Soils, Pesticides, and pH: Interactions and Management

2023 AGVISE Soil Fertility Seminars

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General outline

- What is pH
- Why do we care about soil pH
- How do acid soils form
- General overview of herbicide activity in soil
- Deep dive on pH effects on herbicides
- Takeaways and management of low pH

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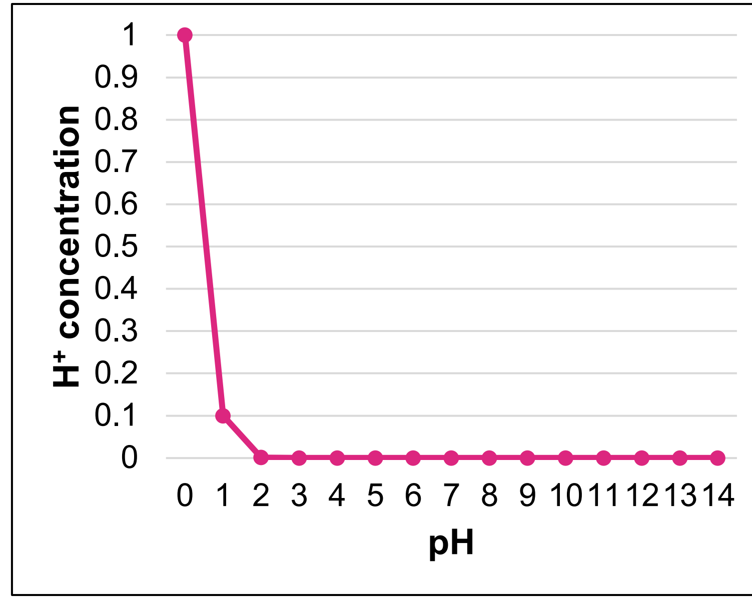
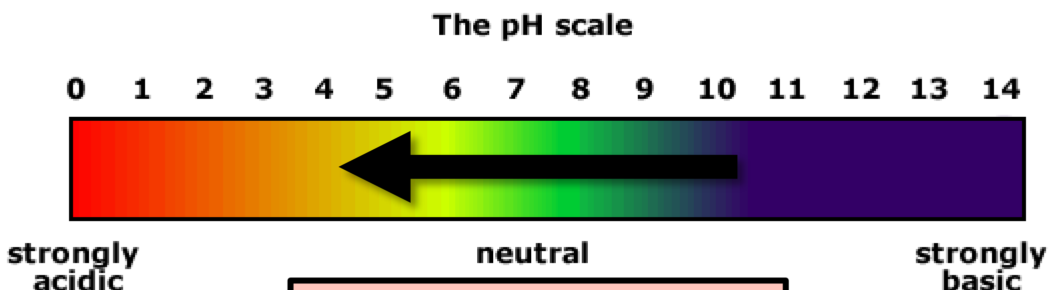
What is pH?

- Measure of hydrogen ion concentration (H^+)
- pH is a logarithmic (log) scale
- A change from pH 7 to pH 5 is therefore a 100x increase in acidity





Lower pH, higher acidity

Highest concentration of H^+ (10^0)

Lowest concentration of H^+ (10^{-14})

https://www.ibchem.com/IB16/08.31.htm

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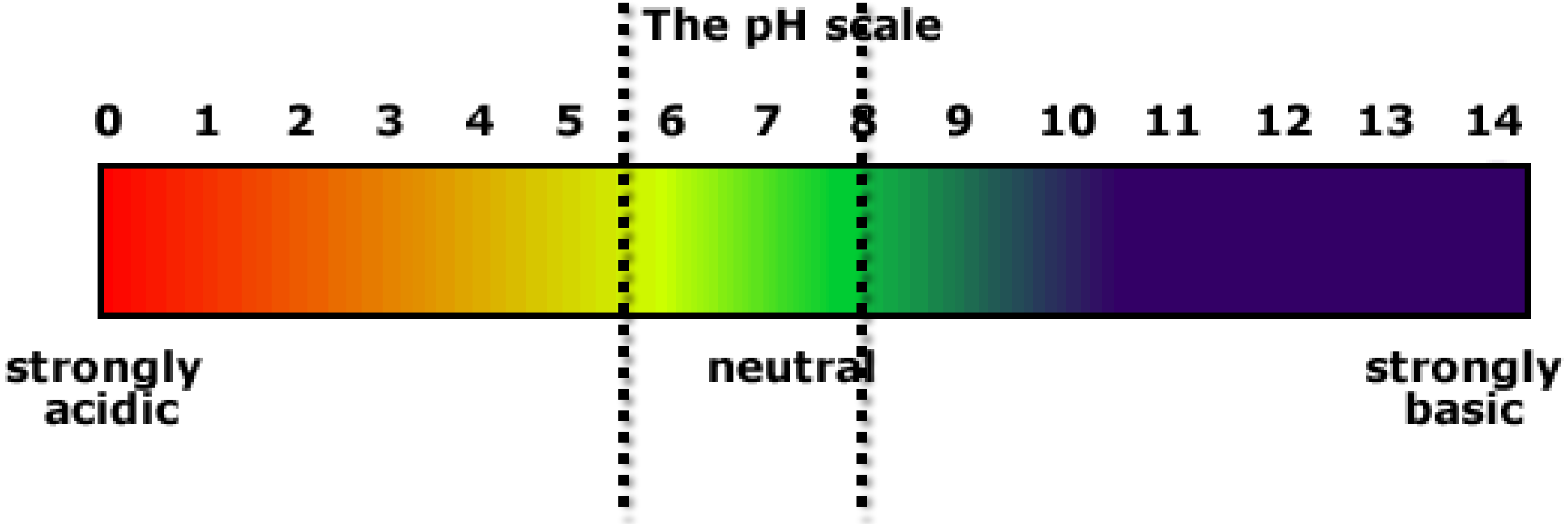
What is a "good" soil pH?

- Productive soils typically have a pH between 5.5 and 8.0



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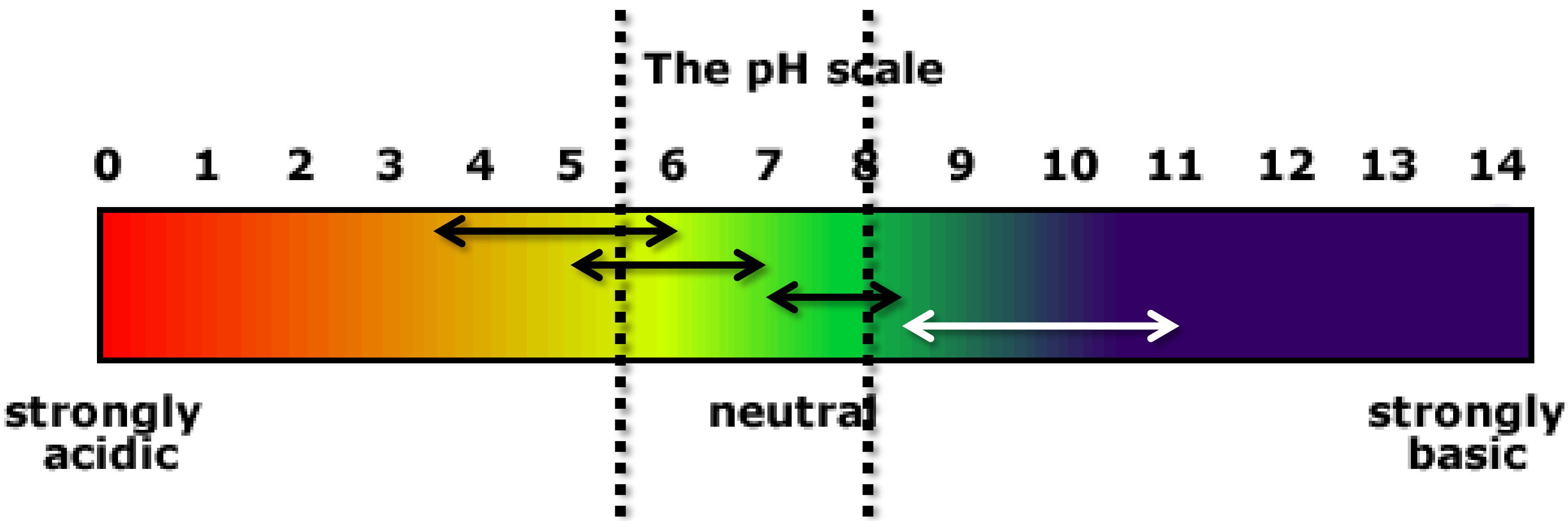
What is a “typical” soil pH?

- Depends on where the soil formed
  - Forest soils: pH 3.5 to 6.0
  - Humid region arable soils: pH 5.0 to 7.0
  - Calcareous soils: pH 7.0 to 8.3
  - Sodic soils: pH 8.3 to 11.0



Why do we care about soil pH?

- Soil pH is a “master control”

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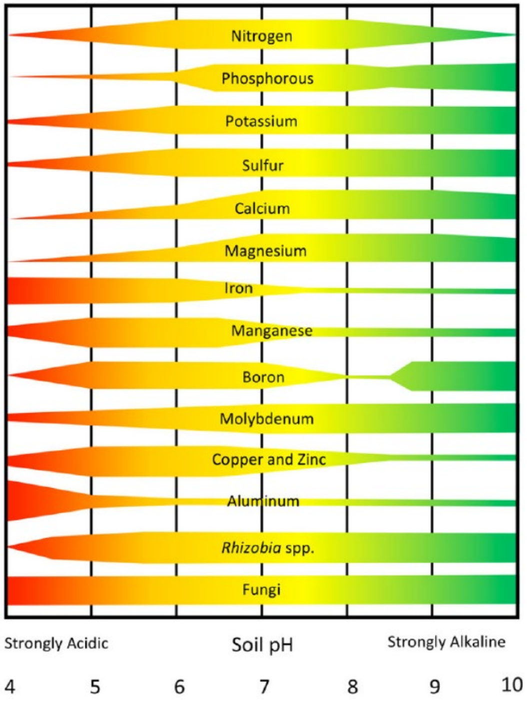
Why do we care about soil pH?

- Soil pH is a "master control"

Crop Growth

Nutrient Availability



Input Efficacy

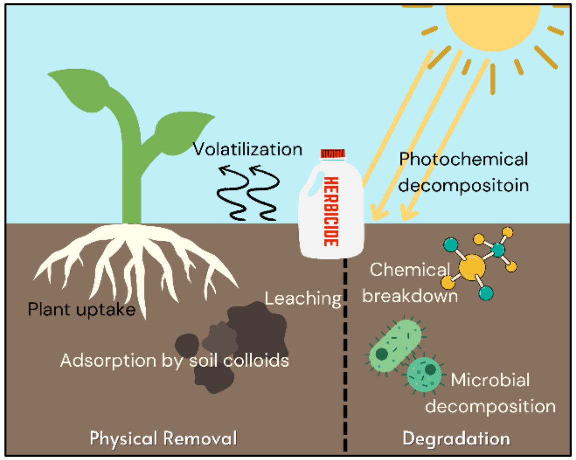


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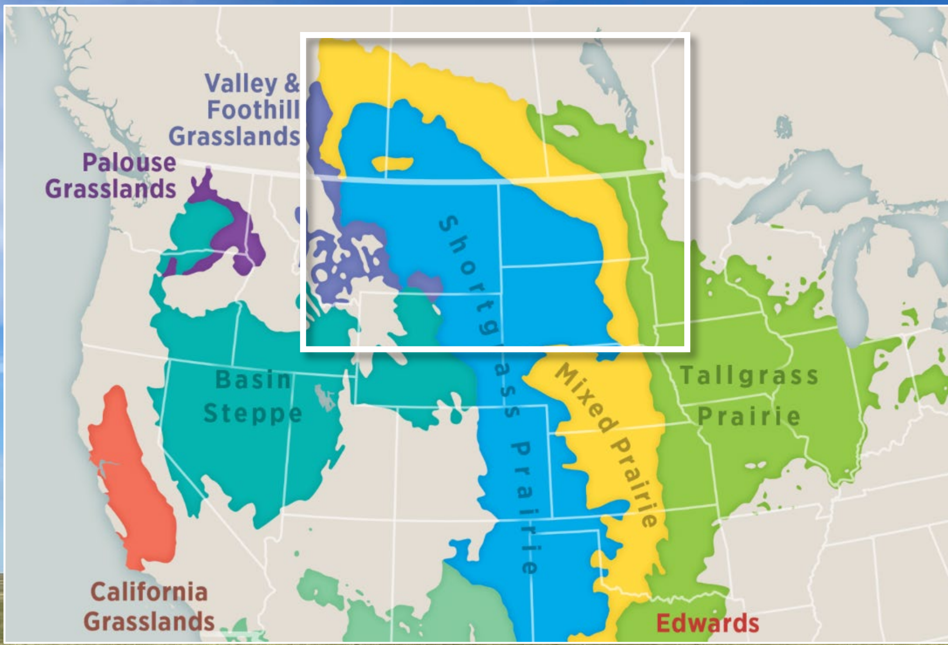
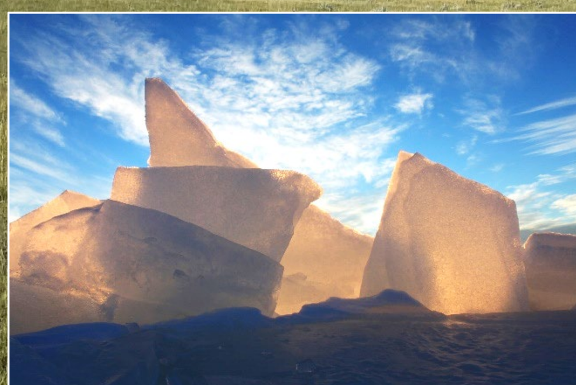
Photo: Gene Hettel/CIMMYT. https://flic.kr/p/8Ke1Jr

Washington State University

But we just have high pH soils here?





