Essential but Unmeasured: A Survey of Mehlich III Extractable Nickel in the Soils of Wisconsin and Illinois

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Introduction:

Nickel is the most recent element found to be essential to the plant life cycle, having been found so by Brown et. al in 1987. Though Ni has been proven essential, little research has been conducted to assess the spatial variability and possibility of growth-limiting Ni levels in soils. Ni atoms have five valences from 0 to +4 and only one of those valences, Ni^{2+}, is considered to be plant available (Horst Marschner, Bryson et al.); yet studies to date of soil Ni levels have focused primarily on the determination of total Ni without regard to the valence or relative plant availability, limiting the agricultural usefulness of the current soil Ni surveys. Here is presented a survey of soils in Wisconsin and Northern Illinois that were submitted to a commercial soil testing laboratory for routine fertility analysis, including Mehlich III extraction. The addition of Ni to the suite of elements analyzed by Mehlich III allowed for Ni levels to be collected on a larger scale than any survey to date.

Nikoli and Matsi in 2014 found that Mehlich III shows promise as an extractant for plant available Ni. Accordingly, Ni was added to the suite of nutrients detected in the Mehlich III extract at Rock River Laboratory, Inc, a commercial soil analysis laboratory in southeast Wisconsin. All samples submitted for routine fertility since the second quarter of 2020 were thus analyzed for Mehlich III extractable Ni along with other routine fertility tests. The goal was to amass a large dataset of Ni values then use statistical analysis to find patterns or relationships that might otherwise go unnoticed. At the time of this writing, the dataset contains 38,000 samples from Wisconsin and northern Illinois. In total, 25 attributes are collected for each sample, yielding a dataset of 950,000 individual data points.

While the majority of research into soil Ni has focused on total Ni, a small number of studies have been conducted to assess the suitability of routine soil nutrient extraction methods for determination of plant available Ni concentrations. The goals of these studies were varied and some sought to employ routine soil testing as an estimate of plant Ni uptake, with an ultimate goal of predicting when excess Ni may enter the food chain (RLF Fontes et al) Others have looked to routine soil extractants such as Mehlich I (Rodak et al), DTPA (Rodak et al; Nikoli et al) and Mehlich III (Nikoli et al) to try and establish an analysis that can be used to add Ni to routine soil fertility testing. In 2016, Nikoli et al became the first to establish critical soil test levels and their findings are used here to determine the extent of possible Ni deficiency, if any.

Methods:

Sample collection was conducted by customers of Rock River Laboratory, Inc. and followed generally accepted sample collection techniques, but no specific sample collection criteria were specified for this study. Once received at the lab, samples were dried at 50C for approximately 24h prior to being pulverized with a flail mill and sieved to pass a 2mm screen.

Sample scooping was conducted using calibrated scoops that conform to the specifications outlined in NCERA-13 publication No. 221, *Recommended Chemical Soil Test Procedures for the North Central Region.* All samples were analyzed for the following suite: Bray-1 (1:10) P with ascorbic acid color development and spectrophotometric detection, Bray-1 (1:10) K with flame photometer detection, water pH (1:1), Sikora buffer pH (1:1:1), loss-on-ignition organic matter (360C, 2 hours), and Mehlich III (1:10) extractable Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, and Zn with ICP-OES detection. Estimated CEC was calculated using the equation: est. CEC = [(K ppm/391)+(Mg ppm/122)+(Ca/200)]*soil density. The est. CEC equation was also used to express Ca, K, and Mg in milliequivalents.

Data were analyzed using JMP Pro 13.1.0 under license of the University of Wisconsin – Madison.

Discussion:

Population distributions show that a distinct and significant separation exists between Ni concentration and state of origin (figure 1) with Illinois having generally higher concentrations. While the precise reasoning for the difference between the states is unclear, there are several factors that warrant investigation. Soil properties that have been reported to impact Ni bioavailability include pH, SOM, clay content, and Fe oxides/hydroxides (Rooney et al). It is also worth noting that the Illinois samples originate primarily from grain operations whereas dairy enterprise is a more significant portion in the Wisconsin samples. There is a possibility that the agricultural enterprise plays a role in Ni concentrations, as these two will differ in manure applications and crop residue. The difference between the populations are even more clearly expressed when the cumulative frequencies of Ni concentrations are plotted by state and overlain (Figure 2)

When comparing to the work of Nikoli et al. in 2016, between 2.4% and 99.9% of samples could be classified as below the critical level for ryegrass (*Lolium perenne* L.) (Table 1). Here again the distribution differences between Wisconsin and Illinois are evident as the most conservative critical limit of 1.3 mg kg^{-1} shows that 37.3% and 2.4% of soils are deficient for each state, respectively.

