Essential but Unmeasured

A survey of Mehlich III extractable nickel in the soils of Wisconsin and Illinois

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ROCK RIVER LABORATORY, INC.
AGRICULTURAL ANALYSIS

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What does essential mean?

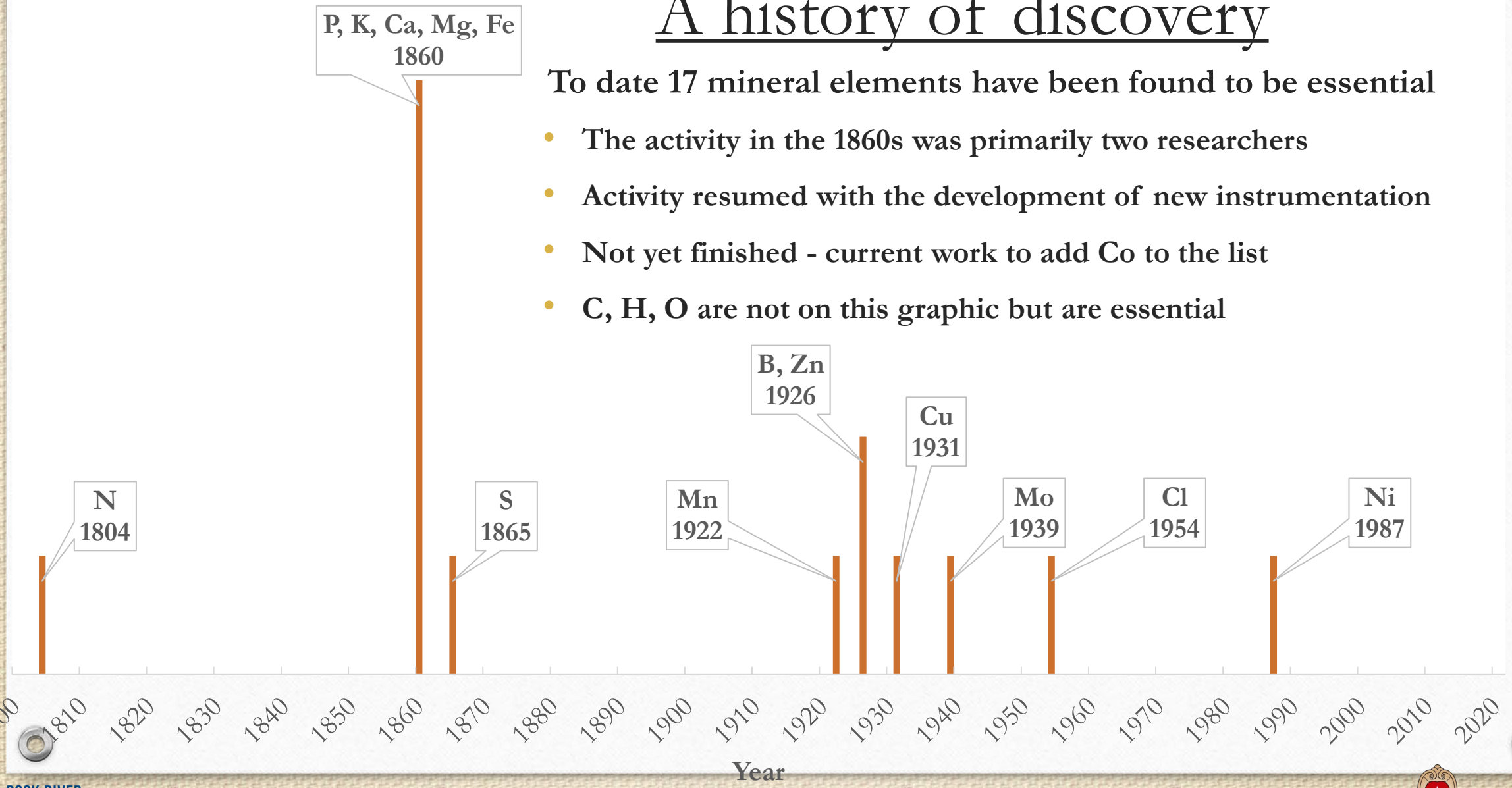
Arnon & Stout (1939) outlined the criteria of essentiality

1. A deficiency of the element makes it impossible for the plant to complete the vegetative or reproductive stage of its life cycle
2. Such deficiency is specific to the element in question, and can be prevented or corrected only by supplying this element
3. The element is directly involved in the nutrition of the plant, rather than correcting an environmental condition that prohibits vigor

A history of discovery

To date 17 mineral elements have been found to be essential

- The activity in the 1860s was primarily two researchers
- Activity resumed with the development of new instrumentation
- Not yet finished - current work to add Co to the list
- C, H, O are not on this graphic but are essential



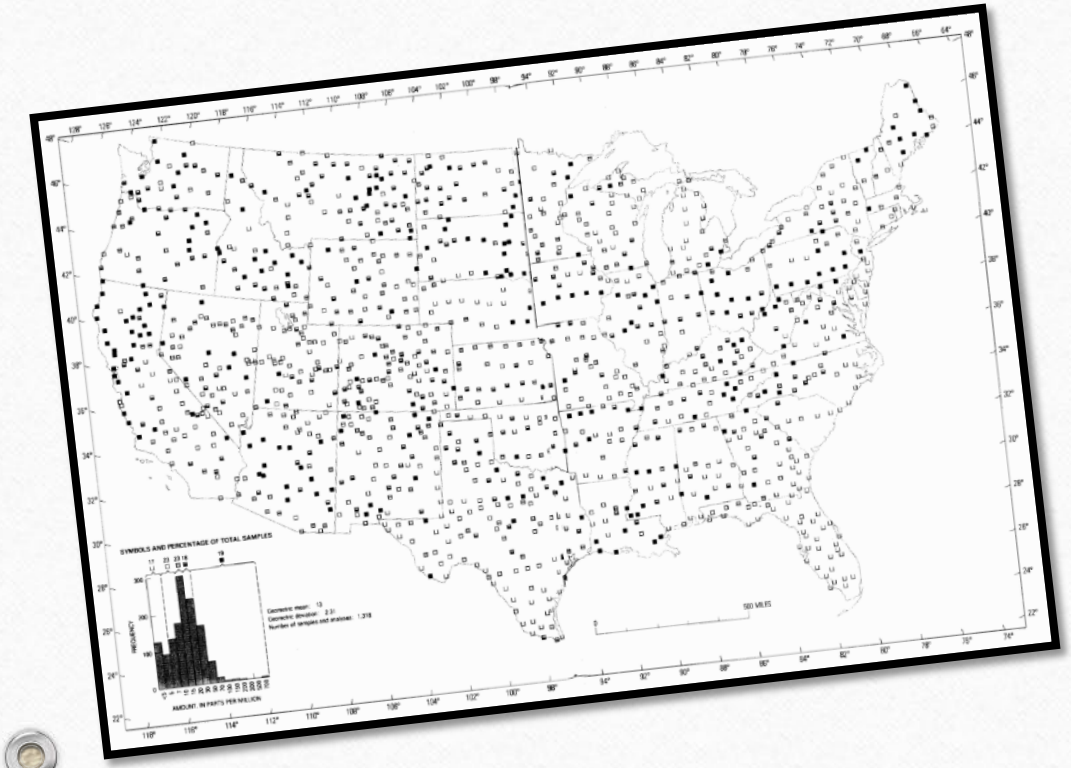
The essentiality of nickel

- In 1987 Brown et al. were able to design an experiment that fulfilled the criteria of Arnon & Stout by breeding successive generations of barley with less and less Ni until the seeds were no longer viable

and then…

Excitement, jubilation, and a flurry of scientific discovery?