- Northern Great Plains
  - Young soils
  - Frigid and semiarid climate
- Soils typically "calcareous" (have free lime); loaded with base cations (K+, Ca+, Mg+)

Daniel Huffman based on NatureServe (Comer et al. 2018) and the International Vegetation Classification and Terrestrial Ecoregions of the World (Dixon et al. 2014)

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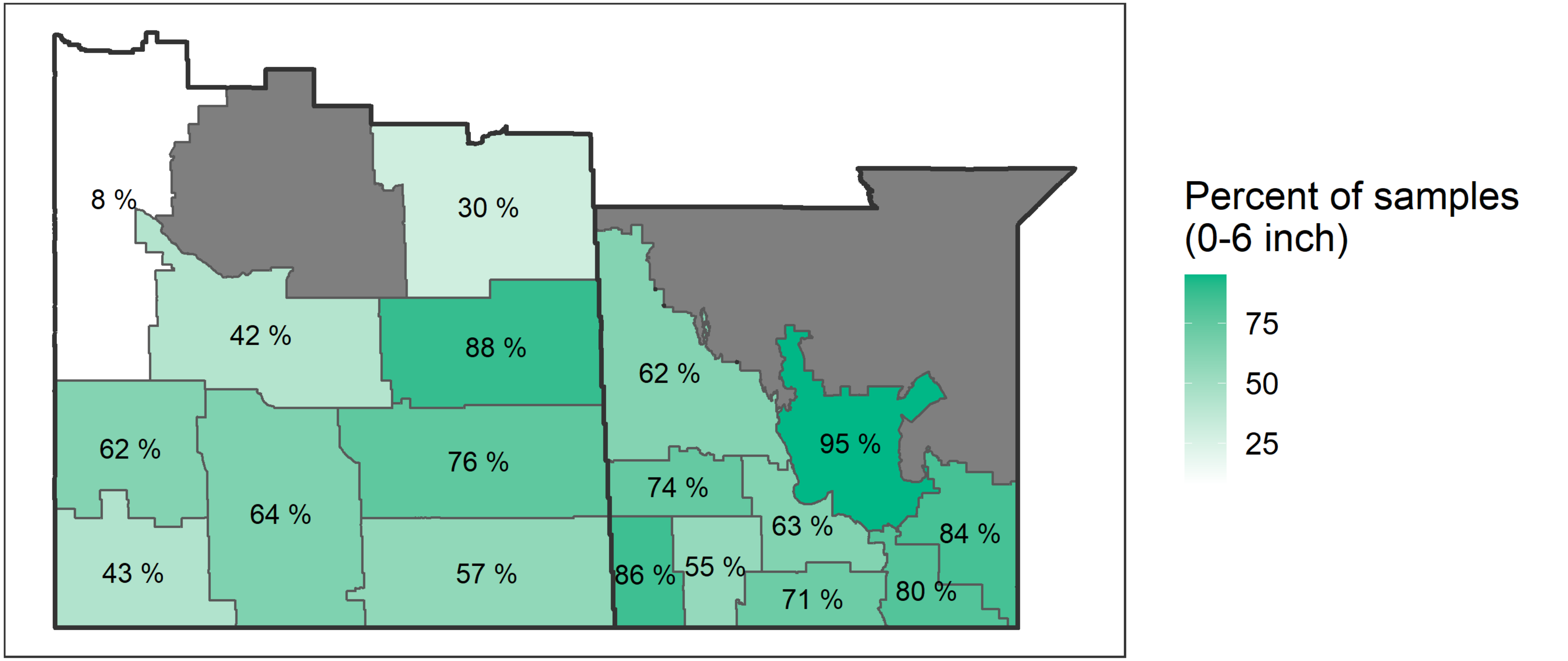
Soil samples with soil pH above 7.3 in 2022



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But we just have high pH soils here?

"There is a mistaken assumption that North Dakota does not have significant areas of low pH."

- Dr. Dave Franzen, 1999

Franzen, 1999 Soil Copper, pH, Zinc, and Boron Levels

But we just have high pH soils here?

"Approximately 17% the state acreage has a pH lower than 6.5 and conceivably could respond to limestone fertilization in sensitive crops."

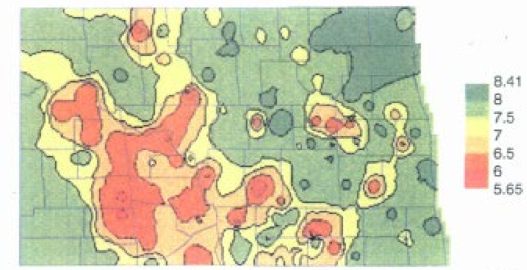

Figure 4. Soil pH levels, upland positions, non-manured sites, 1998.

pH range: 5.65 to 8.41

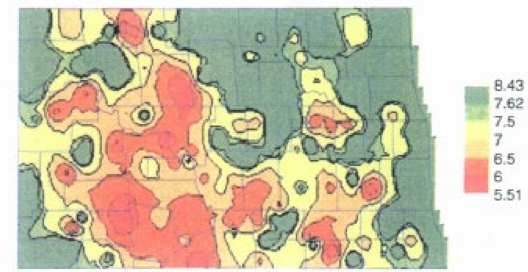

Figure 5. Soil pH on sloping positions on non-manured sites, 1998.

pH range: 5.51 to 8.43

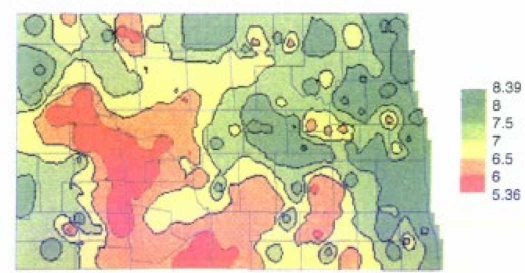

Figure 6. Soil pH in depressional areas, non-manured sites, 1998.

pH range: 5.36 to 8.39

Franzen, 1999 Soil Copper, pH, Zinc, and Boron Levels

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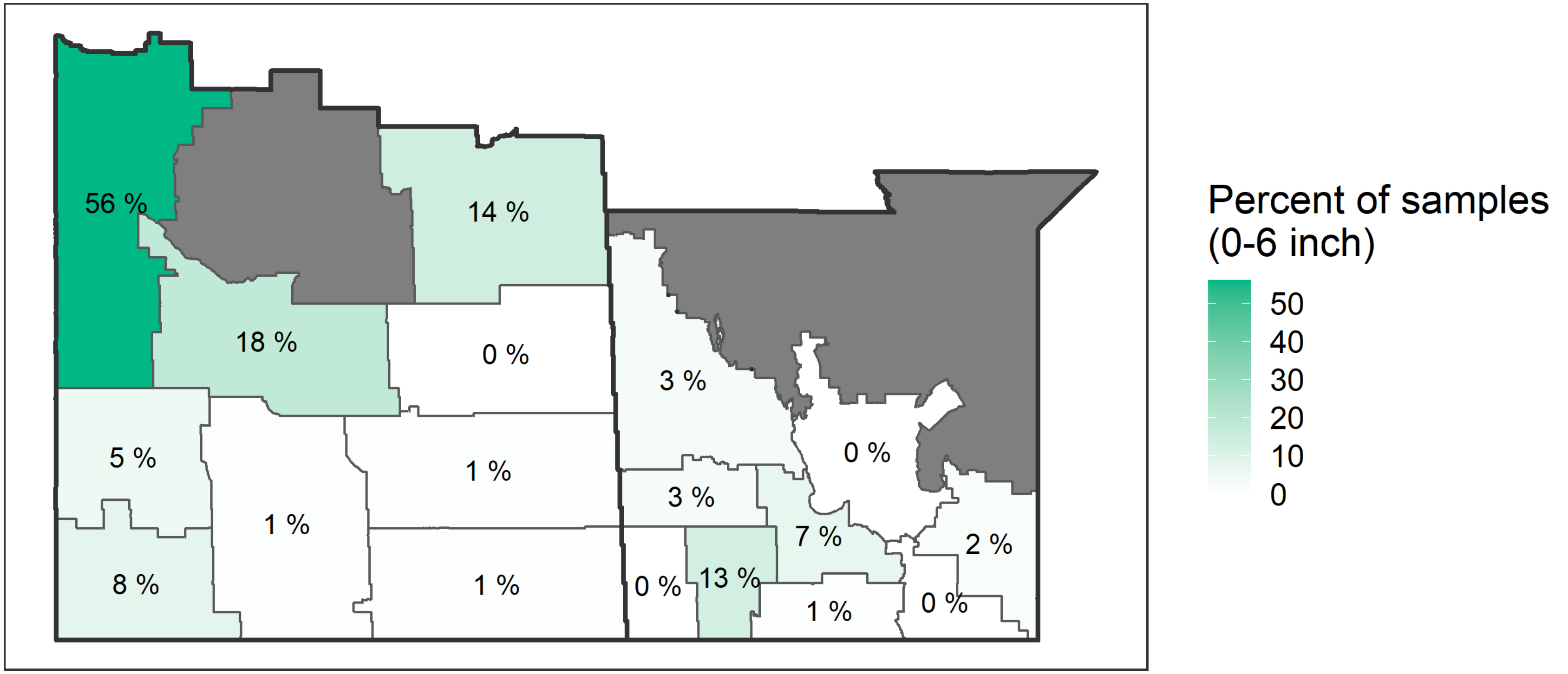
Soil samples with soil pH below 6.0 in 2022



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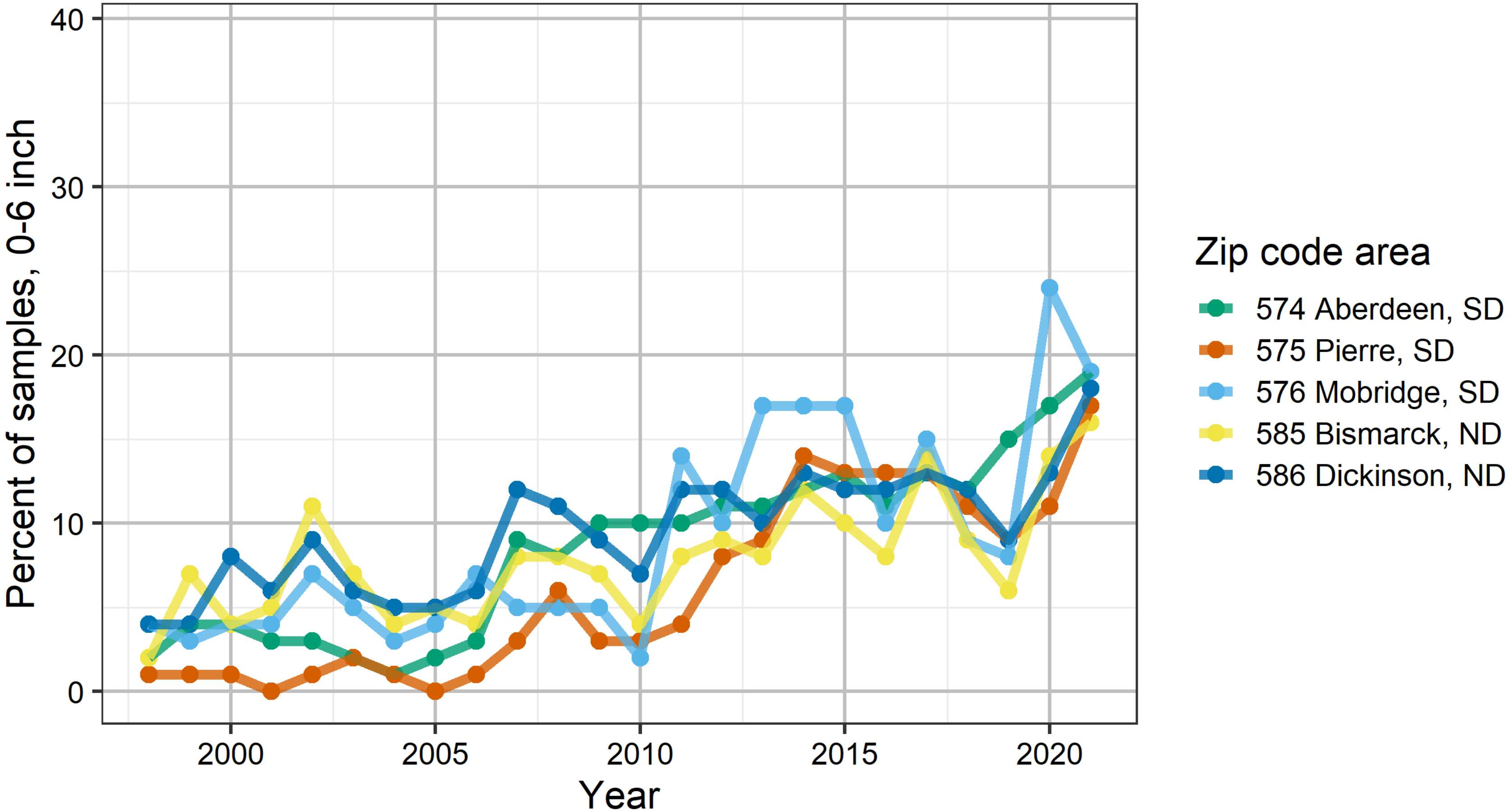
Soil pH trend (pH < 6, 1:1) across the northern Great Plains (Western ND and SD)