Figure 1: Mehlich III extractable Ni Distributions by State of Origin

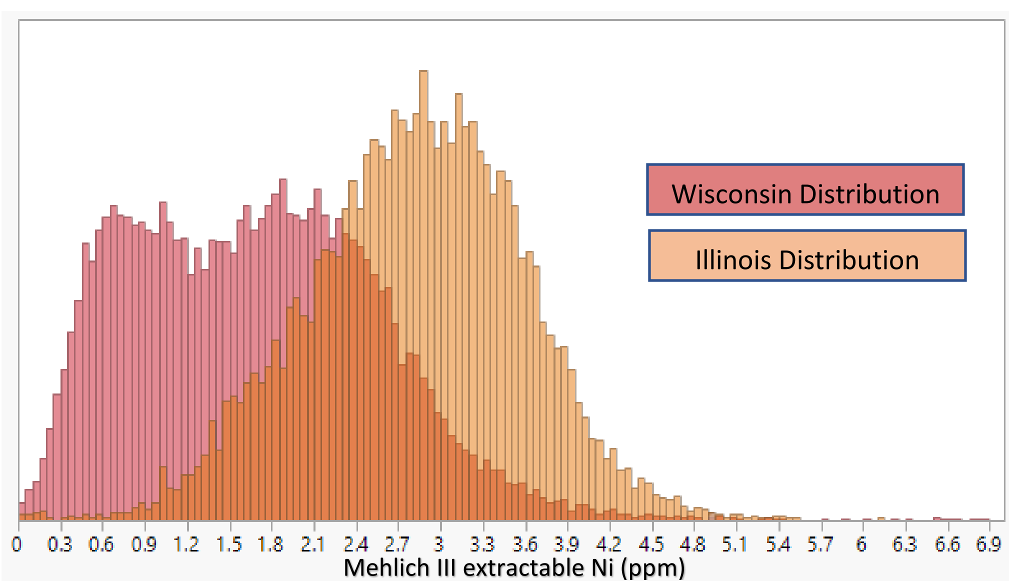

Figure 2: Cumulative Frequency Plot of Mehlich III Ni Values by State, with Three Critical Values of Nikoli et al. Shown for Reference

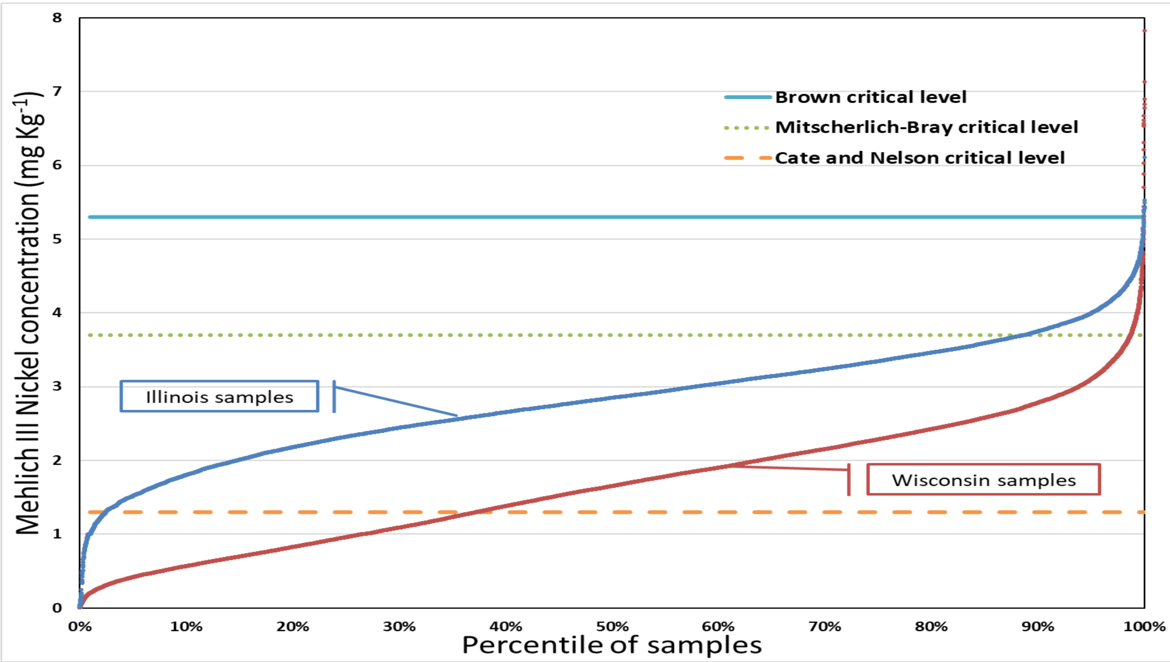

Table 1: Three critical levels of Mehlich III extractable Ni and percentage of samples in each state that fall below (Nikoli, et al., 2016)

Critical deficiency level (mg kg^{-1})	Calibration technique	WI percent below	IL percent below
1.3	Cate and Nelson	37.3	2.4
3.7	Mitscherlich-Bray	98.7	88.7
5.3	Brown et al.	99.9	99.9

Mehlich III Ni concentration appears to be correlated with Mehlich III extractable Mg, soil pH, soil organic matter, and Mehlich III extractable Ca (data not shown). These correlations are visible in scatterplots, but the size of the dataset creates noise and causes a lack of clarity in the statistical analyses. Sorting data by properties such as state of origin, soil pH, or soil organic matter helps to reduce the noise, but not enough to state whether definitive relationships exist. More work will be done in this area to try and better understand the direction and magnitude of any relationships that do exist.

Conclusion:

Mehlich III shows promise as a routine extractant for plant available Ni. This study has shown that there are no significant hurdles to a commercial lab adding the analysis, so widespread adoption of the testing should not pose a challenge. The challenge currently lies in the interpretation of the data. The one attempt to determine a critical value, by Nikoli et al. concluded that the variance in the soil test obscured the data and resulted in an unsatisfactory fitting of the calibration models that were attempted. However, Nikoli et al did see a yield response to additions of Ni and Freitas et al. (2018) has found that soybean can see a benefit from added Ni. These findings tell us that a more intensive study of plant available Ni is necessary and may prove beneficial. This survey will lay the groundwork for a much fuller understanding of soil Ni concentrations, how those Ni concentrations can be determined at a larger scale, and how the results are to be interpreted.

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