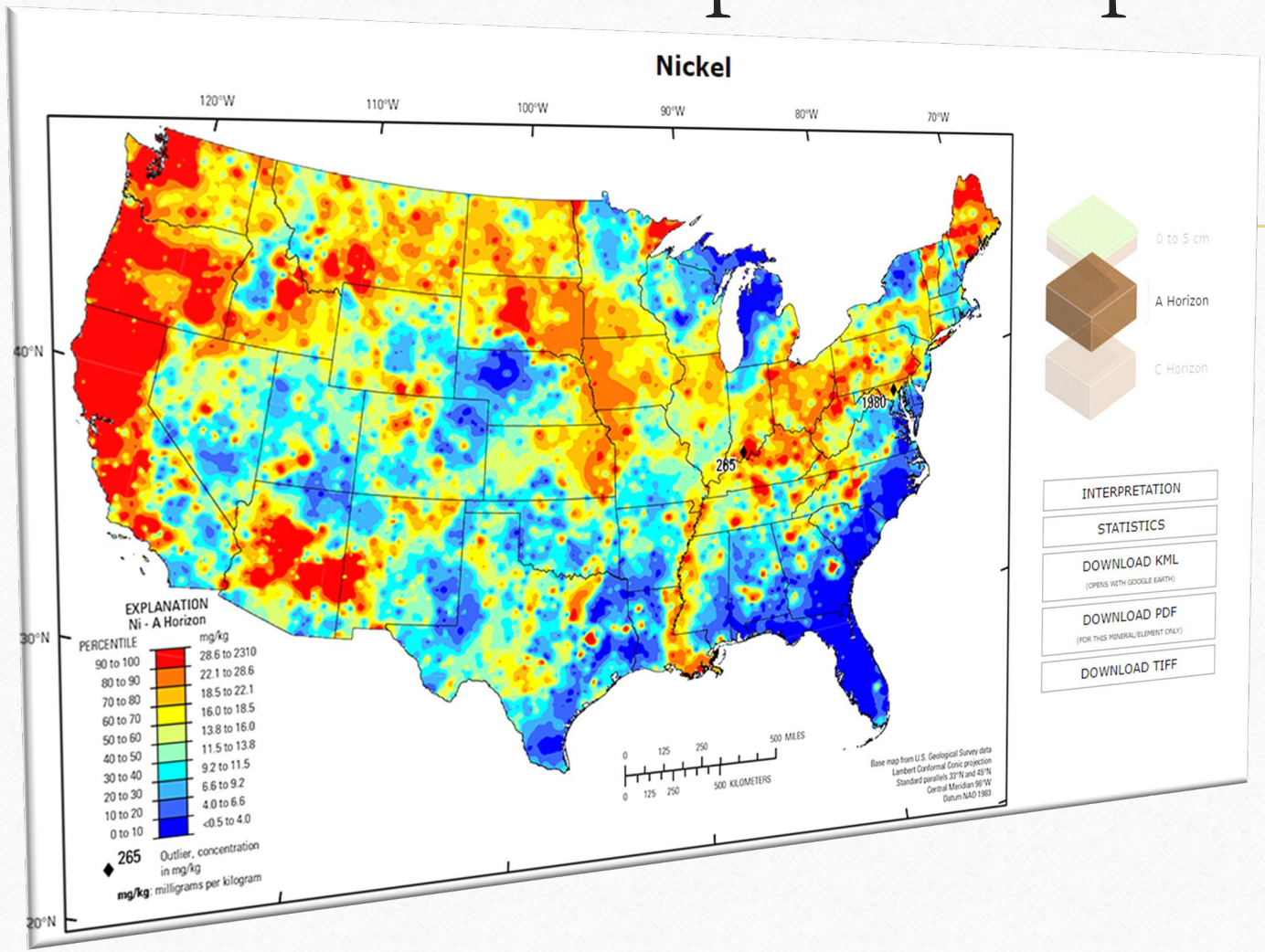
NOPE



1984 USGS Surficial materials survey showed total nickel concentrations in the soils of the conterminous United States

The critical concentration found by Brown et al was so low (90±10 ng g^{-1} dry weight) that a deficiency was deemed unlikely

USGS maps were updated in 2017



Easier to see areas that are relatively lower in total Ni concentrations

- Definite regional variation
  - Ultramafic parent material in the West and Northwest
  - Quartz dominates in the Southwest

- "Low" regions are <0.5 to 4.0 mg kg^{-1} so still no real concern for crops to fall below critical essentiality level

The three faces of nickel

Essential

>Required amount is very low, and natural abundance is not limiting

>This may have led researchers to dismiss the potential of fertility studies

Beneficial

>Yield responses documented in multiple crops over decades

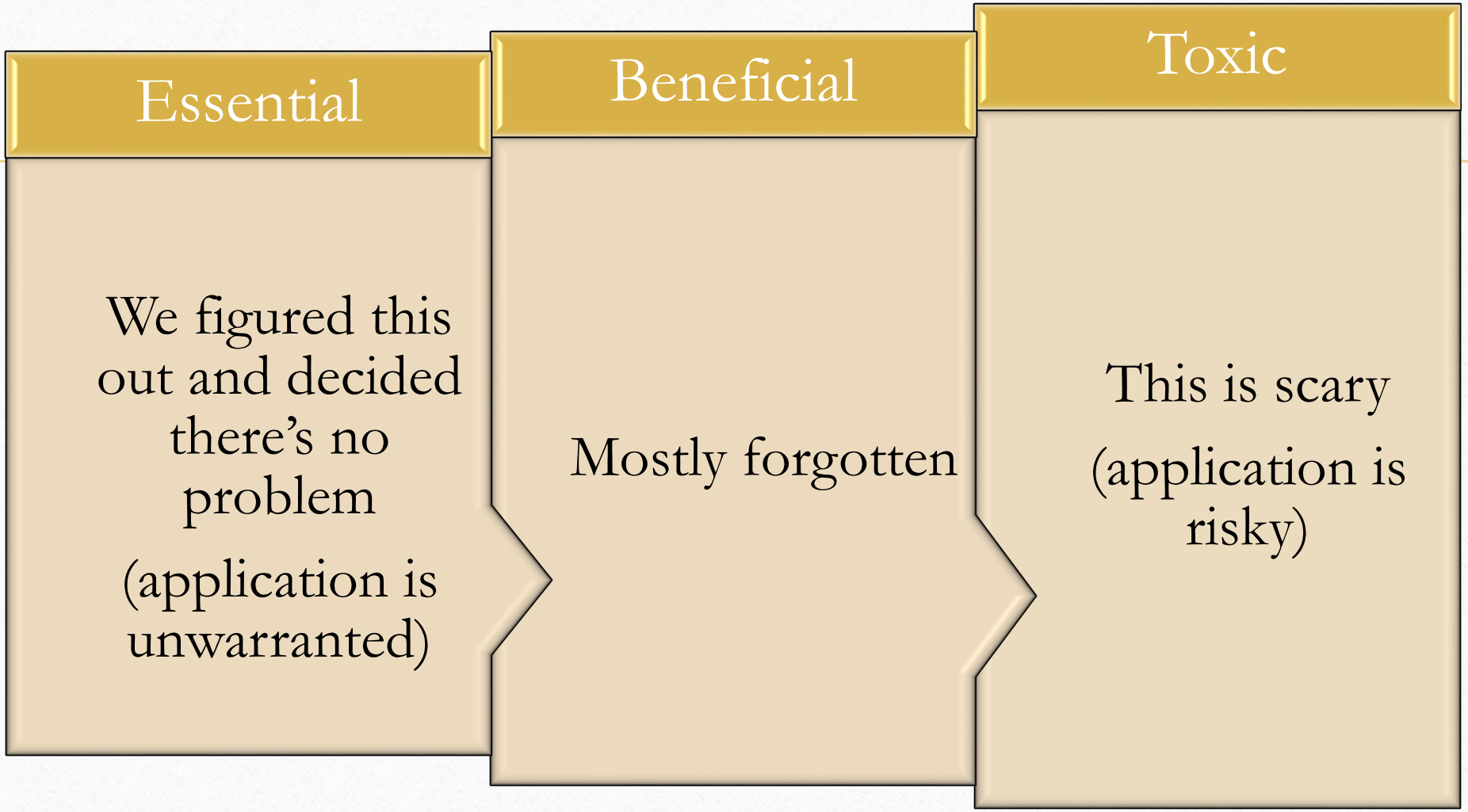
>Nickel was found to be a critical component of urease in 1975

Toxic

>Toxicity to plants begins at 10 ug g^{-1} in sensitive plants while hyperaccumulators can have 30,000 mg g^{-1}

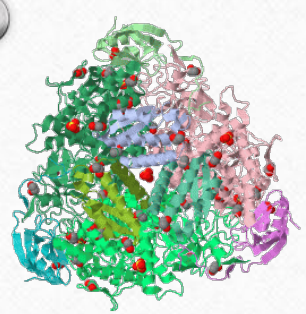
>Downstream toxicity in consumers is also a major concern

