3 extractable Ca (Figure 1). The difference between M3-Ca and AA-Ca was further examined as a function of soil pH using nonlinear regression and an exponential plateau model (Figure 2A). This analysis identified a critical soil pH of 7.33; where M3 extracted exponentially more Ca than AA as soil pH increased beyond this critical pH value. Excluding samples with a soil pH greater than 7.33 resulted in a near 1:1 relationship (slope = 1.047) and substantially improved relationship ($R^2 = 0.9$) between M3- and AA-Ca (Figure 2B).

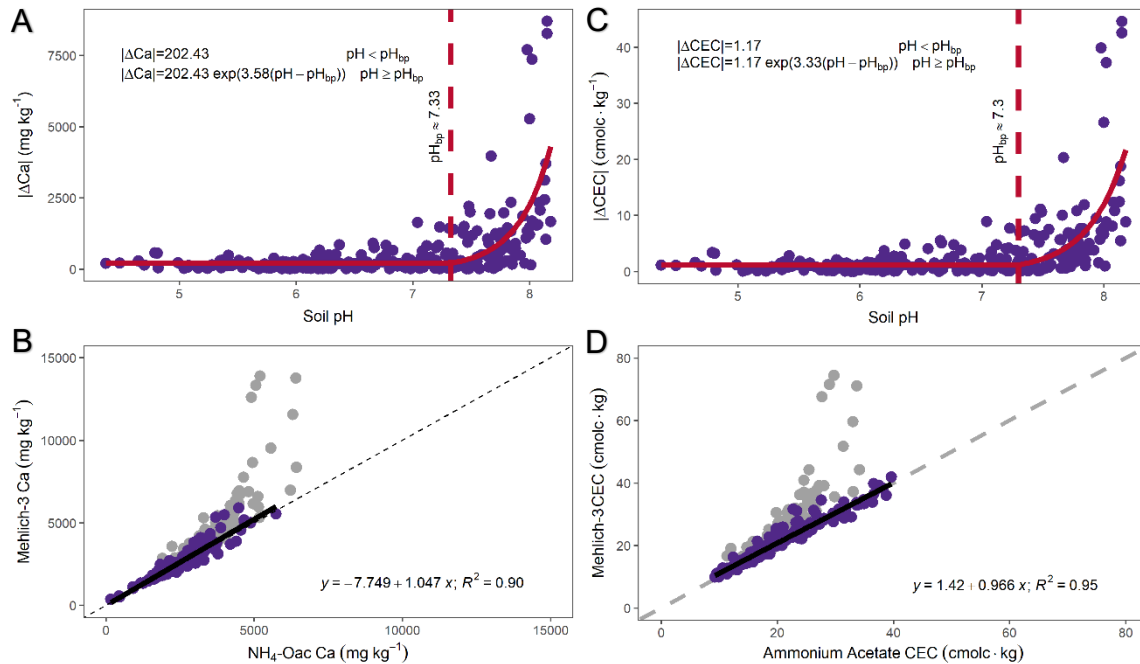


Figure 2. (A) The difference between Mehlich-3 (M3) and ammonium acetate (AA) extractable calcium (ΔCa) as a function of soil pH. The nonlinear model fit is indicated by the solid line. The soil pH breakpoint value is indicated by the dashed vertical line. (B) The relationship between M3 and AA extractable calcium (Ca). (C) The difference in CEC by summation determined from Mehlich-3 and ammonium acetate (ΔCEC) as a function of soil pH. (D) The relationship between CEC determined from Mehlich-3 and ammonium acetate. In panels B and D, the dark points indicate soils with a pH below the critical value, while the grey points indicate soils with a pH above the critical value. The linear models are indicated by solid lines, where samples with $\text{pH} \geq 7.3$ were excluded (grey points).

This relationship and effect of soil pH on M3 and AA extractable Ca has been documented in previous studies, and is primarily attributed to the presence of calcium carbonates and their dissolution during the extraction process (Michaelson et al., 1987; Ketterings et al., 2014; Rogers, 2019). Soil carbonate measurements were performed on a subset of samples, and regressed against the difference between M3- and AA-Ca and -CEC. A strong linear relationship was observed ($R^2 = 0.93$), suggesting the

increased Ca extracted by M3 is due to dissolution of calcite-like minerals (data not shown, see Rutter et al., 2022 for details).

Cation Exchange Capacity

Cation exchange capacity (CEC) was calculated from both AA and M3 extracts using the summation approach (AA-CEC and M3-CEC, respectively). Linear models fit the raw data poorly and appeared to be influenced by soil pH; where M3-CEC was generally greater than AA-CEC in higher pH samples. Regression analysis indicated a similar trend to that of the Ca measurements, where the difference between M3-CEC and AA-CEC (Δ CEC) increased exponentially as soil pH increased beyond 7.3 (Figure 2C). These results are not surprising given that these CEC values are calculated directly from the Ca, Mg, K, and Na measured from the AA and M3 extracts, but clearly illustrate the effect of extracting nonexchangeable-Ca on CEC estimates. Excluding soil samples with a pH equal to or above this critical pH value (pH = 7.3) resulted in a near 1:1 relationship between M3-CEC and AA-CEC (slope = 0.97; $R^2 = 0.94$) (Figure 2D). Regression against soil carbonate content also indicates these differences are likely driven by the dissolution of calcium carbonates in the M3 extracts (data not shown; see Rutter et al., 2022).

CONCLUSIONS

Relationships between CEC by summation for AA and various displacement methods have been reported in some studies (Ciesielski et al., 1997; Jaremko & Kalembasa, 2014; Ketterings et al., 2014; Sumner & Miller, 2018). However, M3-CEC by summation is largely ignored in the literature, and many commercial soil testing laboratories in the US currently report these values on a routine basis. Results from this study clearly illustrate the limitations and difficulties of interpreting these values. Ideally, an individual tasked with this interpretation would also have knowledge of soil pH and the soil's carbonate contents. Unfortunately, soil carbonate tests are relatively time-consuming and costly, and are often not included in routine soil tests for farmers. Given the wide range of soils and environments represented in this study, our results suggest a critical soil pH of 7.3 may be appropriate as an alternative to soil carbonate measurements for Kansas soils; where M3-Ca should not be interpreted as “exchangeable-Ca” or used for CEC estimates in soils with a pH at or above this value.

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