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AGVISE Laboratories, Northwood, ND

Sources of soil acidity (H^+)

- Nitrogen fertilizer
- Breakdown of organic matter
- Rain
  - Normal rainfall in equilibrium with atmospheric carbon dioxide has a pH of 5.0 to 6.0 (carbonic acid)
  - Leaches base cations from the soil (Ca^{2+}, Mg^{2+}, K^+, Na^+) leaving acid cations (H^+ and Al^{3+}) behind
  - Acid rain
- Crop uptake and removal of base cations

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Long-term use of nitrogen

ammonium sulfate

$$(NH_4)_2SO_4 + 4O_2 \rightarrow 2HNO_3 + H_2SO_4 + 2H_2O$$

nitric acid sulfuric acid

breakdown of organic matter (generalized)

$$[C_2H_4ONS] + 5O_2 + H_2O \rightarrow H_2CO_3 + RCOOH + H_2SO_4 + HNO_3$$

carbonic acid strong organic acids nitric acid sulfuric acid

- Microbes oxidize ammonium-based fertilizers and organic matter, resulting in plant-available N
- Produces acids that donate H^+, lowering soil pH

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Long-term use of nitrogen

Lime quantity required to neutralize the soil acidity produced by different N sources if all ammonium-N is converted to nitrate-N		
Nitrogen source	**Fertilizer analysis**	**Lime required (lb CaCO3/lb N)**
Anhydrous ammonia	82-0-0	1.8
Urea	46-0-0	1.8
Ammonium sulfate (AMS)	21-0-0-24	5.4*
Monoammonium phosphate (MAP)	11-52-0	5.4
Urea-ammonium nitrate solutions (UAN)	28 to 32-0-0	1.8

*The estimate for AMS may be 50% too high (Chien et al., 2010)
From Cihacek et al. 2021 as adapted from Wortmann et al., 2015 and Havlin et al., 2005

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Let's do the math for a wheat/canola/field pea rotation

Yield Goals: 60 bu/a (wheat); 40 bu/a (canola); 50 bu/a (pea)

N, P, S Needs: 305 lb N, 80 lb P_2O_5, 35 lb S

		Lime requirement	
	lbs N	lb $CaCO_3$/lb N	total lb $CaCO_3$
560 lbs urea	258	1.8	464
154 lbs MAP	17	5.4	92
146 lbs AMS	35	5.4	189
			745 lbs $CaCO_3$/acre per 3 yr rotation

2,235 lbs $CaCO_3$/a required every 12 years to neutralize acidity produced from N fertilizer

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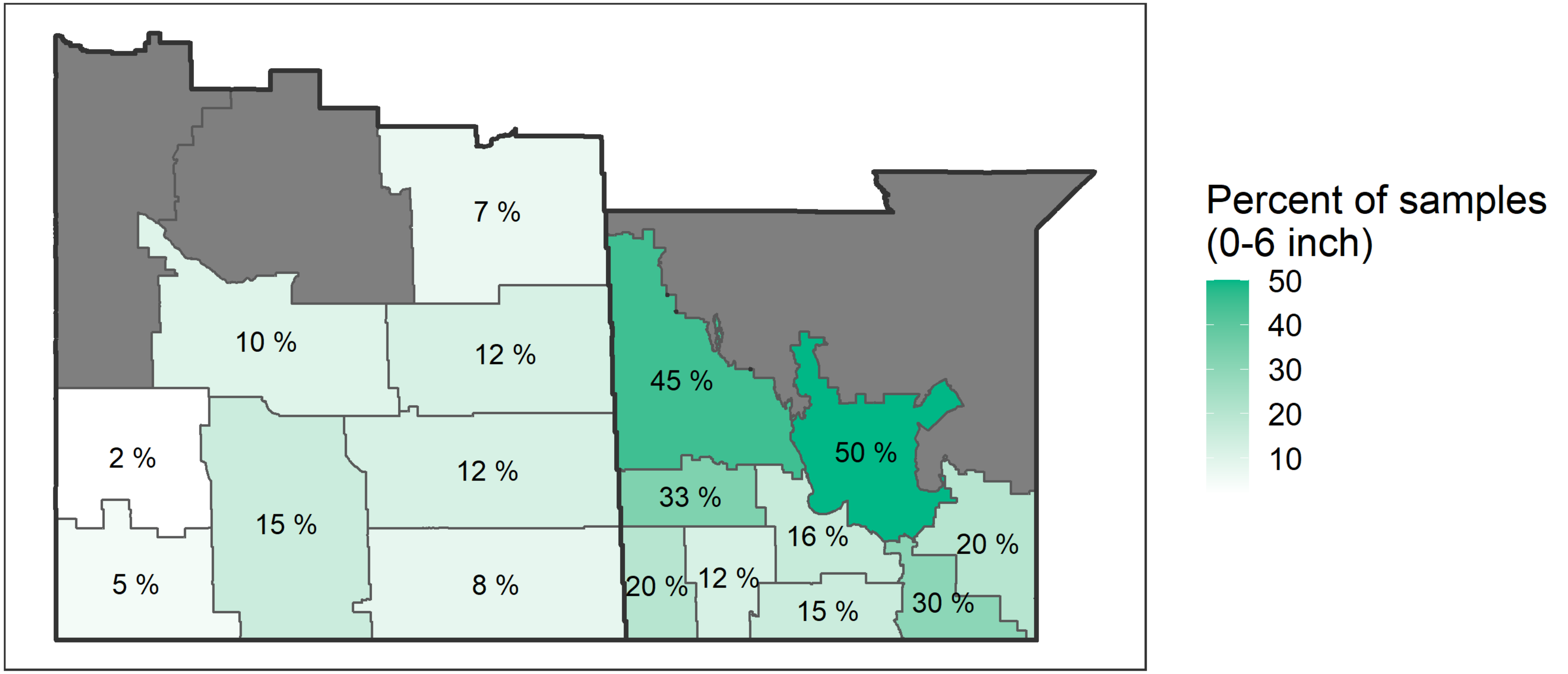
Soil samples with calcium carbonate above 5.0 % CCE in 2022



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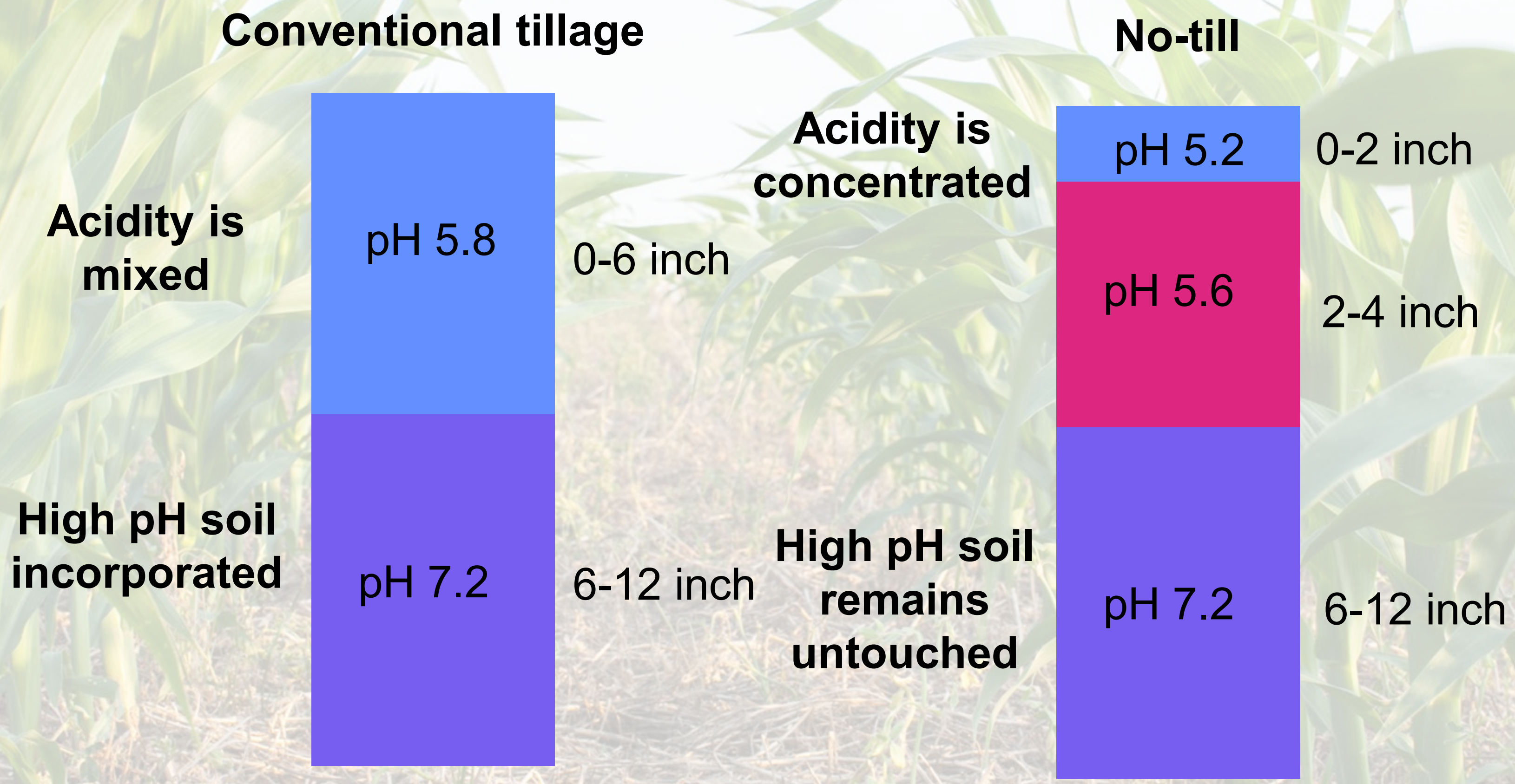
5% CCE $\approx$ 100,000 lb $CaCO_3$