The three faces of nickel simplified



Documented responses to added nickel

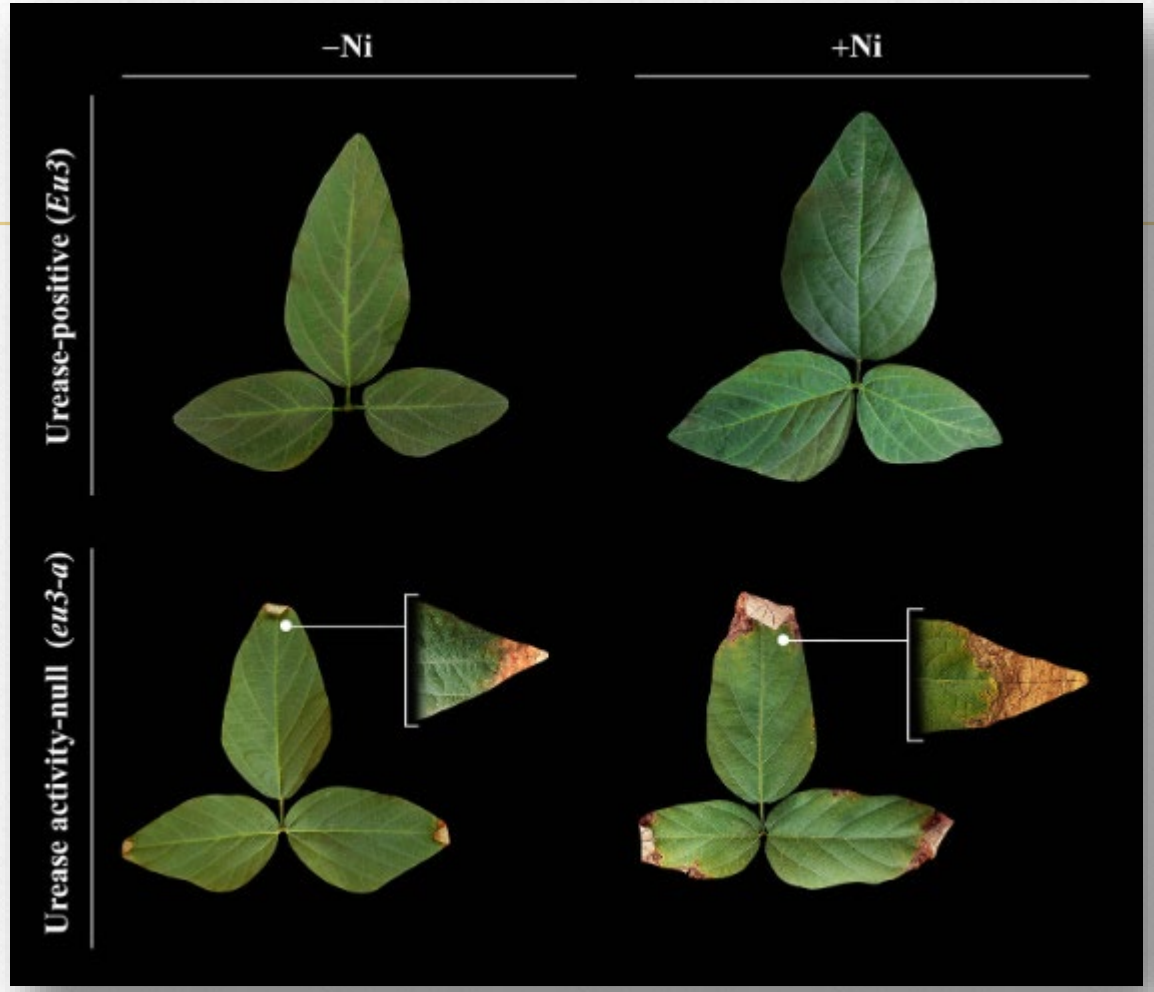
- ***Roach & Barclay, 1945;*** Increased yield in wheat, potatoes, and broad beans, foliar applied; UK
- ***Freitas et al., 2018;*** As much as 1,502 kg ha^{-1} yield increase (22.3 bu ac^{-1}, assuming 60 lbs bu^{-1}); soybeans; soil applied; Brazil
- ***Levy et al., 2019;*** 25% greater biomass accumulation with addition of 0.25 mg kg^{-1}; no yield response; soybeans; soil applied; Brazil
- ***Kumar et al., 2021***; Greatest yield increase with 5.0 kg ha^{-1} soil applied plus 0.2% $NiSO_4$ foliar applied; barley; India



Nickel as a beneficial element

Urease

- Nickel was discovered to be a required constituent in 1975
- Catalyzes the breakdown of urea into ammonium and carbon dioxide
- Without it, we can see urea toxicity in leaves

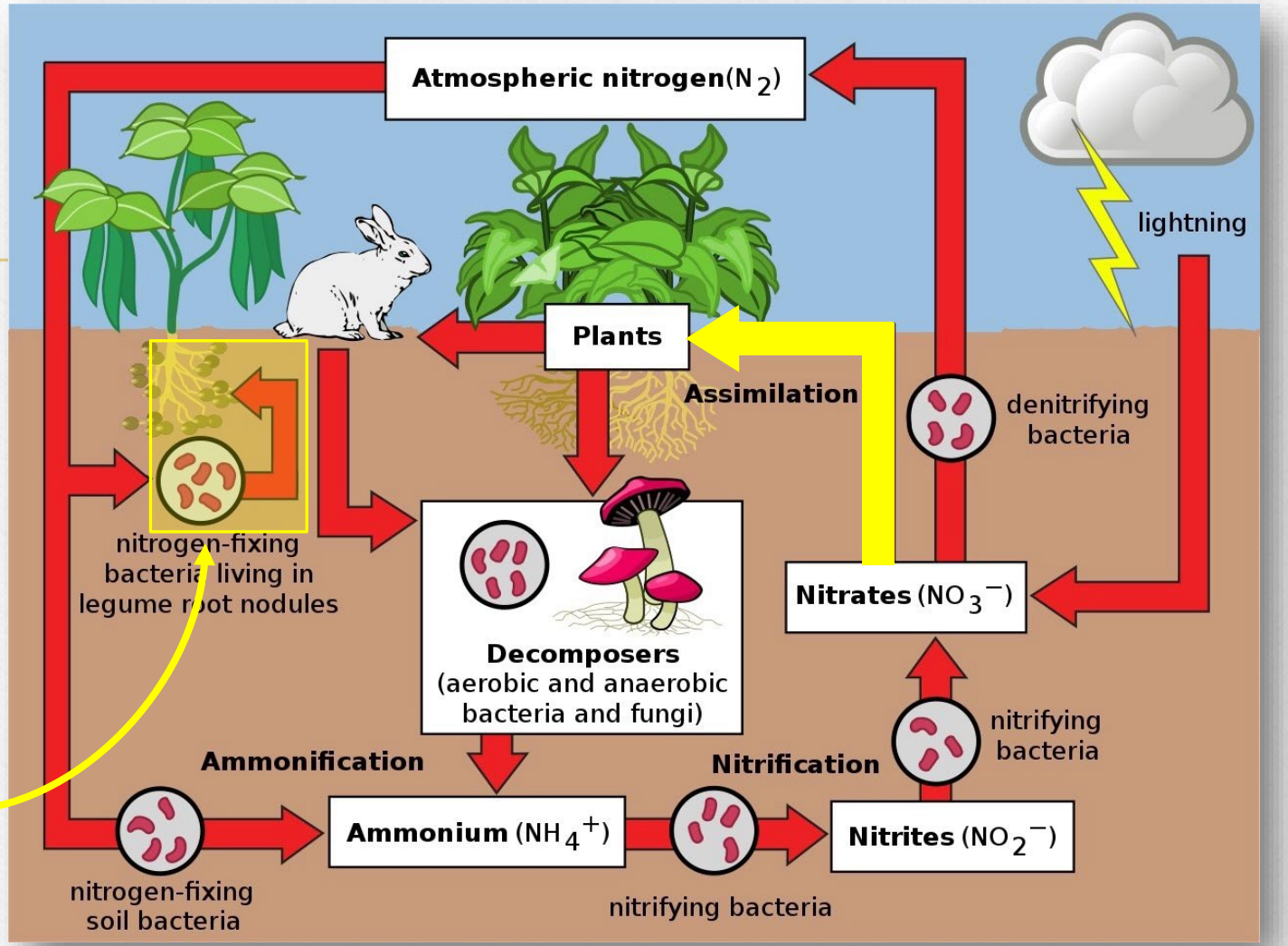


D. Siqueira Freitas et al. *Frontiers in Plant Science*(2018)

Why does urea matter?

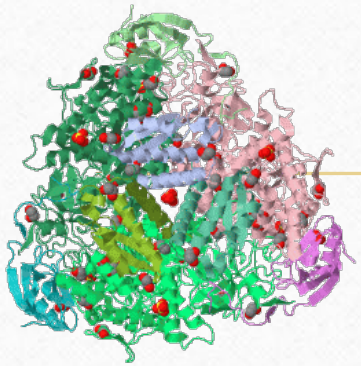
Plants take up nitrate, not urea. It says so right here!

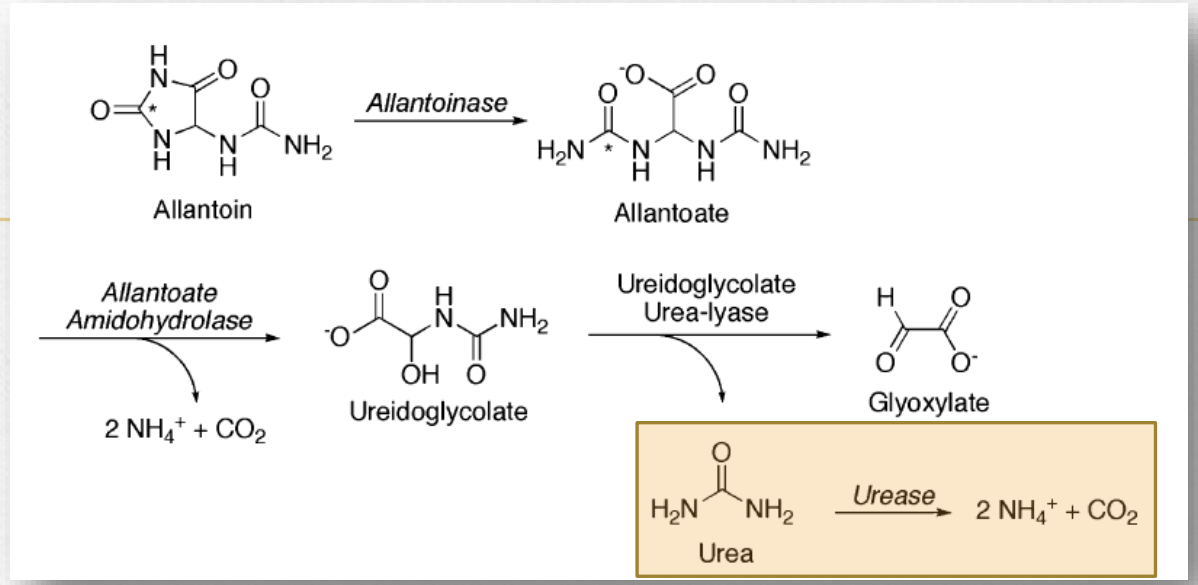
THIS is where it matters



https://www.quora.com/Will-the-nitrogenous-waste-of-animals-like-urine-be-directly-absorbed-by-the-plants

Urea and urease in legumes





Nodules fix ammonia(um) which is transferred to the roots and converted to ureides

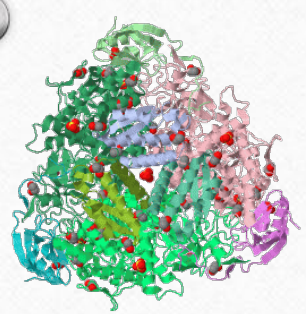
Plant transports ureides from the roots as allantoin and allantoate

Enzymes eventually break these into urea

Urease liberates the NH_4^+

C. D. Todd et al. *Journal of Experimental Botany*(2006)

Nickel as a beneficial element



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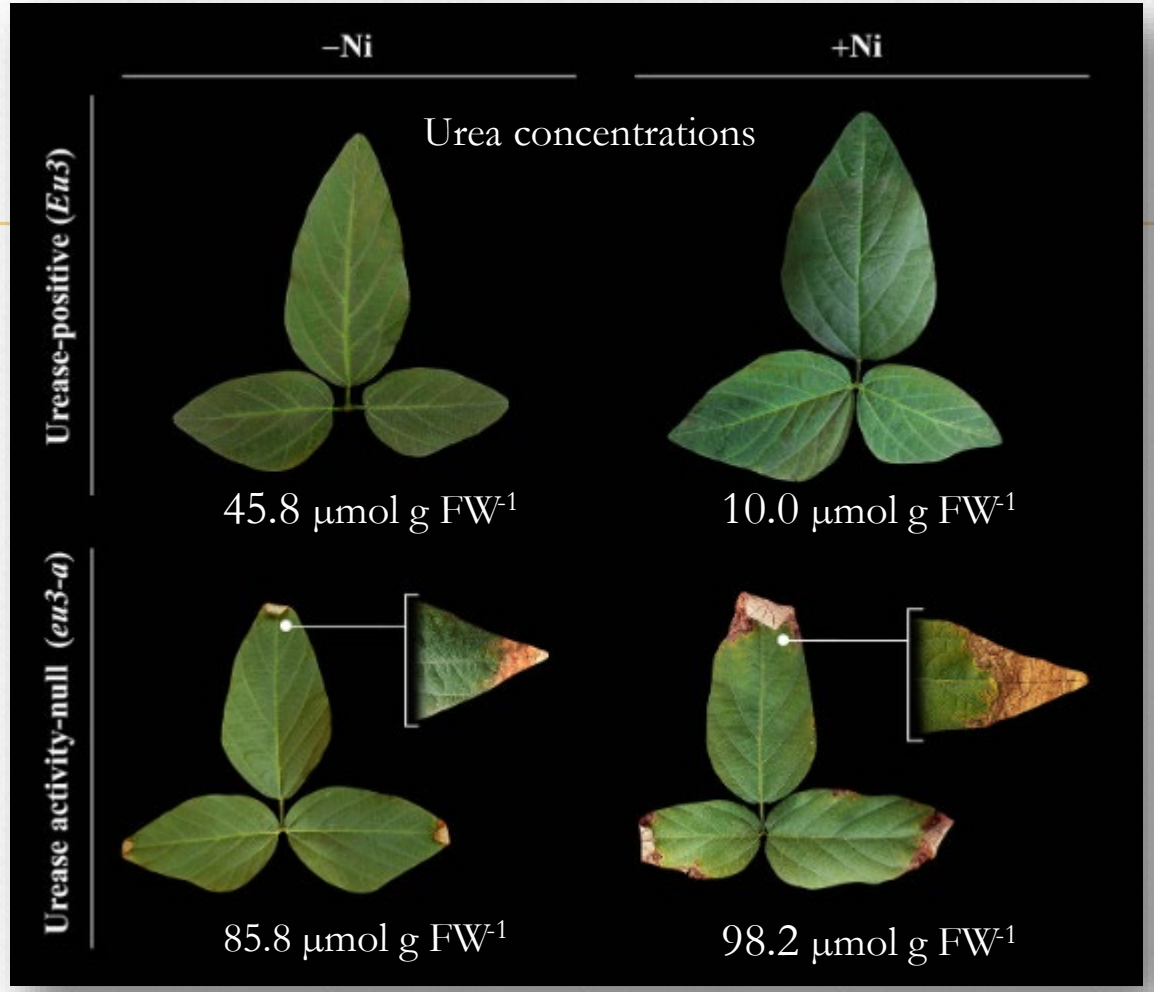

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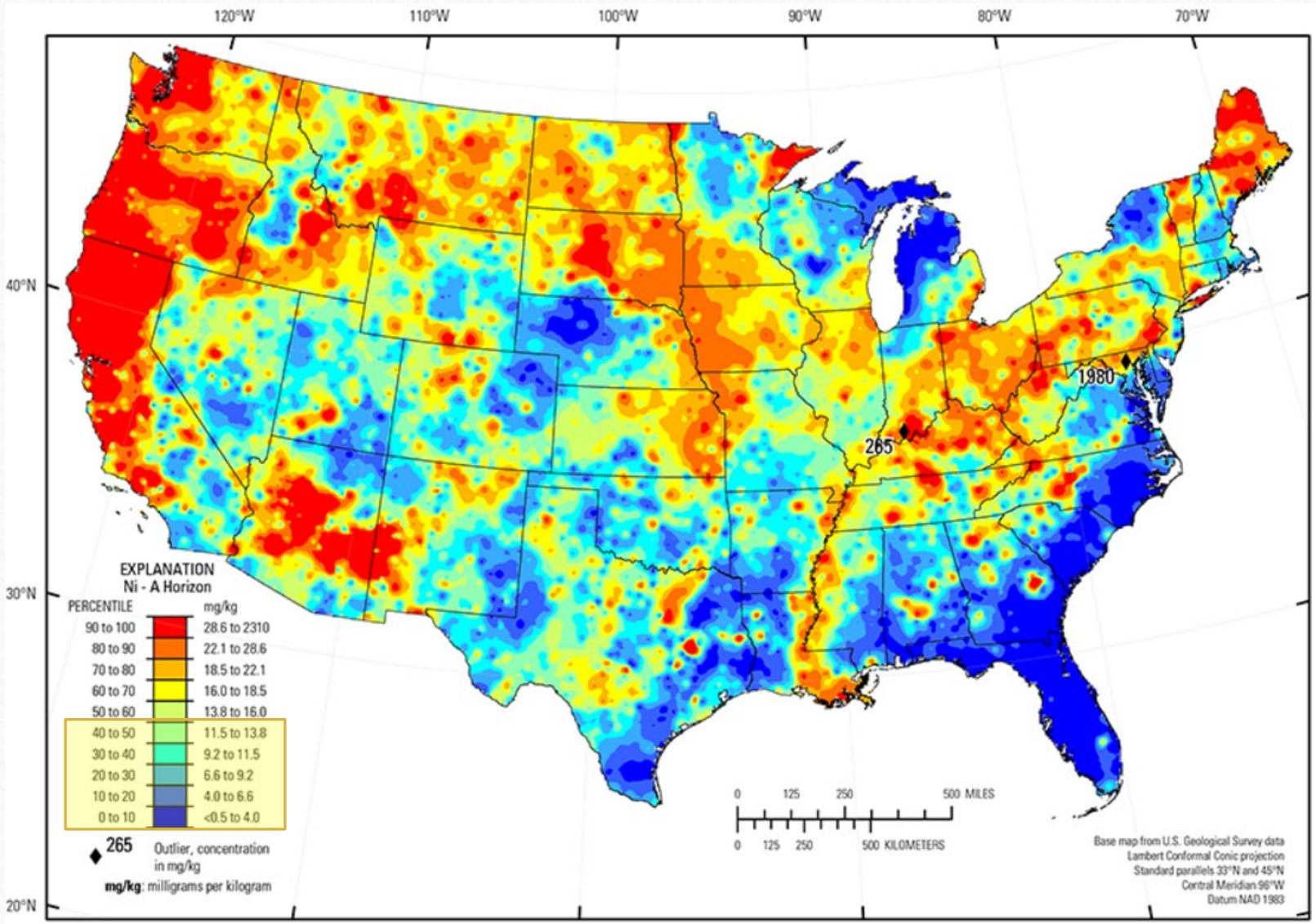