Adoption of long-term no-till



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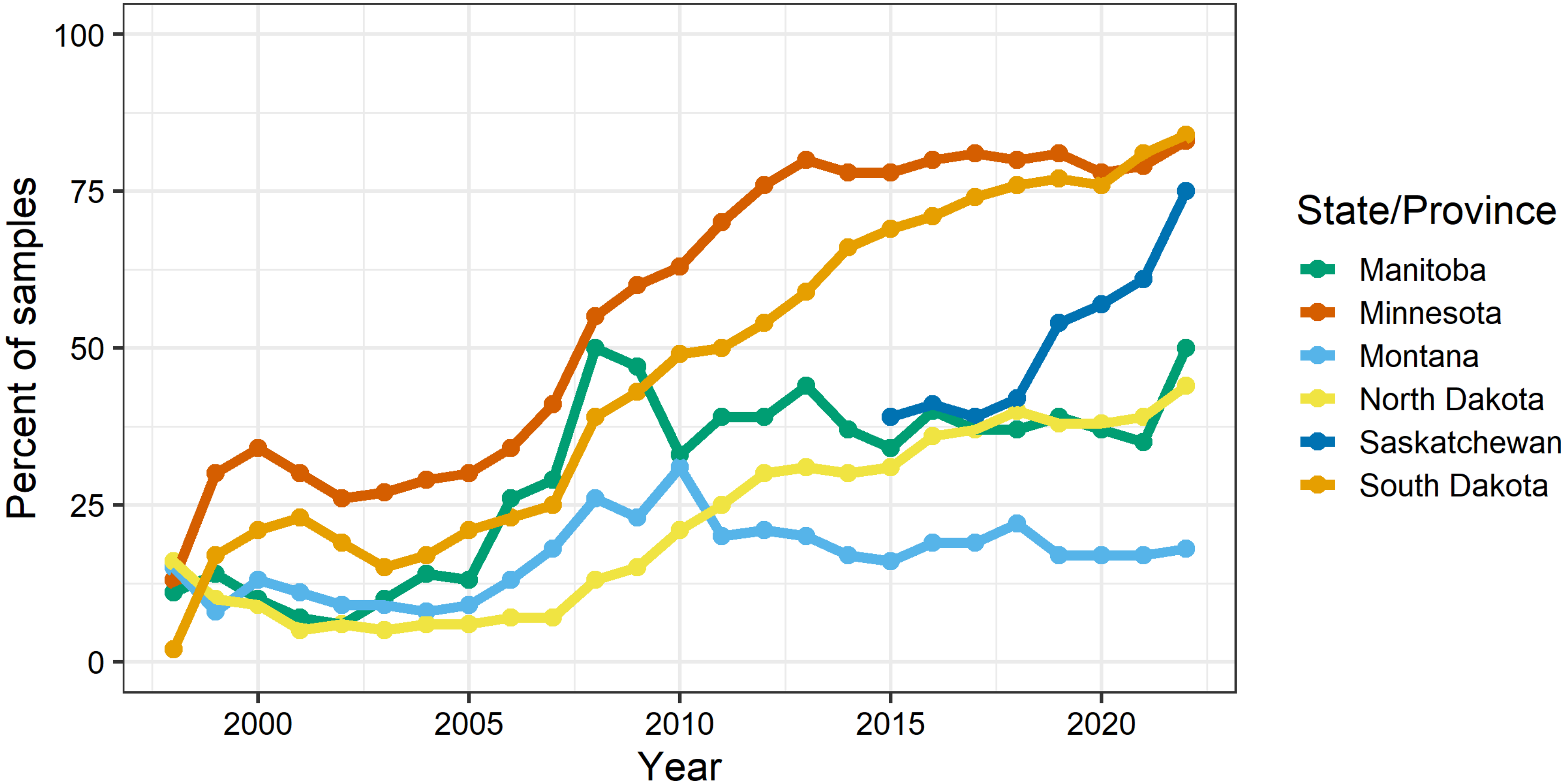
Soil samples collected as a precision sample (grid or zone)

Trend from 1998 to 2022



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Zone sampling reveals field variability

No. zones per field	Average soil pH range within field (high zone – low zone)				
0-6" samples	**Nitrate-N lb/acre, 0-24 inch**	**Olsen P ppm**	**K ppm**	**pH**	**Soil organic matter %**
3	31	9	92	0.6	1
4	29	14	118	0.8	1.2
5	47	17	143	0.9	1.5
6	63	21	175	1.1	1.3
7	69	23	185	1.2	1.3
8	66	28	196	1.4	1.7

Data from 25,000 zone-sampled fields in 2022

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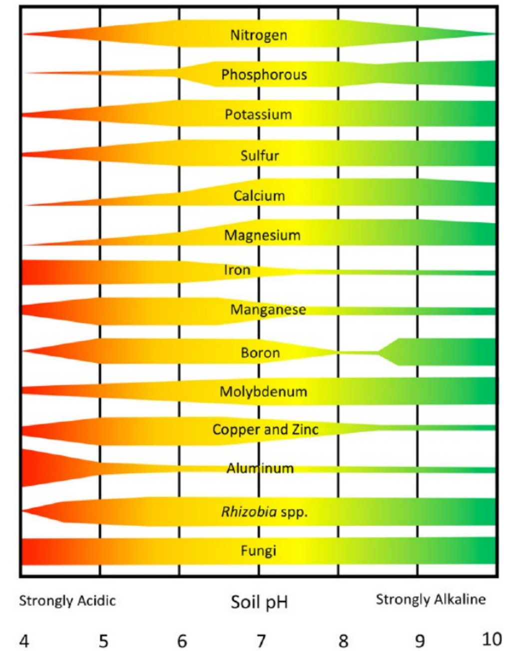
Why do we care about soil pH?

- Aluminum toxicity
  - When soil pH <5.5, aluminum becomes more soluble
  - High levels of aluminum interfere with cell division at root tips, restricting crop growth

Photo by Hal Weiser, NRCS



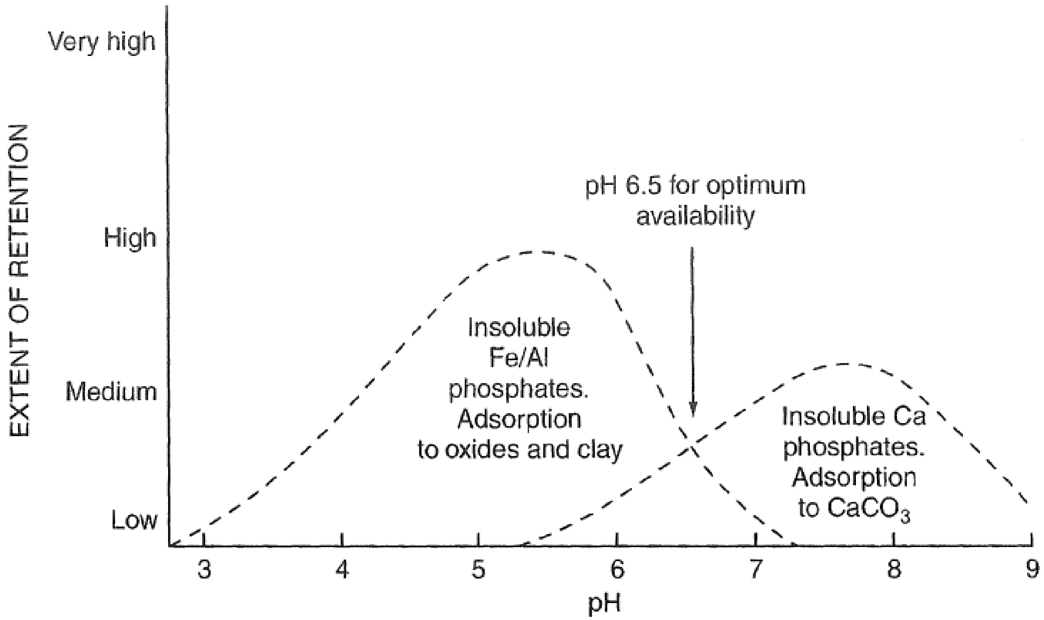
Washington State University

Sunflowers in western North Dakota

Photo by Ryan Buetow, 2022

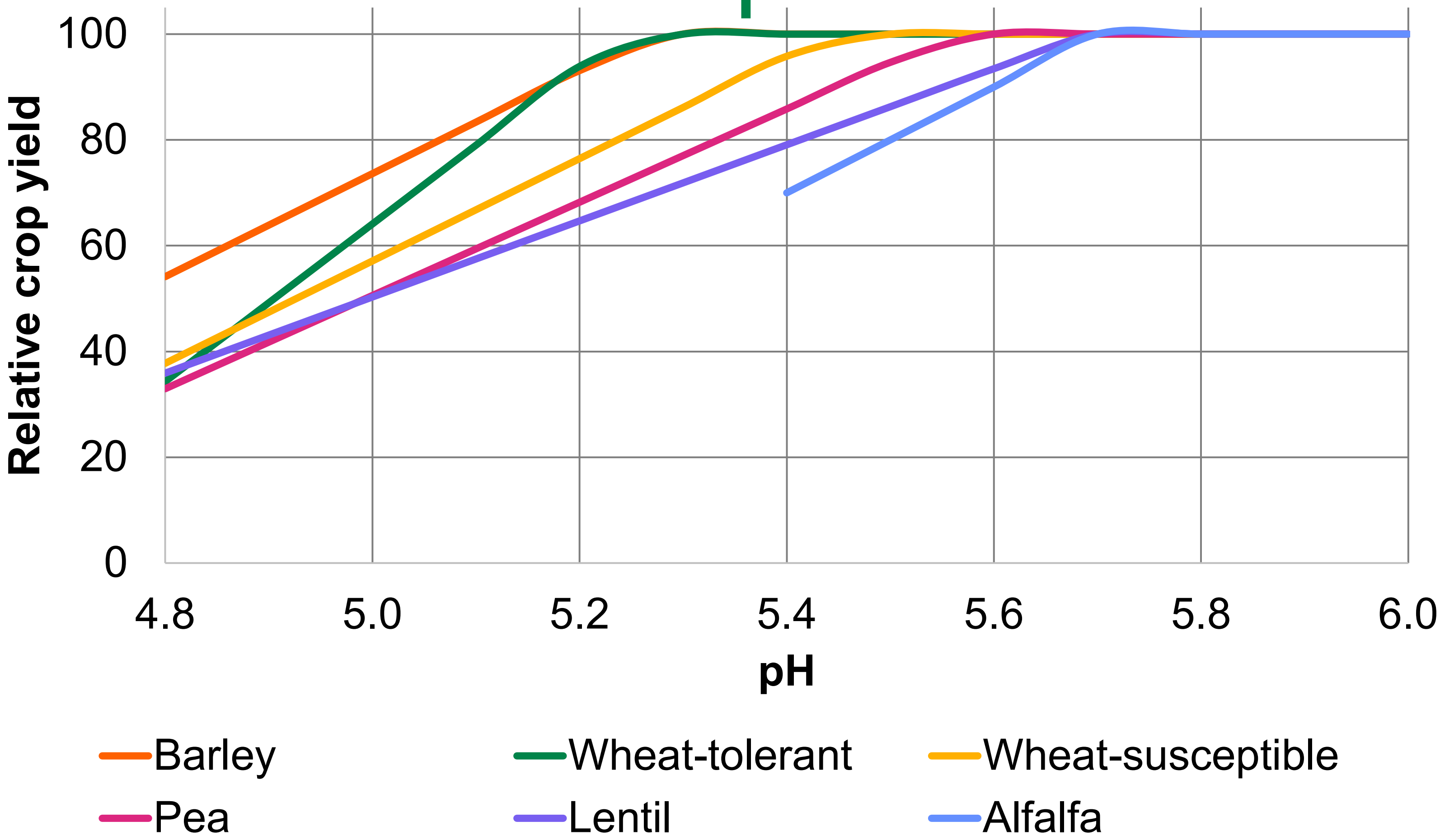
Why do we care about soil pH?

- Nutrient availability
  - Phosphorus complexes with aluminum ions at low soil pH, reducing availability
  - Bacteria (including *Rhizobia sp.*) are less able to survive, reducing legume N fixation



Havlin, J.L., J.D. Beaton, S.L. Tisdale, and W.L. Nelson. 2005. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. 7th ed. Pearson Prentice Hall, Upper Saddle River, NJ.

Low pH tolerance of different crops



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Mahler, R.L., and R.E. McDole. 1987. Effect of soil pH on crop yield in northern Idaho. Agron. J. 79(4):751–755.

Soil acidity (pH <6.0) an emerging soil fertility issue on the Northern Plains

- Long-term use of nitrogen, adoption of long-term no-till, and zone/grid soil sampling have contributed to increased frequency of acid soils
- Soil pH controls availability of plant nutrients
  - Low pH decreases phosphorus availability and increases availability of plant toxic aluminum
  - Soil pH 5.0-5.5, aluminum toxicity
  - Soil pH 6.0-6.6, reduced legume N fixation

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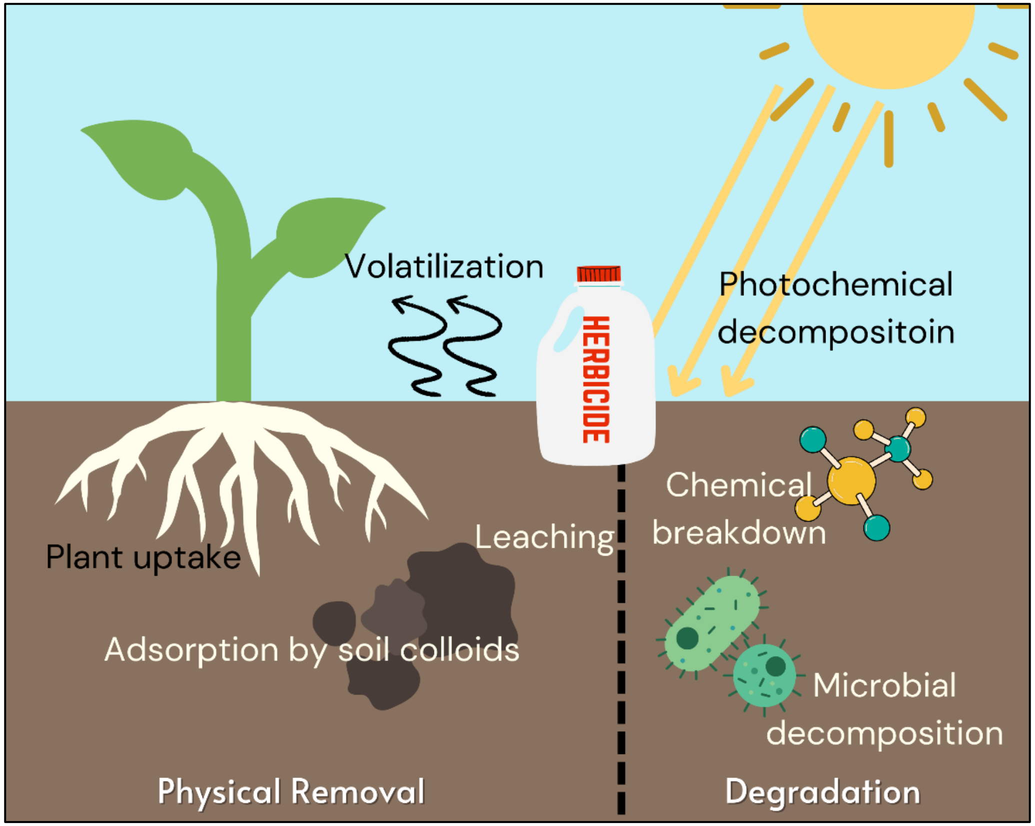
Why do we care about soil pH?