Increased urease activity

1985 Dalton et al. found increased urease activity in response to added Ni in a soil with 13 ppm total Ni.

13 ppm is roughly the median value in the conterminous US

Things I've said
That should bother you

1. The USGS surveys quantify total nickel concentrations

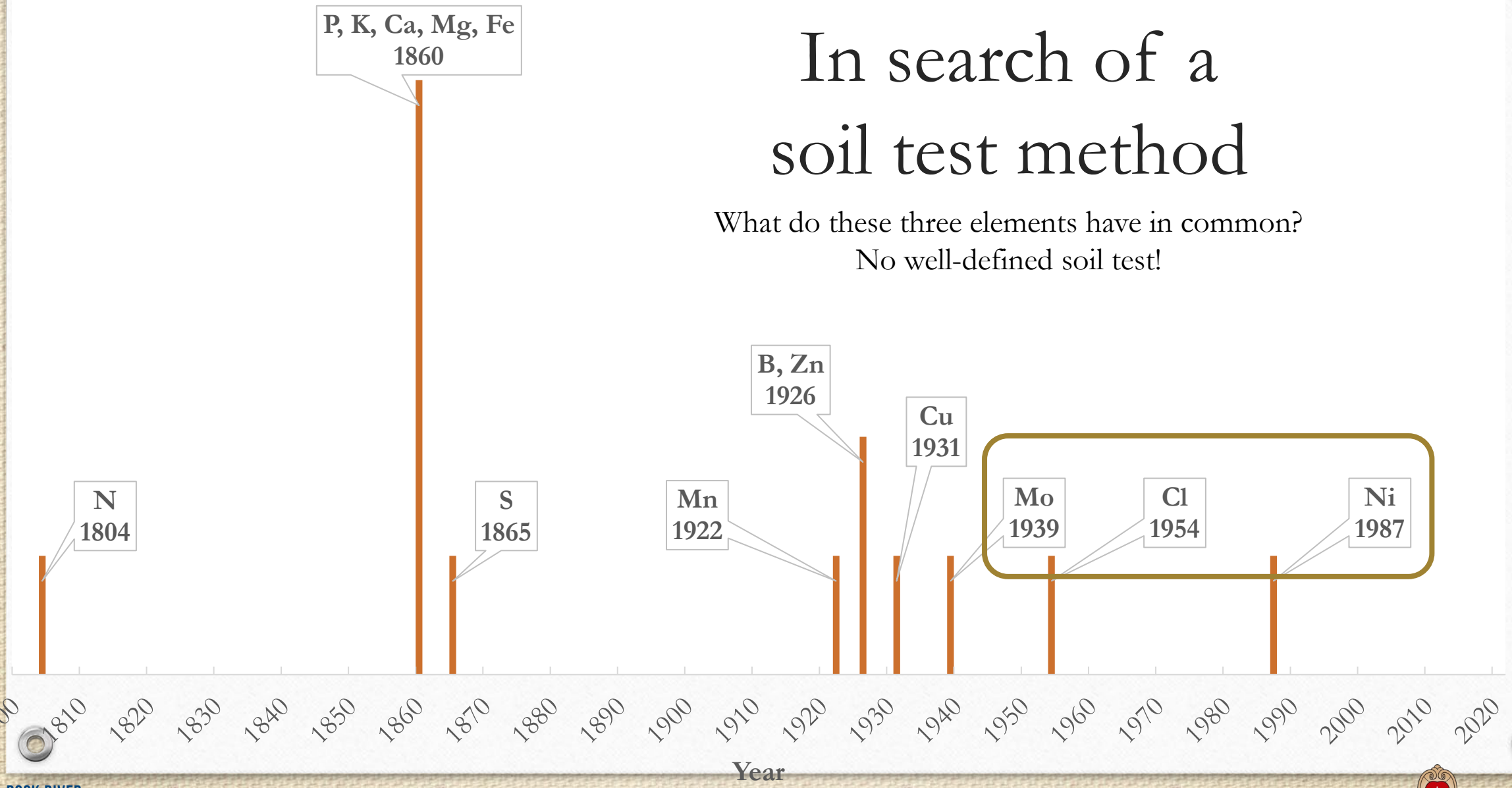
We need a plant available test

2. Brown et al. critical level (90 ppb in tissue) is not helpful agronomically

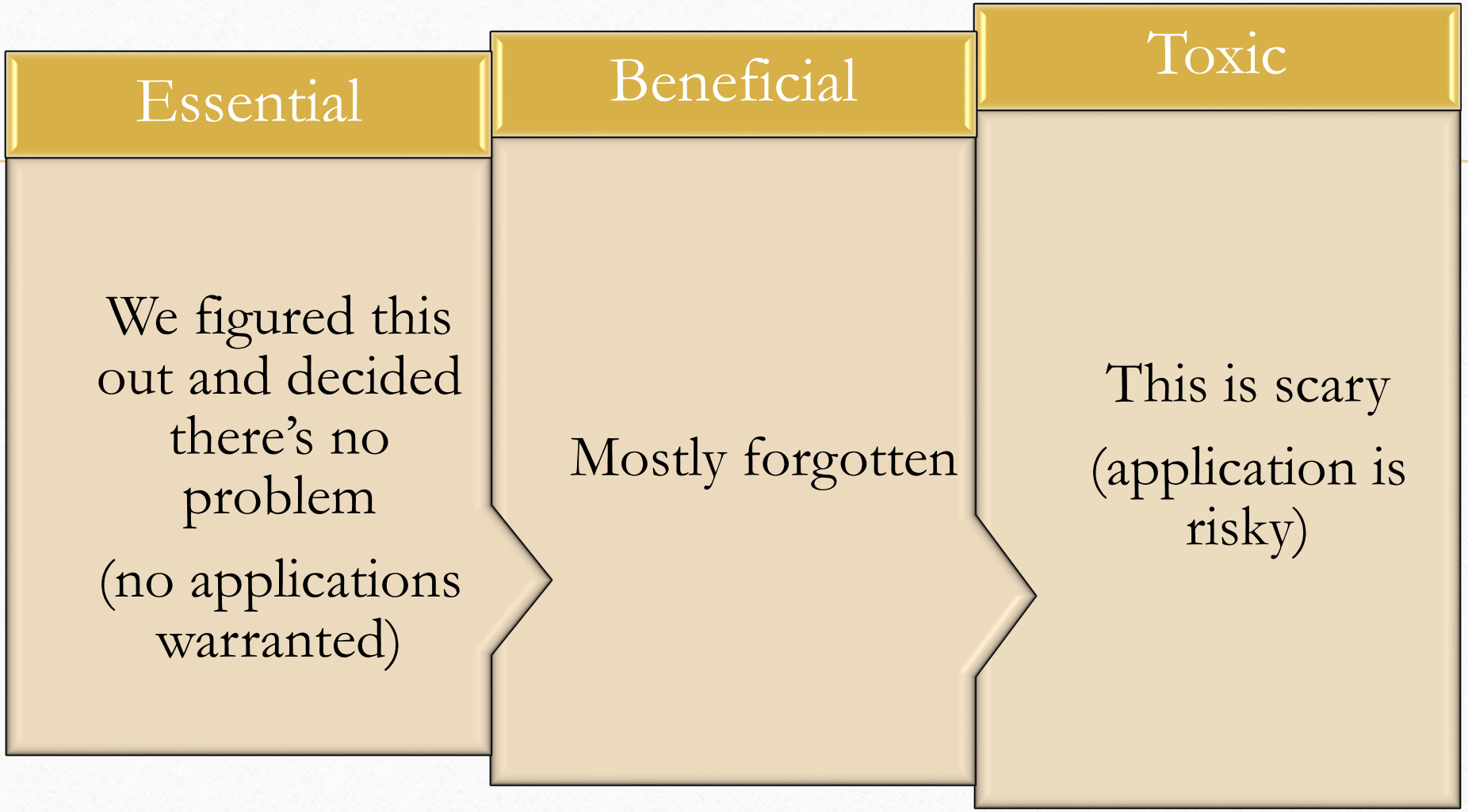
We need to know the agronomic critical level

In search of a soil test method

What do these three elements have in common?
No well-defined soil test!



The three faces of nickel simplified



Nikoli & Matsi 2014

Evaluated several existing soil extractants for efficacy with nickel

- DTPA, AB-DTPA, AAAc-EDTA, Mehlich III, 0.1 M HCl, 0.1 M HNO_3
- First attempt to develop sufficiency critical levels in the soil
- Best efficacy with AAAc-EDTA and Mehlich-3
- Determined critical level to be ~2 mg kg^{-1} for these methods, using Cate-Nelson procedure
- Used ryegrass as the crop

Rodak et al. 2015

Evaluated Mehlich-1 and DTPA extractions along with tissue analysis

- Both extractants tracked well with nickel additions to the soil
- Grain tissue analysis tracked better with soil analysis than did shoot or leaf
- Some soil nickel levels were too low to be quantified by either method
- Did not seek to determine critical level
- Used soybeans as the crop

Nikoli et al. 2016

Multiple extractants and multiple calibration techniques

- DTPA, AB-DTPA, AAAc-EDTA, Mehlich III extractants
- Mitscherlich-Bray equation, Graphical technique of Brown et al., Cate-Nelson graphical technique
- Still used ryegrass

Nikoli et al. 2016

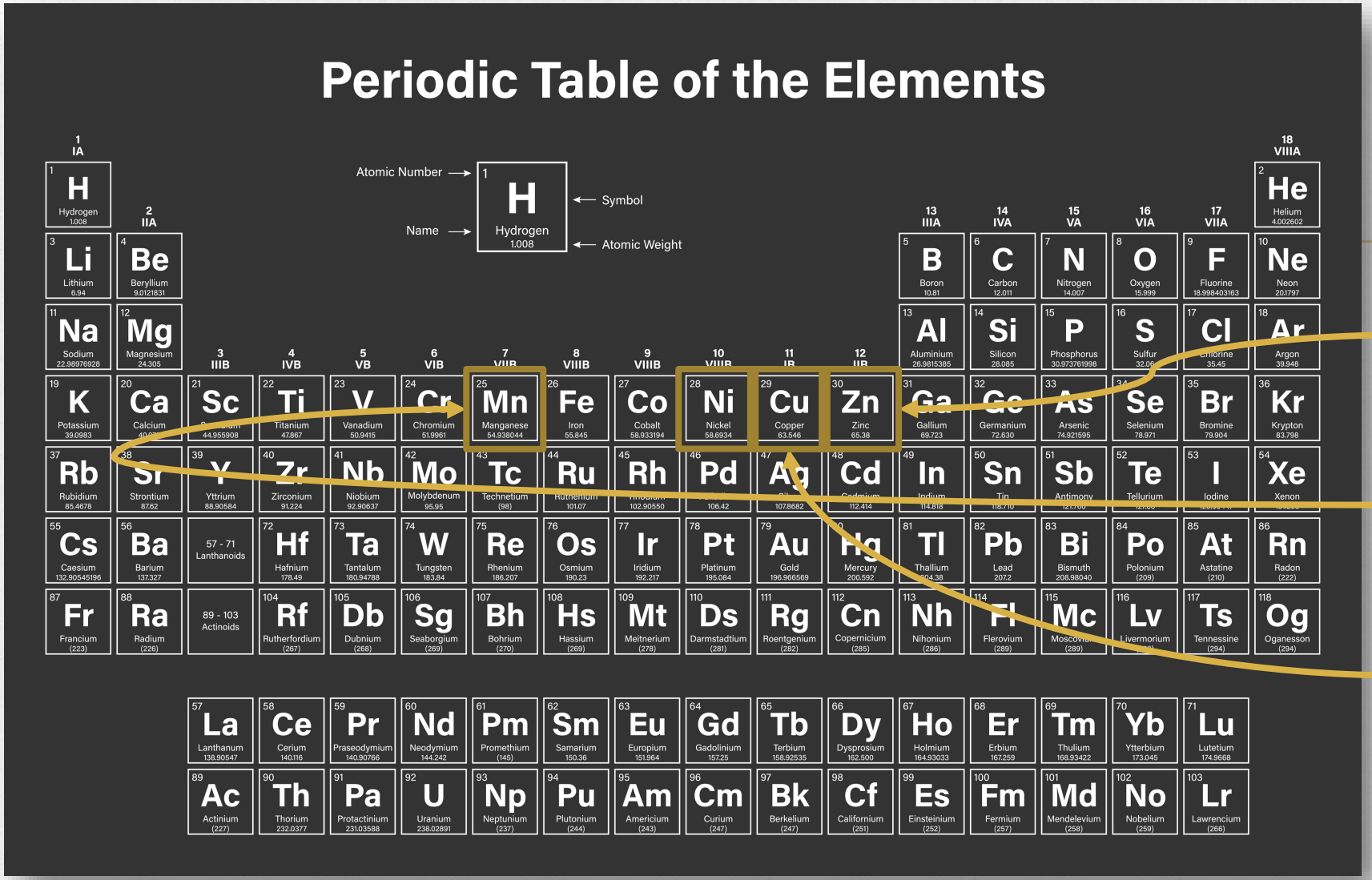
Table 1: Critical levels of extractable Ni (mg kg $^{-1}$)				
Calibration technique	DTPA	AB-DTPA	Mehlich III	AAAc-EDTA
Cate and Nelson	0.5	1.0	1.3	1.1
Mitscherlich-Bray	2.1	2.2	3.7	5.1
Brown et al.	2.3	1.8	5.3	6.0

Sidebar: A brief history of the Mehlich extractant

Dr. Adolf Mehlich working at North Carolina State University

- 1953?: Mehlich I, AKA Double Acid extractant is the first universal extractant. A general success, it doesn't work well in all soil types, particularly non-acid soils
- 1978: Mehlich II tried to rework Mehlich I to include more soil types, broader pH range. Again, mostly successful but lost efficacy of Cu extraction
- 1984: Mehlich III aimed to reduce the corrosivity of Mehlich II, and improve Cu extraction with addition of EDTA (published posthumously)

Mehlich III Vs Mehlich II



Zn +25%

Mn +50%

Cu +170%

Sawyer, Schroeder & Barak, 2020

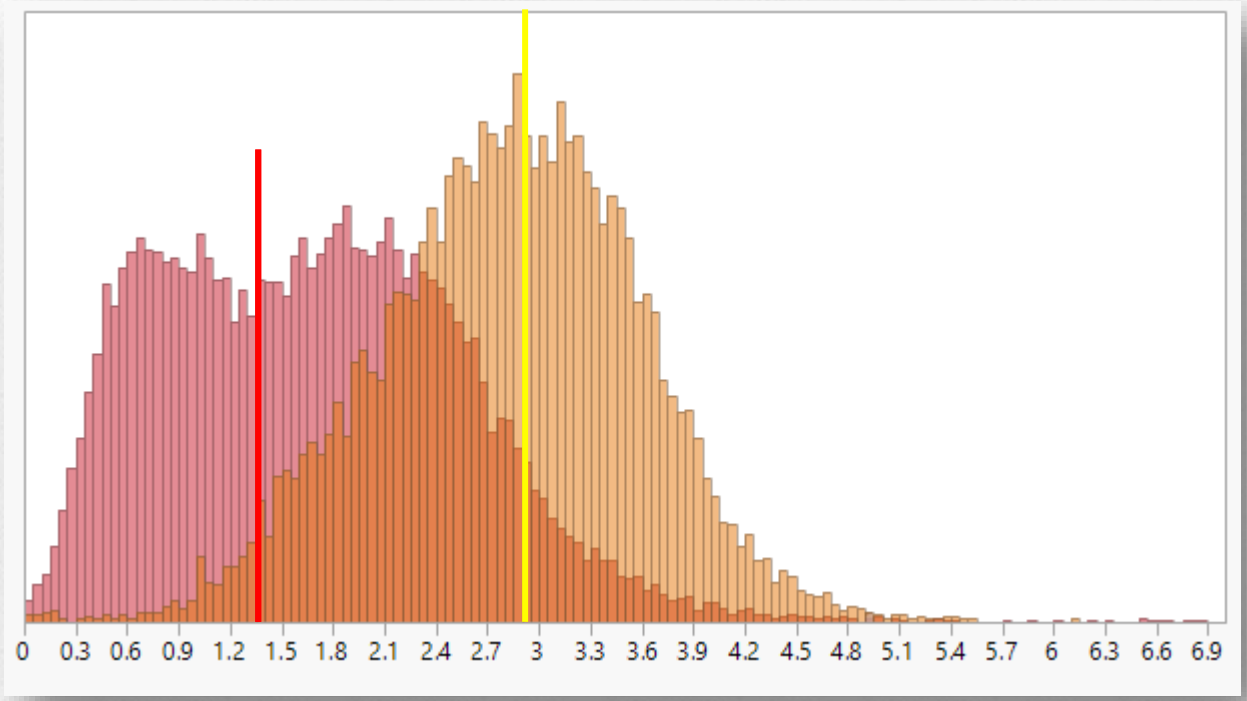
Aimed to assess Mehlich III extractable nickel content in Midwestern USA and compare to critical levels determined by Nikoli et al., 2016