Input Efficacy



Low soil pH can affect weed control

- Reduced crop stand increases weed competition
- Some weeds are less stressed at low soil pH, increasing weed competition
- Affects length of certain herbicide residual activity
  - Can lengthen residual… sometimes too much (carryover)
  - Can reduce residual activity

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Sunflowers in western North Dakota

Photo by Ryan Buetow, 2022

Some weeds like acid soils

Reduced weed control in durum
Scranton, ND

soil pH ranged 4.0 to 5.0

“Growth of green foxtail was greater at pH 4.8 than at pH 7.3”
Weaver and Hamill, 1985

Field site, August 14, 2022
Reduced weed control
Soil pH 5.3

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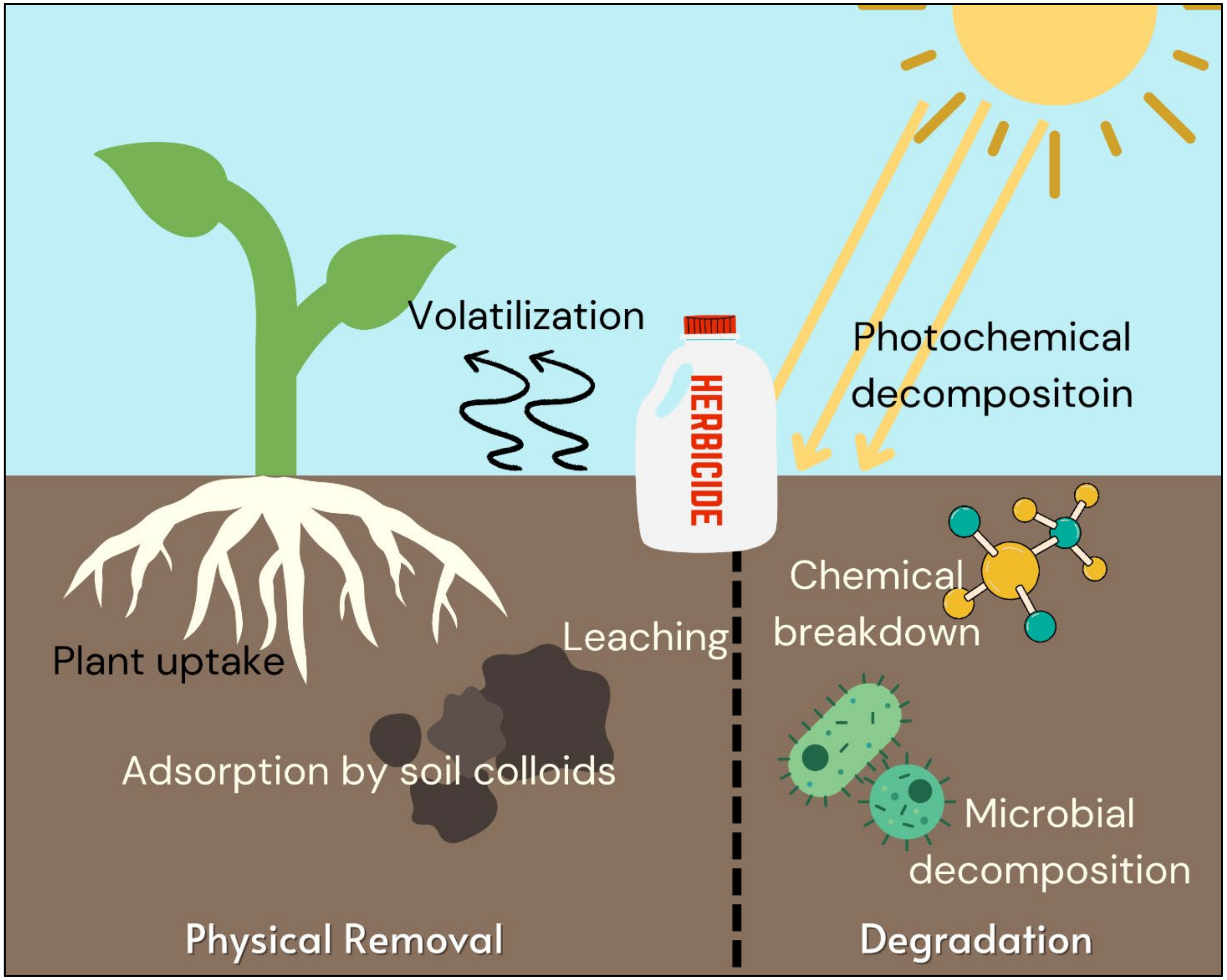
Soil-residual herbicide activity is affected by soil properties



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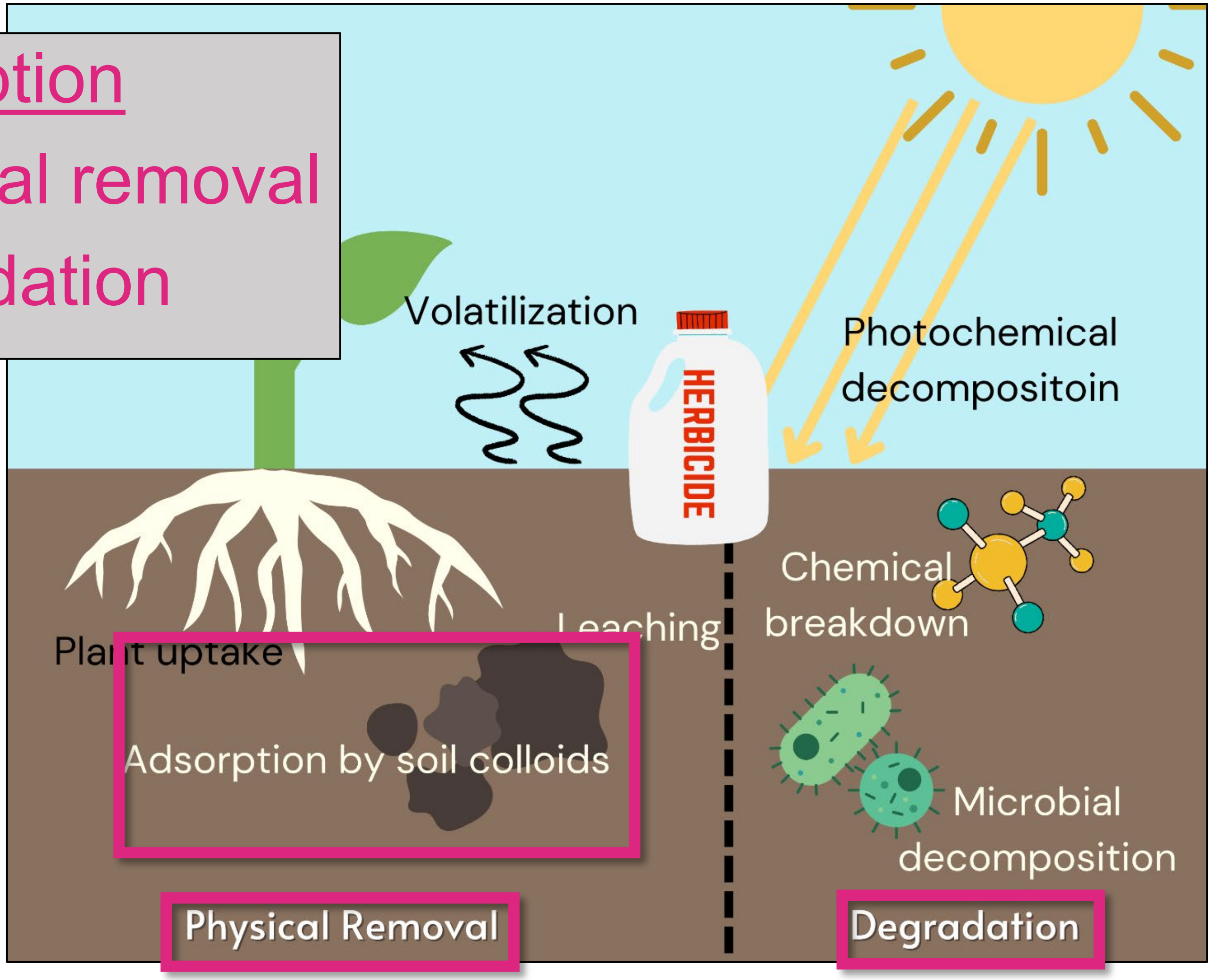
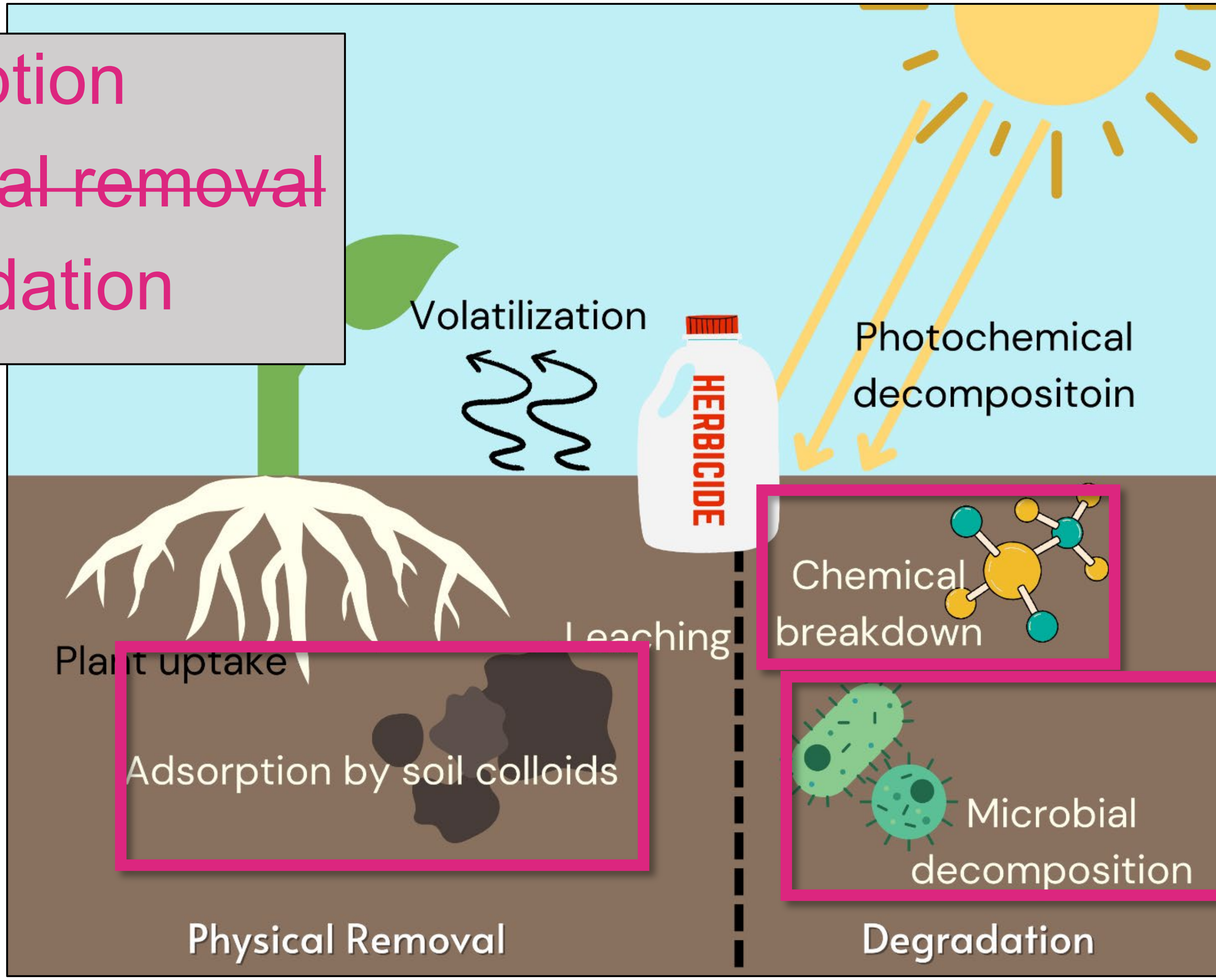
Three main loss pathways of herbicides once they are applied