- Will data indicate that nickel fertilization may provide a benefit to soybean production in these soils?
- Assess regional differences in nickel concentrations as well as relationships among nickel and other soil properties
- Observational study with no experimental variables

Sawyer, Schroeder & Barak, 2020

- Nickel analysis was added to all samples submitted to the lab for Mehlich III analysis
- ~39,000 samples collected throughout Wisconsin and Illinois April to October 2020
- Samples collected by customers following a myriad of protocols
- Little known about the fields in the study

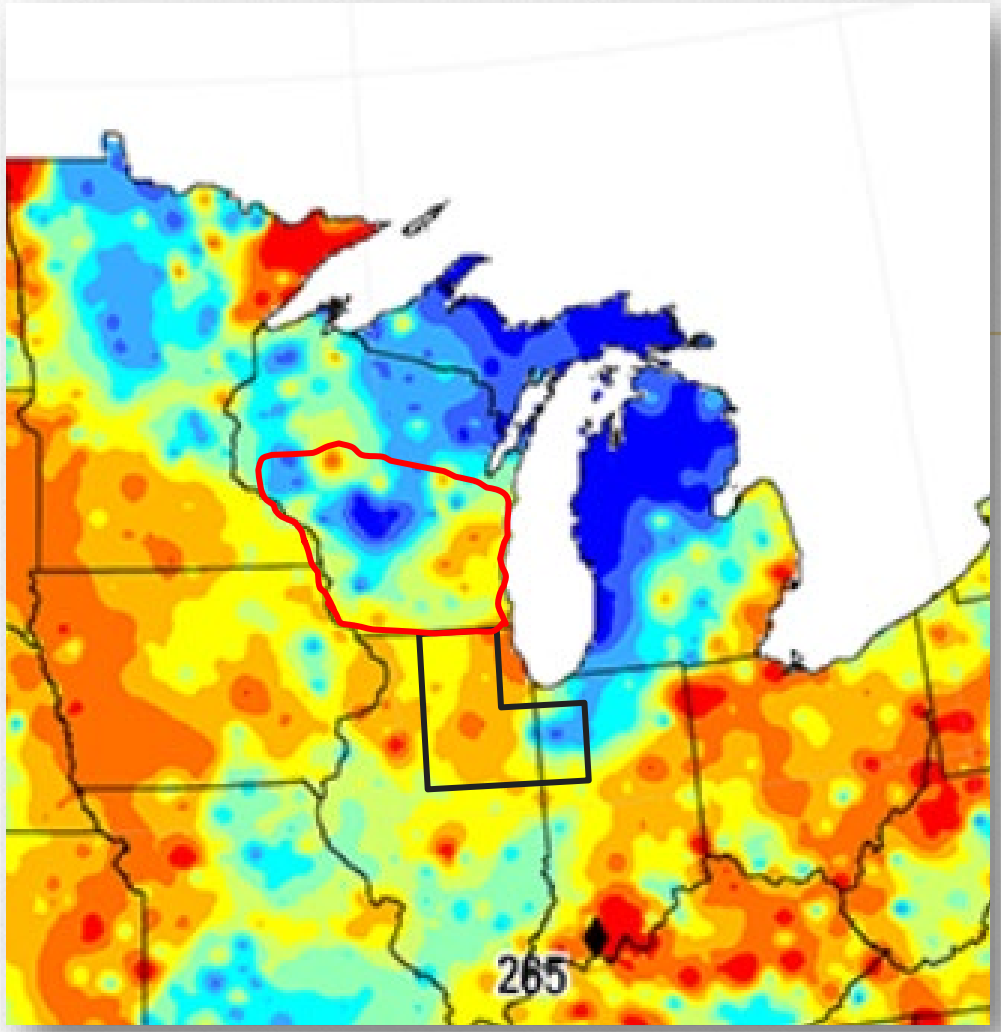
Sawyer, Schroeder & Barak, 2020



Mehlich III extractable nickel concentration distribution by state

"Wisconsin" samples

"Illinois" samples

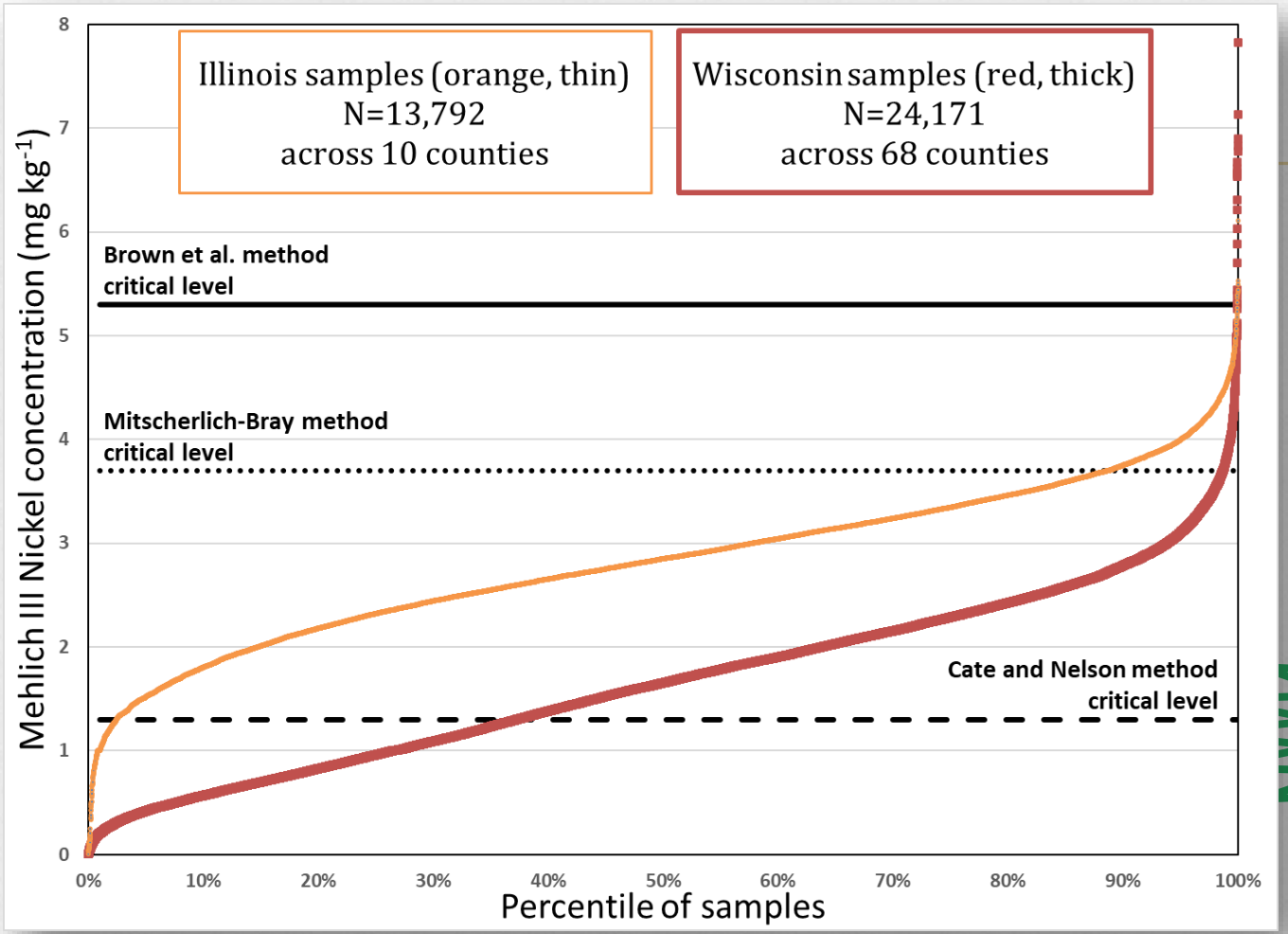


USGS total nickel concentrations, 2017

- "Illinois" samples come from an area more uniformly high in total nickel than "Wisconsin" samples
- "Wisconsin" samples have more diversity of dairy/grain operations whereas "Illinois" samples are predominantly grain
- What is the relationship between total and Mehlich III extractable?

Sawyer, Schroeder & Barak, 2020

Cumulative distribution by state



Compare to Nikoli 2016 critical levels

Critical 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

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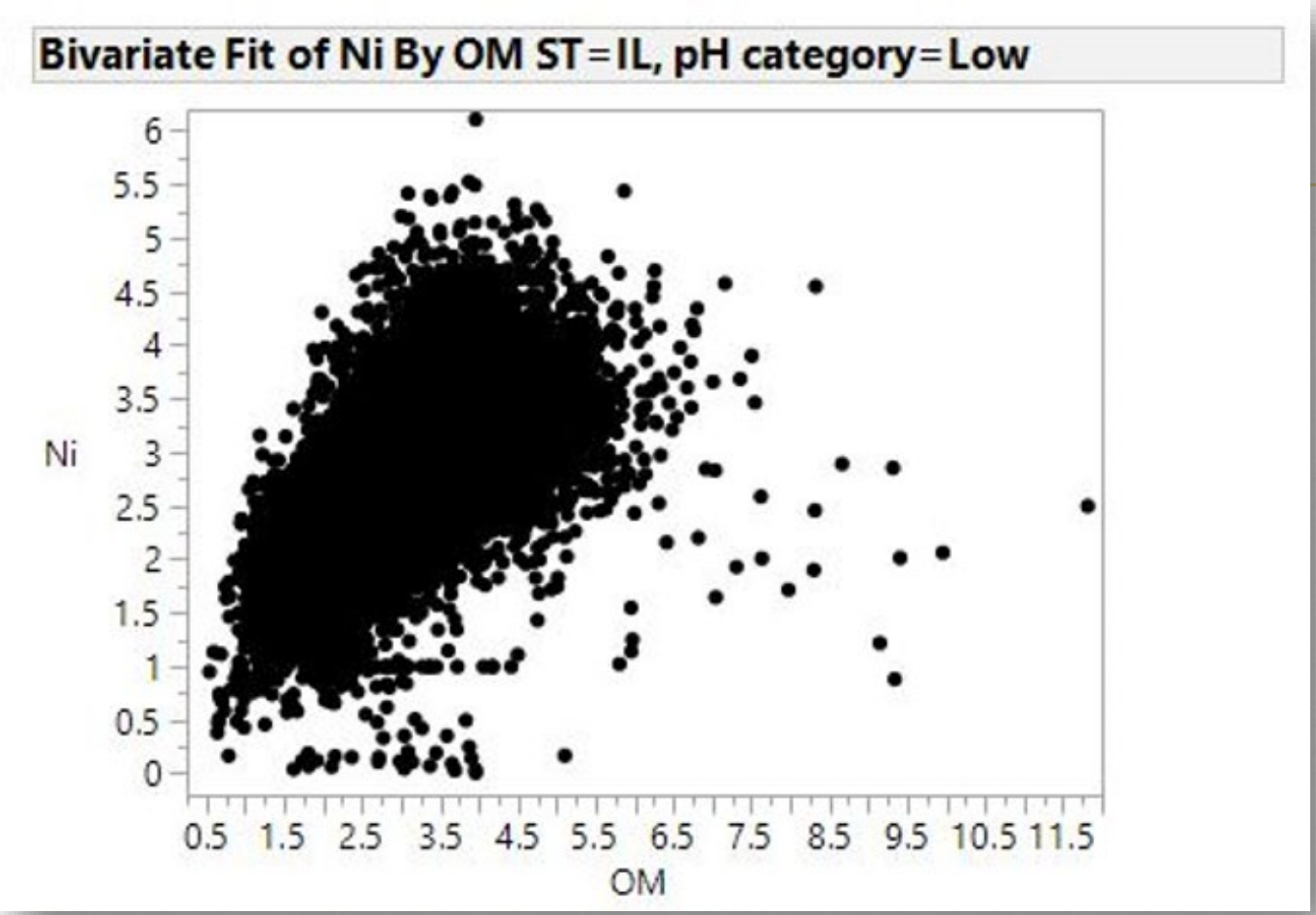
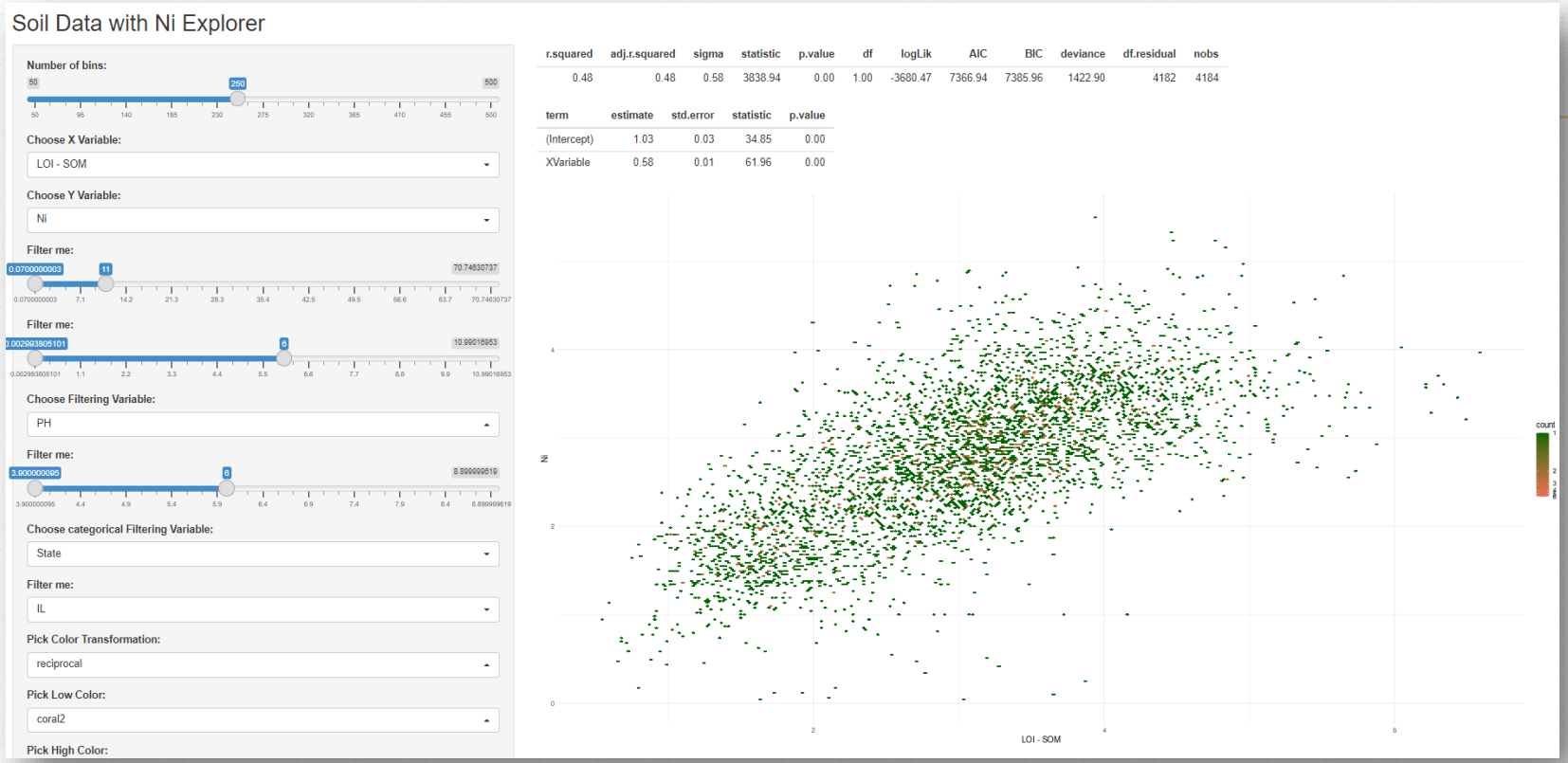
Interesting correlations



So much data!! Relationships are difficult to visualize, so data were being binned into categories

Interesting correlations



So much data!!

We needed to build a web-based data explorer to better bin, sort, and display the data

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What's next?

- Further explore regional differences
- Looking for nickel everywhere in agriculture
  - Manure, plant tissue, forages, fertilizers, irrigation water
  - 200,000+ soil samples
- Mehlich III Ni X soybean yield observational study in WI and IL in conjunction with Dr. Shawn Conley, UW Dept. of Agronomy
- Determine critical levels in Midwestern soils for soybeans

Interesting nickel facts

- Swedish mineralogist Axel Fredrik Cronstedt was the first person to realize that nickel was a new element in 1751
- The name comes from the German word Kupfernickel, meaning "Old Nick's copper."
- Twice as abundant as copper, nickel constitutes about 0.007 percent of Earth's crust
- Nickel is only one of three naturally occurring elements that is strongly magnetic. The other two are iron and cobalt.
- Adding nickel to glass gives it a green color.

http://justfunfacts.com/interesting-facts-about-nickel/