- Adsorption
- Physical removal
- Degradation



Soil pH affects:

- Adsorption
- ~~Physical removal~~
- Degradation



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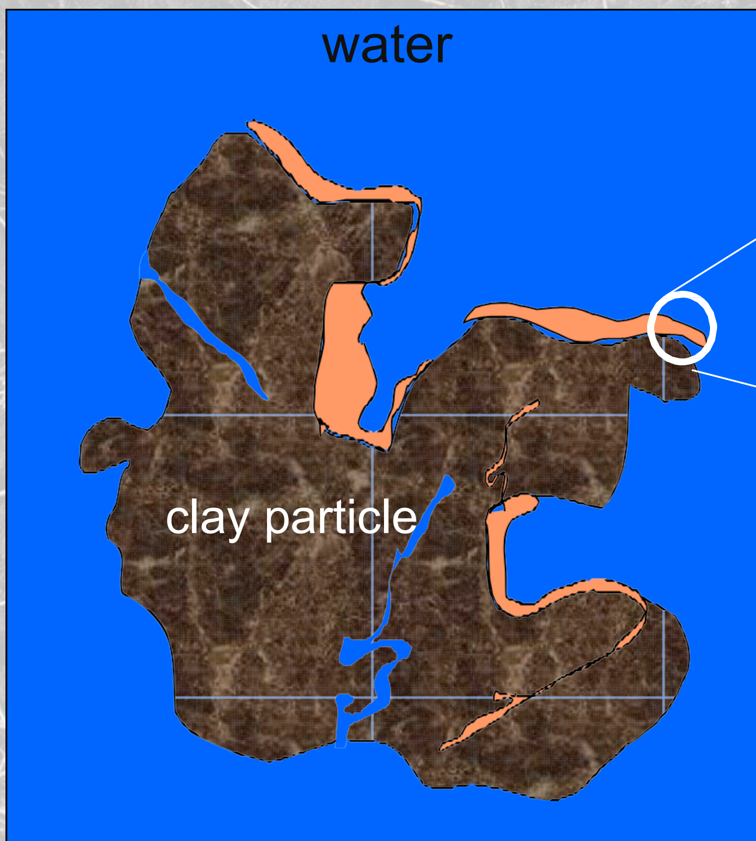
What is adsorption?

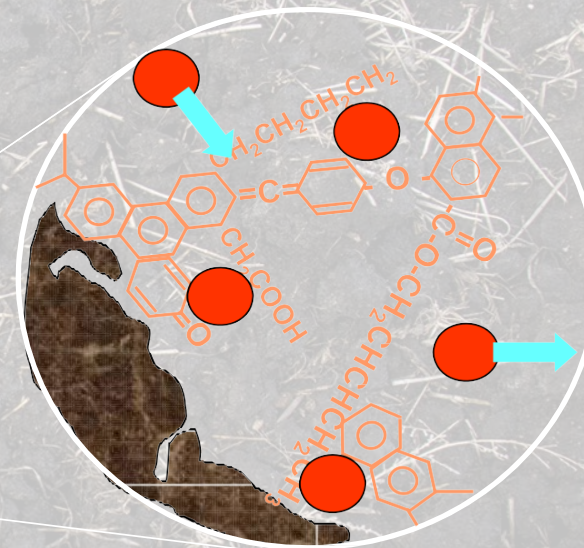


soil organic matter – humic material

Slide courtesy of Dr. Bill Johnson, Purdue University

What is adsorption?

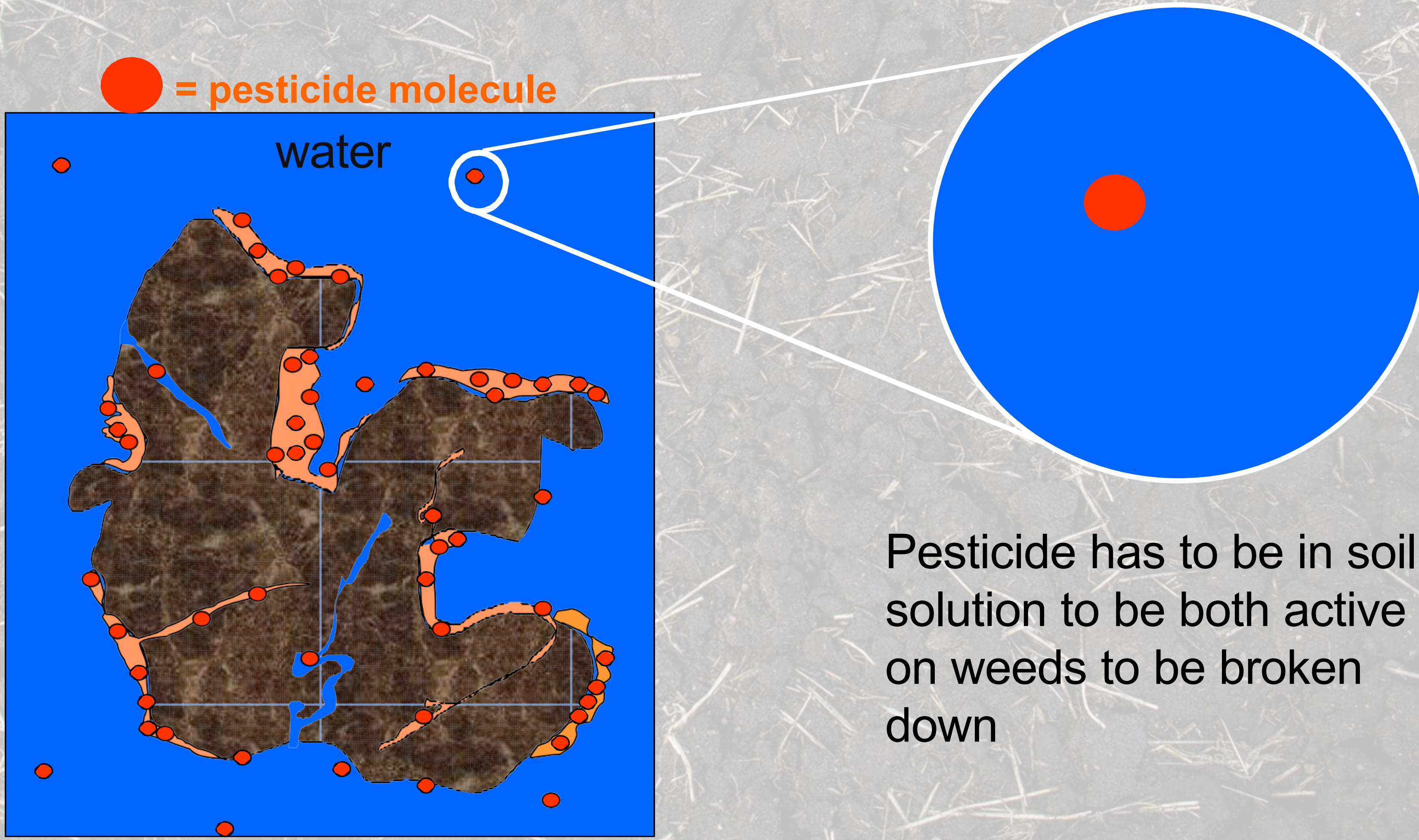
= pesticide molecule



adsoprtion
and
desorption

Slide courtesy of Dr. Bill Johnson, Purdue University

What is adsorption?



Pesticide has to be in soil solution to be both active on weeds to be broken down

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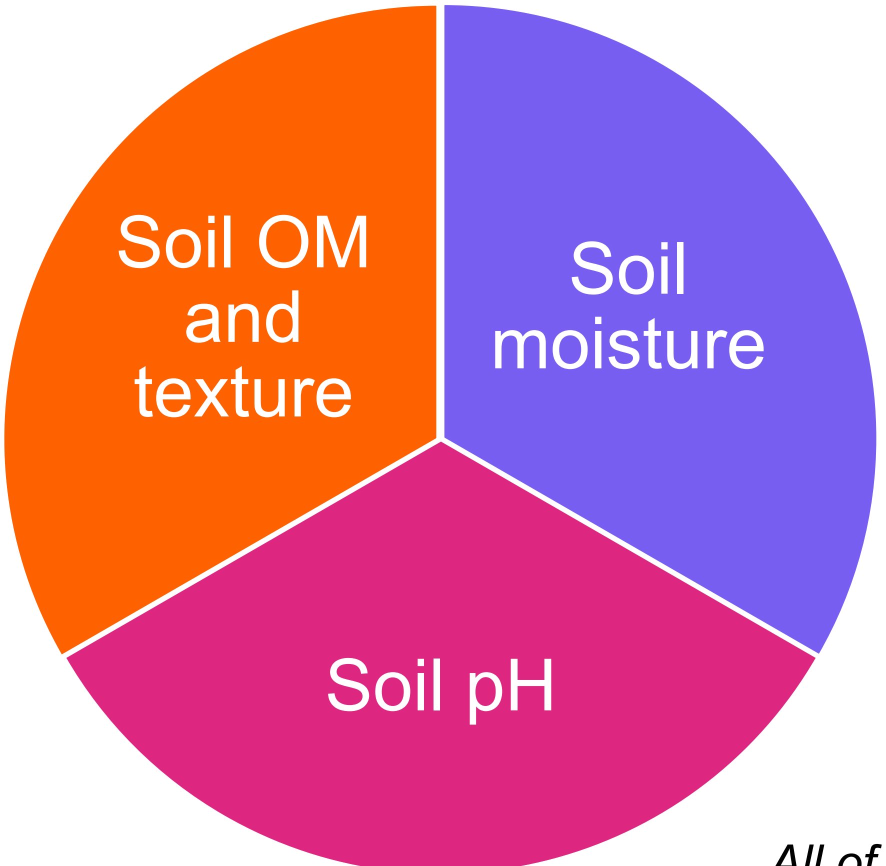
Slide courtesy of Dr. Bill Johnson, Purdue University

What soil factors determine herbicide residual length



All of these factors affect herbicide adsorption

Soil organic matter and texture

- Soil OM and texture contribute to a soil's cation exchange capacity (CEC; measure of a soil's ability to hold onto cations)
- More clay = higher CEC
  - Smectite (80-150 meq/100g)
  - Illite (10-40 meq/100g)
  - Kaolinite (3-15 meq/100g)
- Organic matter a huge contributor to CEC (150-400 meq/100g)
  - OM often a more important factor than texture in determining herbicide residual length
- Higher organic matter means higher microbial degradation

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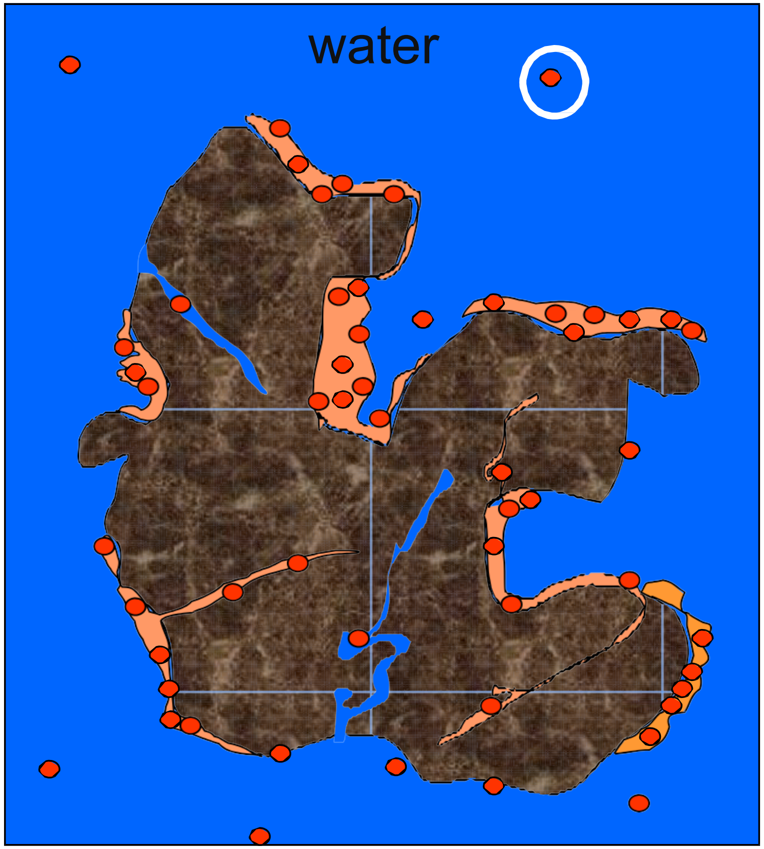
Generalizations on soil texture/OM on residual length

- Higher OM/clay content
  - Herbicide less biologically active; herbicide binds to soil OM
  - Higher potential for microbial breakdown
- Lower OM/clay content
  - More of herbicide stays in soil solution; more biologically active
  - Less microbes in the soil,

Adsorption and microbial activity is dependent on soil moisture and soil pH



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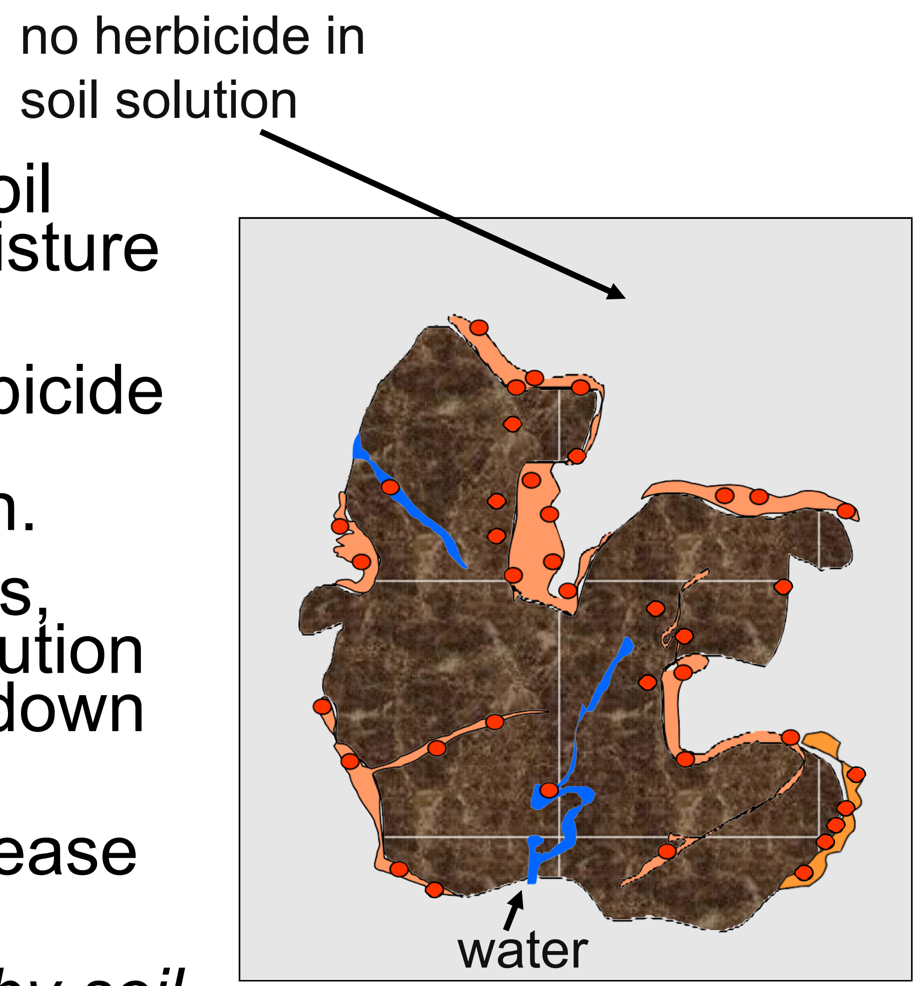
Soil moisture

- Binding of herbicides to soil particles increases as moisture content decreases
- Under dry conditions, herbicide is bound to the soil and unavailable for breakdown.
- When soil moisture returns, herbicide desorbs into solution and is available for breakdown and plant uptake.
- Prolonged conditions increase likelihood of carryover

Soil moisture is influenced by soil texture and organic matter



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Soil pH effect on soil adsorption

- Higher soil pH means soil has more OH^- groups on clay edges and OM (pH dependent charge)
  - More negatively charged sites can potentially hold onto more herbicide, greater adsoprtion
- Lower soil pH means soil has less OH^- groups and can hold onto less herbicide
- Atrazine and imidazolinones are the opposite – adsorption decreases as pH increases

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Soil pH effect on herbicides in solution

- Higher concentration of H^+ in acid soils favors neutrally-or positively-charged form of herbicides (if they are ionizable)
- Lower concentration of H^+ in basic soils favors negatively-charged form of herbicides
- Higher pH = deprotonation = negatively-charged herbicide, increasing the solubility of the herbicide
  - For example, mesotrione (Callisto), saflufenacil (Eragon LQ)
  - As pH increases, water solubility increases
  - General rule: higher water solubility, decreased adsorption

Herbicide	pH	Water Solubility (mg/L)
Callisto	4.8	2,200
Callisto	6.9	15,000
Callisto	9.0	22,000
Eragon LQ	5.0	30
Eragon LQ	7.0	2100

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Shaner, D.L., ed. 2014 Herbicide Handbook. 10th ed. Lawrence, KS: Weed Science Society of America. 294, 409 p.

Always read and follow pesticide label instructions.

Soil pH

- Affects chemical degradation, specifically acid hydrolysis
  - Cleavage of OH, Cl, or F functional groups off of herbicide
  - Acid hydrolysis ceases at soil pH 6.8 and above
- Affects microbial degradation
  - Bacteria less able to survive at lower pHs
  - Soil pH extremes can negatively effect microbes that typically breakdown herbicides
  - Optimized from soil pH 6.5 to 8

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Factors outside of soil that affect herbicide residual length

- Herbicide chemistry
- Rate of herbicide
- Herbicide use history
- Application method
- Plant cover

Herbicides in our region most affected by soil pH

Herbicide	Group	Trade Name	Primary degradation
Chlorimuron	2	Classic	Acid hydrolysis
Imazethapyr, imazamox	2	Pursuit, Solo ADV II	Microbial
Atrazine	5	Aatrex	Microbial, acid hydrolysis
Metribuzin	5	Sencor	Microbial
Fomesafen	14	Reflex	Photodegradation, anaerobic microbes
Sulfentrazone	14	Authority	Microbial
Mesotrione	27	Callisto	Microbial

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North Dakota Weed Control Guide, 2023

Always read and follow pesticide label instructions. Not an exhaustive list of active ingredients

Herbicides in our region most affected by soil pH

Herbicide family	Group	Trade Name
Sulfonylureas (SUs)	2	Classic, Ally

- Most SU herbicides broken down by acid hydrolysis
- Acid hydrolysis ceases at soil pH above 6.8
- The SUs used in the northern Great Plains (e.g. Refine SG, UpBeet) are broken down by soil microbes and not dependent on acid hydrolysis for breakdown
- SUs dissociate at soil pH > 7.0 and become negatively charged and do not bind with soil CEC, becoming available for plant uptake

Sulfonylureas become less persistent at low pHs

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Always read and follow pesticide label instructions.

Herbicides in our region most affected by soil pH

Herbicide family	Group	Trade Name
Imidazolinones (IMIs)	2	Pursuit, Solo ADV II

- Breakdown occurs by soil microbes
- Breakdown occurs more rapidly and herbicide activity increases as soil pH increases
- Weakly bound to soil, strongly bound to OM
- IMIs negatively charged at soil pH > 6.5; strongly bound to OM at pH <6.5
- For IMIs, when pH <6.5, a pH reduction as small as 0.2 pH units can double amount adsorbed
- When strongly bound to OM, residues can affect future crops for years

Imidazolinones are more persistent at low pH due to increased adsorption

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North Dakota Weed Control Guide, 2023

Always read and follow pesticide label instructions.

Herbicides in our region most affected by soil pH

Herbicide family	Group	Trade Name
Triazine, triazinone	5	Aatrex, Sencor

- Triazines (atrazine) are broken down by acid hydrolysis (like SUs)
- Atrazine molecules become positively charged at soil pH <7.5 and bind with soil CEC, making them unavailable for plant uptake and breakdown.
- Metribuzin is mainly broken down by soil microbes
- Soil adsorption of metribuzin decreases as soil pH increases, meaning it is more available at higher pHs

Atrazine is less persistent at low pHs, more active at high pH
Metribuzin becomes more active at higher pHs

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North Dakota Weed Control Guide, 2023

Always read and follow pesticide label instructions.

Herbicides in our region most affected by soil pH

Herbicide family	Group	Trade Name
Triketones	27	Callisto

- Primarily broken down by microbes
- Solubility of triketones increases in high soil pHs (>7.0)
- At soil pH <7.0, solubility decreases and triketones are more likely to adsorb to soil CEC

Callisto is more persistent at low pH due to increased adsorption

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North Dakota Weed Control Guide, 2023

Always read and follow pesticide label instructions.

Herbicides in our region most affected by soil pH

Herbicide family	Group	Trade Name
Fomesafen, Sulfentrazone	14	Reflex, Authority

- Fomesafen is primarily broken down by anaerobic microbes
- Solubility of fomesafen increases as soil pH becomes >6.5
  - Higher risk of crop injury at higher pH
  - Needs water for anaerobic microbes (soil moisture extremely important for breakdown)

- Sulfentrazone is primarily broken down by microbes
  - Solubility of sulfentrazone increases as soil pH becomes >6.5
    - More available at higher pH; less at lower pH
    - Sulfentrazone becomes more available in coarse-textured and low-organic matter soils as well
    - Opportunity to vary rate to account for these soil differences (increase rate in acid soils, decrease rate in non-acid soils)

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North Dakota Weed Control Guide, 2023

Always read and follow pesticide label instructions.

Do I have to remember all of this?

GROUP	14	HERBICIDE

AUTHORITY® 480 HERBICIDE

COMMERCIAL

(Agricultural)

Suspension Concentrate
Flowable

Do not use on soils with less than 3% organic matter.
Use the higher rates within the rate range for soils with pH less than 7.0.
Do not apply to soils classified as coarse-textured soils.
Do not apply in any type of soils with an organic matter content greater than 6%.
Do not use on soils with a pH of 7.8 or greater.

Always read and follow pesticide label instructions.

Practical tips to manage herbicide residual

- Always read and follow label instructions
- Fields are variable. Create management zones to monitor soil OM% and pH
- Soil pH is not static; monitor this value over time to avoid possible herbicide issues
- Investigate and diagnose areas of poor crop growth and/or poor weed control
  - If you suspect the issue is pH related, sample from 0-3” and test for OM% and pH
- Keep records of all herbicide applications and rates used + as-applied maps
- Opportunity to VRT herbicide applications

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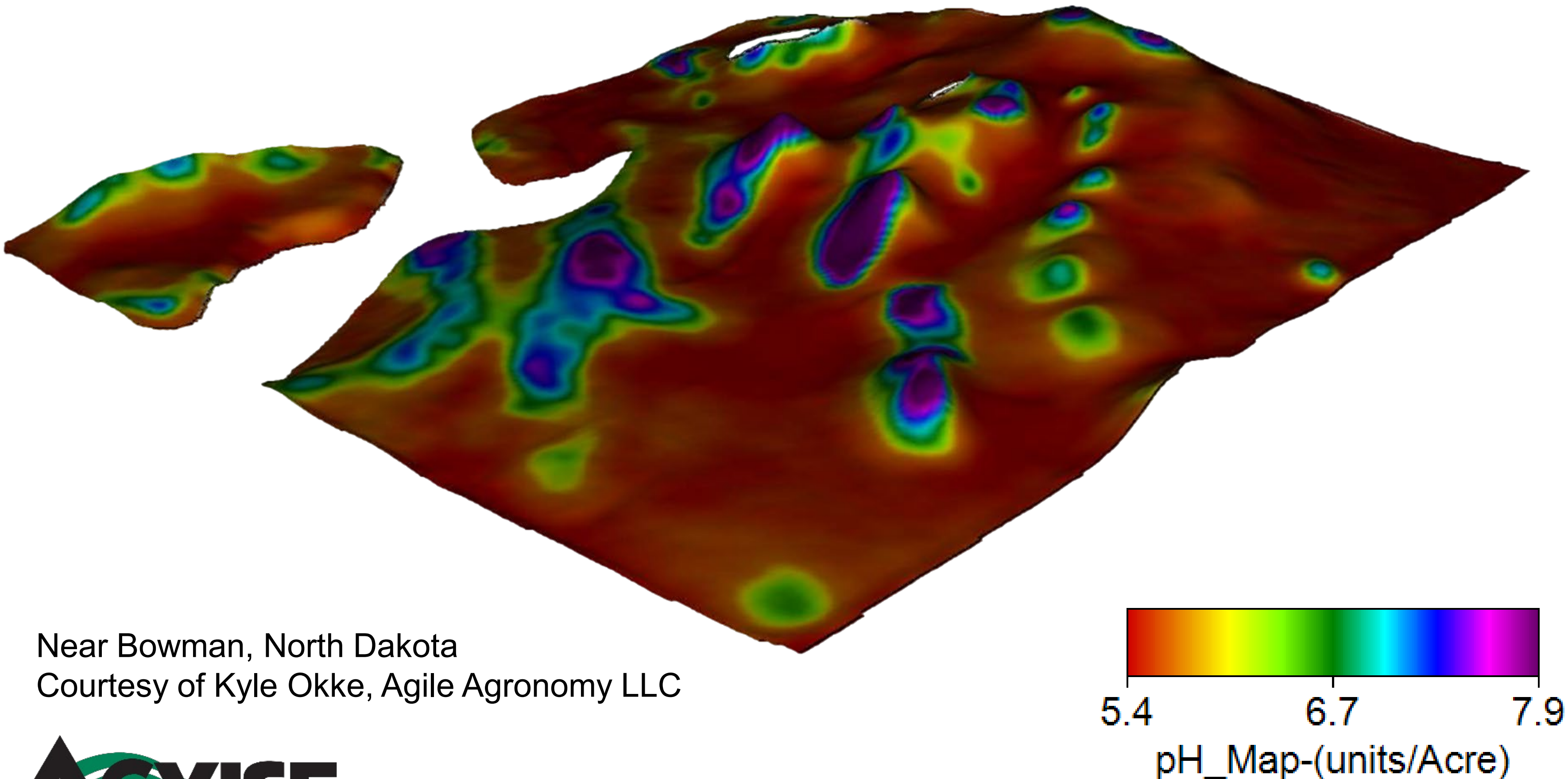
Low pH areas aren't always in the same position on the landscape



Near Bowman, North Dakota
Courtesy of Kyle Okke, Agile Agronomy LLC

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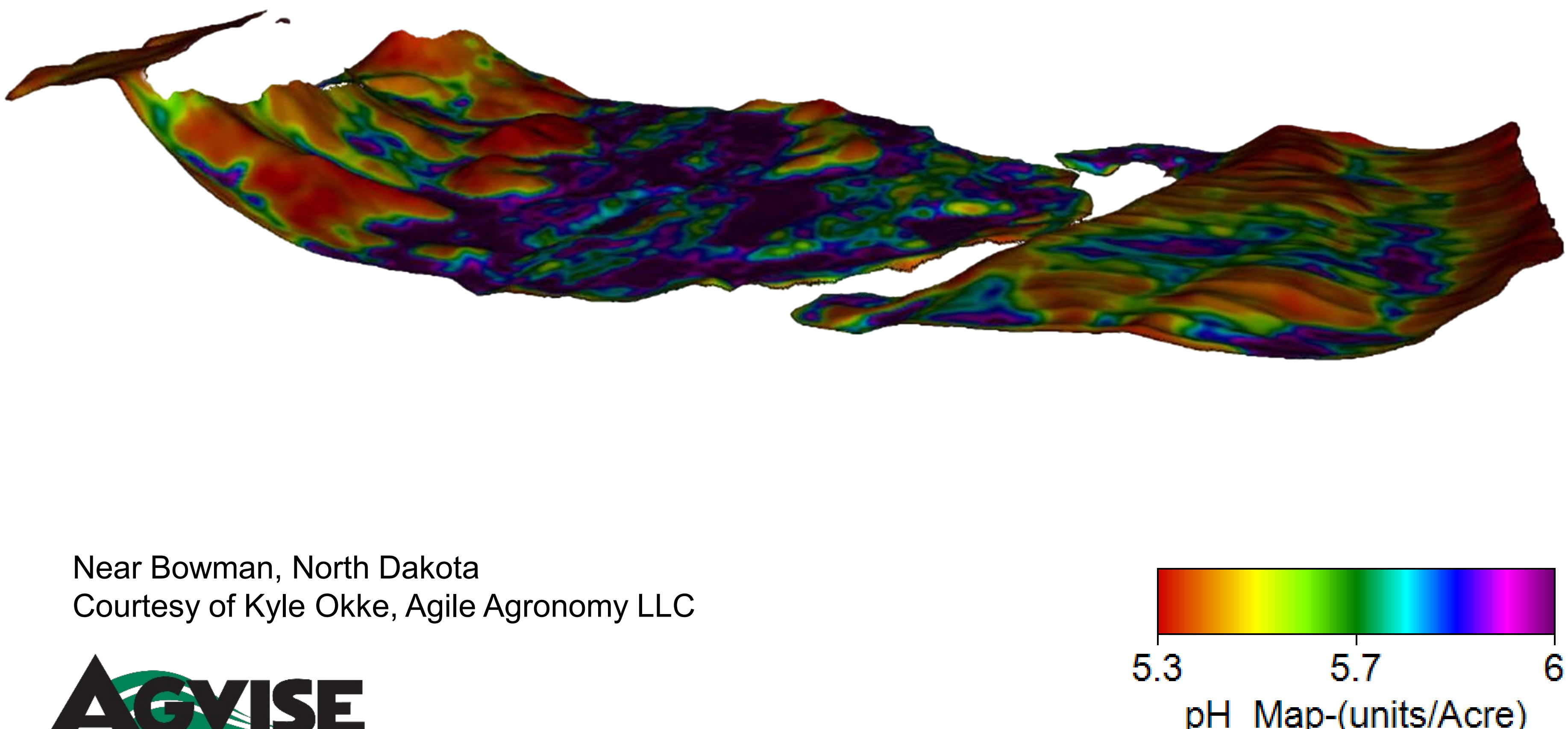

Near Bowman, North Dakota
Courtesy of Kyle Okke, Agile Agronomy LLC

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Long-term solution to acid soils: liming

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2(g) \uparrow$$

lime *hydrogen* *calcium* *water* *carbon dioxide*

- Lime ($MgCO_3$ or $CaCO_3$) reacts with hydrogen in the soil solution, reducing H concentration, increasing soil pH
- Carbonate (CO_3) is important, as this is the part of the material that neutralizes acidity
- In eastern Corn Belt, lime is applied every 3 to 6 years
- Very limited sources of lime in Northern Great Plains
- Unknown how frequent liming will need to be in our climate regime or cropping systems

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Managing low pH soils

- Use zone-sample soil test results to inform nitrogen rates; avoid applying unneeded to reduce acidification through N mineralization
- Keep as much soil residue in the field as possible to reduce base cation removal
- High rates of seed-placed P (40 lb P_2O_5/acre) bind with soluble aluminum, reducing the effects of aluminum toxicity
- Utilize aluminum-tolerant crops and varieties

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AGVISE Western ND Lime Project

Objective: determine the amount of surface-applied lime required to raise pH to 6.5 and determine how long the effect lasts

Site: Golden Valley, ND
Grail silty clay loam
average initial soil pH:
- 0-3”: 5.2
- 3-6”: 5.4

average initial buffer pH:
- 0-3”: 6.3
- 3-6”: 6.4

Treatments: 0 to 2.5 tons/A ENP, surface-applied (lime product had 1,782 lbs ENP/ton)

Trial Initiated: May 5, 2021

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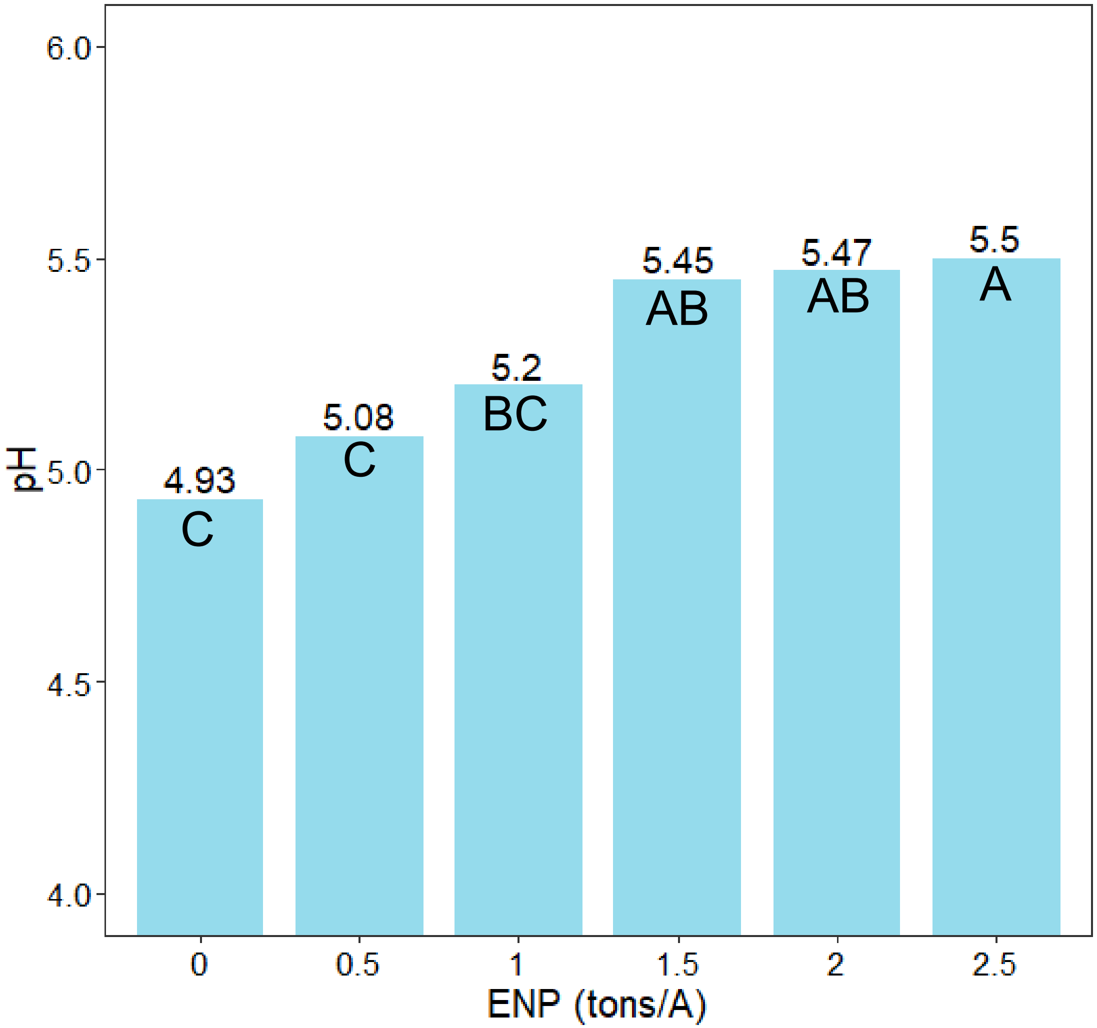
Effect of lime on soil pH, 1.25 years after application, 0-3” depth



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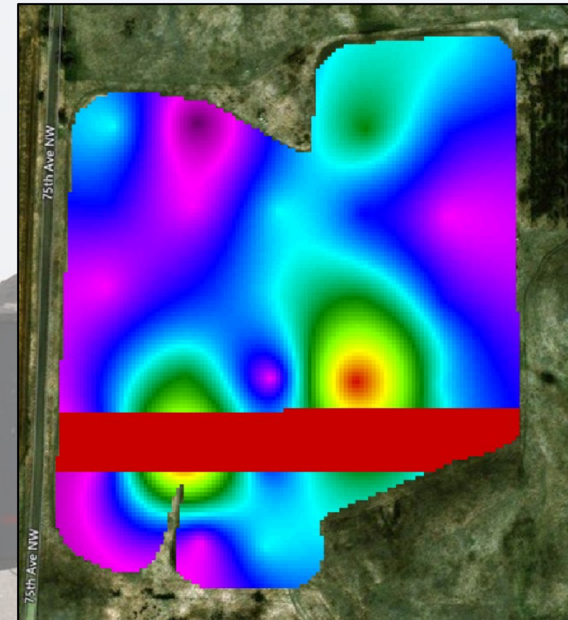
Cost of liming in W ND in 2022

- $0/ton Beet lime from Sidney Sugar in Sidney, MT
- $39/ton to haul lime ~ 136 miles
- $16.50 + $5.00 for every additional ton/acre
- Approximately $100/acre
- Flat rate of 2 ton beet lime/acre
- One field VRT based on 1-acre grid (0 to 4 ton beet lime/acre)
- Lime disced to 3" after application



VRT map made GK Technology Inc.'s ADMS 32

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Resources

- North Dakota Weed Control Guide (Herbicide Carryover section) https://www.ndsu.edu/agriculture/extension/publications/2023-north-dakota-weed-control-guide
- North Dakota Survey of Soil Copper, pH, Zinc, and Boron https://library.ndsu.edu/ir/handle/10365/16271
- Ehmke T. 2015, Managing acidified soils on the Plains https://acsess.onlinelibrary.wiley.com/doi/epdf/10.2134/cs2015-48-1-2
- Soil Residual Herbicides: Science and Management https://www.weedscience.ca/wp-content/uploads/2021/04/Vol-3-Winnipeg_Full_book.pdf

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Thank you!

What questions can I answer?

Questions later?

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